INVESTIGATIONS ON THE SOLVENT EXTRACTION AND LUMINESCENCE OF LANTHANOIDS WITH MIXTURES OF HETEROCYCLIC β-DIKETONES AND VARIOUS NEUTRAL OXO-DONORS

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BY

RANI PAVITHRAN

UNDER THE SUPERVISION OF
Dr. M.L.P. REDDY

CHEMICAL SCIENCES DIVISION
REGIONAL RESEARCH LABORATORY (CSIR)
THIRUVANANTHAPURAM - 695 019, KERALA, INDIA.
MARCH 2005

Regional Research Laboratory
Council of Scientific & Industrial Research
Industrial Estate P.O.,
Thiruvananthapuram - 695 019, Kerala, India
Phone : 91 - 471 - 2515360 [O], 0471-2494906 [R]
Fax : 91- 0471 - 2491712, E-mail : reddy@csrrltrd.ren.nic.in, mlpreddy@yahoo.co.uk

r. M. L. P. Reddy
cientist

CERTIFICATE

This is to certify that the work embodied in the thesis entitled **"INVESTIGATIONS ON THE SOLVENT EXTRACTION AND LUMINESCENCE OF LANTHANOIDS WITH MIXTURES OF HETEROCYCLIC β-DIKETONES AND VARIOUS NEUTRAL OXO-DONORS"** is the result of investigations carried out by Mrs. Rani Pavithran under my supervision in the Chemical Sciences Division of Regional Research Laboratory (CSIR), Thiruvananthapuram, and the same has not been submitted elsewhere for any other degree.

Dr. M.L.P. Reddy
(Thesis Supervisor)

Dr. M.L.P. REDDY
Scientist
Regional Research Laboratory (CSIR)
Thiruvananthapuram - 695 019

Thiruvananthapuram
March 2005

LIST OF PUBLICATIONS

1. Steric effects of polymethylene chain of 4-acylbis(pyrazolones) on the solvent extraction of trivalent lanthanoids: Synergistic effect with mono and bifunctional neutral organophosphorus extractants, **Rani Pavithran** and M.L.P. Reddy, *Anal. Chim. Acta*, 2005 (In Press).

2. Crown ethers as synergists in the extraction of trivalent lanthanoids with 3-phenyl-4-(4-fluorobenzoyl)-5-isoxazolone, **Rani Pavithran** and M.L.P. Reddy, *Radiochim. Acta*, *92*, 31-38, 2004.

3. Synergistic solvent extraction of trivalent lanthanoids with mixtures of 1-phenyl-3-methyl-4-pivaloyl-5-pyrazolone and crown ethers, **Rani Pavithran**, R. Luxmi Varma and M.L.P. Reddy, *Solv. Extr. Ion Exch.* **21(6)**, 797-813, 2003.

4. Enhanced extraction and separation of trivalent lanthanoids with 3-phenyl-4-(4-fluorobenzoyl)-5-isoxazolone and dicyclohexano-18-crown-6, **Rani Pavithran** and M.L.P. Reddy, *Radiochim. Acta*, **91**, 163-168, 2003.

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CONTENTS

PREFACE

The thesis entitled **"INVESTIGATIONS ON THE SOLVENT EXTRACTION AND LUMINESCENCE OF LANTHANOIDS WITH MIXTURES OF HETEROCYCLIC β-DIKETONES AND VARIOUS NEUTRAL OXO-DONORS"** embodies the results of investigations carried out on the solvent extraction of trivalent lanthanoids with various heterocyclic β-diketones in the presence and absence of neutral oxo-donors and also on the luminescent studies of Eu^{3+}-heterocyclic β-diketonate complexes with Lewis bases. The primary objective of the present work is to generate the knowledge base, especially to understand the interactions of lanthanoid-heterocyclic β-diketonates with various macrocyclic ligands such as crown ethers and neutral organophosphorus extractants, with a view to achieve better selectivity. The secondary objective of this thesis is to develop novel lanthanoid luminescent materials based on 3-phenyl-4-aroyl-5-isoxazolones and organophosphorus ligands, for use in electroluminescent devices. The thesis comprises of seven chapters.

The introductory chapter highlights the need for the development of new mixed-ligand systems for the separation of lanthanoids. A general introduction on the solvent extraction chemistry has also been given in this chapter. Further, the development and importance of novel luminescent lanthanoid-β-diketonate complexes for display devices have been brought out towards the end of this chapter.

The second chapter gives a comprehensive review of literature on the recent developments in the synergistic solvent extraction of trivalent lanthanoids with heterocyclic β-diketones in the presence of various neutral oxo-donors. This chapter also incorporates the latest developments on the luminescence of lanthanoid-β-diketonate complexes.

The syntheses of various para substituted derivatives of 4-aroyl-5-isoxazolones and their characterization by various spectroscopic techniques have been described in chapter 3. This chapter also brings out the results of the investigations carried out on the solvent extraction behaviour of trivalent lanthanoids with 4-aroyl-5-isoxazolones in the presence and absence of various crown ethers such as 18C6, DC18C6, DB18C6 and B18C6. An attempt has also been made to understand the interactions of crown ethers with 4-aroyl-5-isoxazolonate complexes of lanthanoids using elemental analysis, IR and ^{1}H NMR spectral studies.

Chapter 4 embodies the results of the studies carried out on the synergistic extraction of trivalent lanthanoids with sterically hindered 1-phenyl-3-methyl-4-pivaloyl-5-pyrazolone in the presence of various structurally related crown ethers. The correlation between the selectivity and the distance between the donating oxygen atoms of 1-phenyl-3-methyl-4-pivaloyl-5-pyrazolone has been detailed in this chapter.

4-Acylbis(pyrazolones) of varying polymethylene chain length have been synthesized and utilized for studying the extraction behaviour of trivalent lanthanoids in the presence and absence of neutral organophosphorus extractants and the results are given in chapter 5. The extraction efficiency of lanthanoids has been correlated with the polymethylene chain length, phosphoryl oxygen donor basicity values and ^{31}P NMR chemical shift values of the complexes of Eu^{3+} with 4-sebacoylbis(1-phenyl-3-methyl-5-pyrazolone) in the presence of various organophosphorus extractants.

The syntheses, characterization and photophysical properties of Eu^{3+}-4-aroyl-5-isoxazolonate complexes in the presence of Lewis bases like trioctylphosphine oxide or triphenylphosphine oxide have been described in chapter 6. The photophysical properties of these complexes have been compared with the commercial phosphor Y_2O_3:5%Eu.

The contributions to the new knowledge arising out of this thesis have been highlighted in the concluding chapter. The relevant references used in this work have been cited towards the end of the thesis.

ABBREVIATIONS

acac	acetylacetone
BA	benzoyl acetone
bathophen	4,7-diphenyl-1,10-phenanthroline
B2EHSO	bis(2-ethylhexyl)sulphoxide
bipy	2,2'-bipyridine
br	broad
btfa	4,4,4-trifluoro-1-phenyl-1,3-butanedione
bzac	1-phenyl-1,3-butanedione
B15C5	benzo-15-crown-5
B18C6	benzo-18-crown-6
CE	crown ether
CMP	bis(2-ethylhexyl)-N,N-diethylcarbamoylmethyl phosphonate
CMPO	octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide
Cyanex 272	bis(2,4,4-trimethylpentyl)phosphinic acid
18C6	18-crown-6
15C5	15-crown-5
d	doublet
DAB	1,4-diaza-1,3-butadiene
DBM	dibenzoyl methane
DB18C6	dibenzo-18-crown-6
DBSO	dibenzoylsulphoxide
DC18C6	dicyclohexano-18-crown-6
D2EHPA	di-(2-ethylhexyl)phosphoric acid
DMSO	dimethyl sulfoxide
DPM	dipivaloylmethanato

EHEHPA	2-ethylhexylphosphonic acid mono-2-ethylhexyl ester
EL	electroluminescence
EPBM	1-ethyl-2-(2-pyridyl)benzimidazole
HFAA	hexafluoroacetyl acetone
HFBPI	3-phenyl-4-(4-fluorobenzoyl)-5-isoxazolone
HP	4-acyl-5-pyrazolones
HPBI	3-phenyl-4-benzoyl-5-isoxazolone
HPBM	2-(2-pyridyl)benzimidazole
HPMAP	1-phenyl-3-methyl-4-acetyl-5-pyrazolone
HPMBP	1-phenyl-3-methyl-4-benzoyl-5-pyrazolone
HPMOP	1-phenyl-3-methyl-4-octanoyl-5-pyrazolone
HPMPP	1-phenyl-3-methyl-4-pivaloyl-5-pyrazolone
HPMTFP	1-phenyl-3-methyl-4-trifluoroacetyl-5-pyrazolone
HTPI	3-phenyl-4-(4-toluoyl)-5-isoxazolone
HTTA	2-thenoyltrifluoroacetone
H_2AdBP	4-adipoylbis(1-phenyl-3-methyl-5-pyrazolone)
H_2DdBP	4-dodecandioylbis(1-phenyl-3-methyl-5-pyrazolone)
H_2SbBP	4-sebacoylbis(1-phenyl-3-methyl-5-pyrazolone)
H_2SuBP	4-suberoylbis(1-phenyl-3-methyl-5-pyrazolone)
LCMD	light conversion molecular devices
m	multiplet
MBDPO	methylenebis(diphenylphosphine oxide)
MHD	6-methyl-2,4-heptanedione
5Mphen	5-methylphenanthroline

NTA	1-(2-naphthoyl)-3,3,3-trifluoroacetonate
OLED	organic light emitting diodes
Phen	1,10-phenanthroline
PhenNO	1,10-phenanthroline-N-oxide
PL	photoluminescence
PMIP	1-phenyl-3-methyl-4-isobutyryl-5-pyrazolone
PMMA	poly(methylmethacrylate)
ppa	3-phenyl-2,4-pentanedione
s	singlet
t	triplet
TBP	tri-n-butylphosphate
TFA	trifluoroacetylacetone
TOPO	trioctylphosphine oxide
TPhPO	triphenylphosphine oxide
TTFA	thenoyltrifluoroacetone-4,4,4-trifluoro-1-(2-thenoyl)-1,3-butanedione

Chapter 1

Introduction

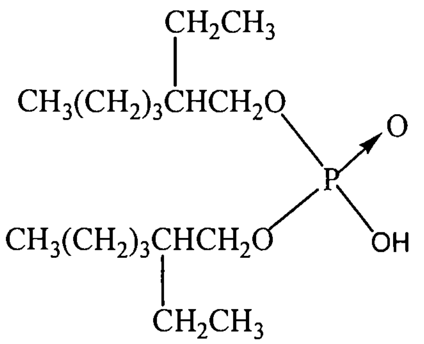
Inspite of the fact that β-diketones represent one of the oldest classes of chelating ligands, their coordination chemistry continues to attract much interests due to the recent industrial applications of several of their metal derivatives [Pettinari et al. 2004]. Several research groups recognize the potential of β-diketones as complexing agents in the extraction separation of lanthanoids in combination with many adduct forming reagents [Bond et al. 2000; Mathur 1983]. Lanthanoid-β-diketonates were also found to be useful as NMR shift reagents [Mehrotra et al. 1978]. They were extensively used in the synthesis of electro-ceramics e.g., superconductors such as $LnBa_2Cu_3O_{7-\delta}$ and $La_{2-x}Sr_xCuO_4$, piezoelectrics such as $LaCuO_2$ and buffer layers of $LaAlO_3$ [Malandrino et al. 1998]. They may also find application in the synthesis of LaF_3 films [Malandrino et al. 1995; Malandrino et al. 1996]. Progress has been made in the search for new lanthanoid-β-diketonates as sources of luminescence, with application in the fabrication of polymer, light emitting diodes for low cost, full color, flat-panel displays [Huang et al. 2001; Kido and Okamoto 2002; Thompson et al. 2002; Molina et al. 2003]. Recently, some lanthanoid-β-diketonate adducts containing particular Lewis bases such as 1-N-alkyl-4-alkyloxy-2-hydroxy-benzaldimines were also proven to exhibit interesting mesomorphic properties [Binnemans and Lodewyckx 2001].

The primary objective of the present work is to generate the knowledge base, especially to understand the interactions of lanthanoid-heterocyclic β-diketonates with various macrocyclic ligands such as crown ethers and neutral organophosphorus extractants, with a view to achieve better selectivity. The secondary objective of this thesis is to develop new lanthanoid luminescent materials involving heterocyclic β-diketones such as 3-phenyl-4-aroyl-5-isoxazolones and neutral oxo-donors for use in electroluminescent devices.

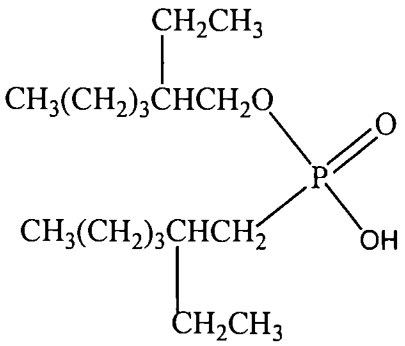
1.1. Separation of Lanthanoids: Solvent Extraction

The separation of trivalent lanthanoids offers a formidable challenge in the field of separation science in view of their similar physico-chemical properties. With increasing demand for lanthanoid elements and their compounds individually and collectively, based on their newer and proven applications in modern technology, the separation and purification of these elements has gained considerable importance over the years. It is well known that separation processes based on ion exchange technique yield high purity compounds of lanthanoids. However, these processes are time consuming and inherently expensive. Methods based on liquid-liquid extraction emerged as a novel and unique technique for the separation of metal ions because of its simplicity, versatility, easy recovery and ready adaptability to scaling up of the process. Various kinds of acidic organophosphorus extractants such as D2EHPA, EHEHPA and Cyanex 272 have been widely used in the Rare Earth Industry for the separation and purification of these metal ions [Powell 1979; Reddy et al. 1995b]. However, even with these extractants, a large number of separation steps are necessary to obtain highly purified lanthanoids in view of their lower separation factors. The average separation factors between adjacent lanthanoids in most cases vary between 1.5 and 2.5 [Pierce and Peck

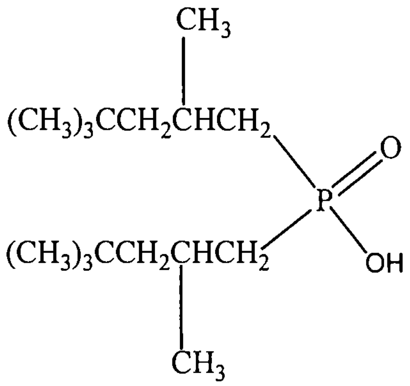
1963]. Thus there is a growing interest in the development of new extraction systems including the use of ion-specific compounds and mixed-ligand systems for the separation of lanthanoids.



D2EHPA



EHEHPA



CYANEX 272

The introduction of cation-selectivity into synergistic solvent extraction systems is best accomplished by the use of crown ethers that form both stable in-cavity complexes with the target cation and have adequate functionalisation to impart organophilicity. The former criterion requires some understanding of the coordination chemistry and particularly, knowledge of the solution speciation of the cation and extractants. However, remarkably few studies of synergistic extraction have probed the cation coordination environment [Mathur and Choppin 1993; Bond et al. 2000]. Significant fundamental and developmental research is still required; however, only with well-planned and carefully executed research, will the potential of size selective synergism be realized. Hence, in the present work, an attempt has been made to understand the interactions of various neutral oxo-donors with lanthanoid-β-diketonate complexes.

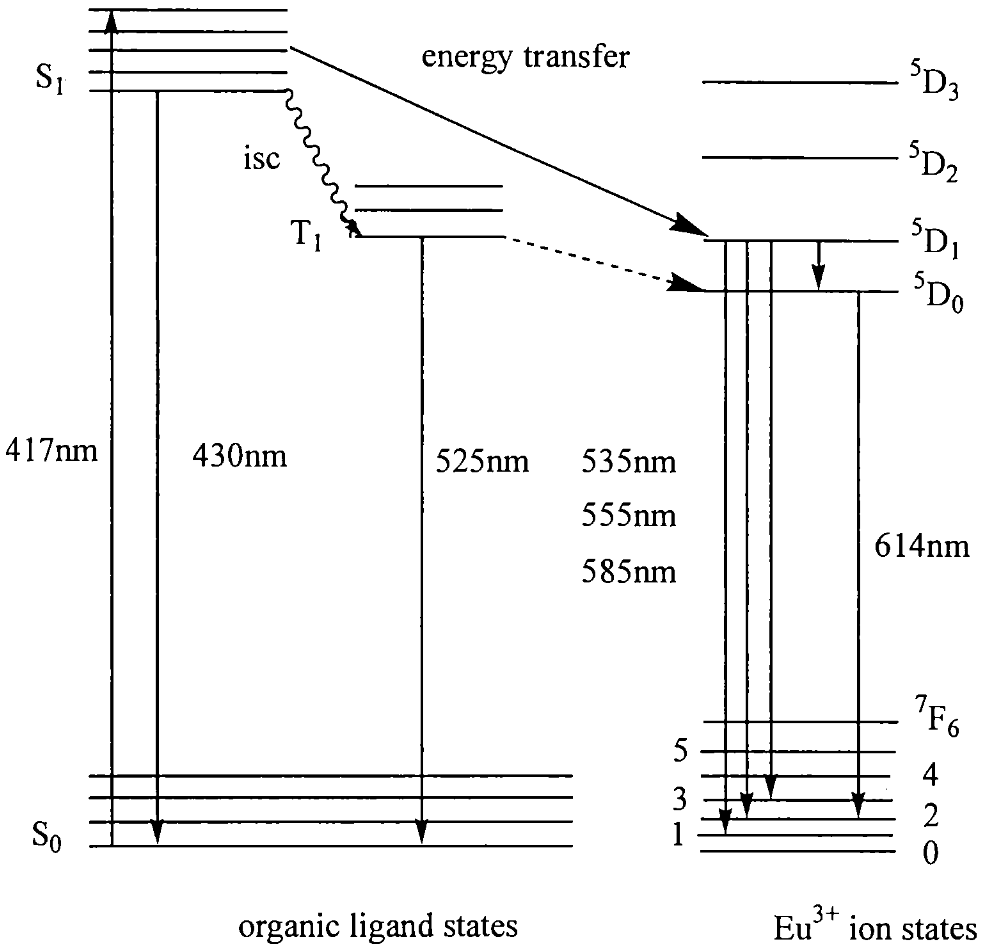
1.2. Luminescence of Lanthanoid-β-diketonate Complexes

Efficient light converting molecular devices (LCMDs) may find several applications, such as luminescent probes, in biomedical assays and time resolved microscopy, fluorescent lighting, luminescent sensors for chemical species, electroluminescent devices, UV-dosimeters, or antireflection coating for solar cells. Besides the quantum yield of a LCMD, other aspects, such as light output, solubility, volatility and photo-, thermal-, and thermodynamic stabilities may be critical to many applications and must also be controlled [de Sa et al. 2000].

Molecular lanthanoid chelates containing β-diketonates have been successfully used in the production of emission layers in organic electroluminescent devices [Kido and Okamoto 2002; de Sa et al. 2000]. Organic light emitting diodes (OLEDs) have been intensively studied throughout the world owing to their potential application in the next generation of full-color, flat panel displays. Organic and polymeric electroluminescence across the whole visible region from blue to red has been demonstrated and the efficiency, brightness and device lifetime are rapidly approaching commercial target figures. However, it is difficult to achieve pure emission colors from small organic molecules or conjugated polymers because their emission spectra typically have a full-width at half maximum wavelength of ca.100 nm, which is not well suited for actual display applications.

Luminescent lanthanoid complexes are good candidates to solve this problem because lanthanoid-based materials can generate extremely pure emission due to the $^5D_0 \rightarrow {}^7F_2$ transition from central Eu^{3+} ion [Kido et al. 1990; Baldo et al. 1998; Robinson et al. 2000; Wang et al. 2001; Hong et al. 2001; Sun et al. 2002]. In addition to the spectral profile of the complexes, the excitation mechanism of the central metal ion also differs widely from that of organofluorescent compounds. Further, in the organic fluorescent compounds, the excited energy of the triplet state will be degraded through thermal deactivation processes without the emission of photons. In contrast, for lanthanoid complexes with π-conjugated ligands such as β-diketonates, the lanthanoid ions are excited via intramolecular energy transfer from the triplet excited states of the ligands.

The interest in the photophysical properties of Ln^{3+} ion complexes has been greatly intensified after Lehn's proposition that such complexes could be seen as LCMDs, coining the term "antenna effect" to denote the absorption, energy-transfer, emission sequence involving distinct absorbing (the ligand) and emitting (the lanthanoid ion) components of the supramolecular species, thus overcoming the very small absorption coefficients of the lanthanoid ions. Luminescence in lanthanoid organic compounds is due to intramolecular energy transfer from the excited ligand triplet state to the chelated ion. The efficiency of this energy transfer depends on the efficiency of the organic ligand absorption, the ligand-to-metal energy transfer and the lanthanoid luminescence [Sabbatini et al. 1993; de Sa et al. 2000]. To improve the energy transfer to the lanthanoid ions, the triplet states of the ligands must be closely matched to or slightly above the emitting resonance levels of the metal ion.



Energy transfer in lanthanoid complexes

The excitation energy of the ligand triplet state, which may be directly generated by carrier recombination, can also utilize to excite the emitting center. Thus there is no limitation, upto 100%, of the internal quantum efficiencies for devices using lanthanoid ion-chelate as emitters.

Therefore, in the present work, investigations have been carried out to develop novel europium complexes as the emitting layer involving heterocyclic β-diketones in the presence of various neutral organophosphorus reagents.

1.3. Solvent Extraction: General

Solvent extraction highlights the usefulness of phase distribution and is based on the principle that a solute can distribute itself in a certain ratio between two immiscible solvents. In this method, a solute distributes itself between an aqueous and organic phase. According to Gibbs phase rule,

$$P + V = C + 2 \qquad (1)$$

(where P, the number of phases, V, the variance or degrees of freedom and C, the number of components). The distribution of a solute between two immiscible solvents is univariant at constant temperature and pressure. That is, if we choose the concentration of the solute in one phase, its concentration in the other phase is fixed.

The distribution law, stated by Berthelot and Jungfleisch, states that at a particular temperature for a solute 'X' distributing between two immiscible solvents 1 and 2, at equilibrium, the ratio of concentrations of the two phases is a constant, provided the nature of the species is the same in both the phases.

$$D = [X]_1/[X]_2 \qquad (2)$$

The constant, D, is known as the distribution or extraction coefficient. The chemical potential of the solute is the same in each phase at equilibrium, provided temperature and pressure are constant, i.e.,

$$\mu_1 = \mu_2 \qquad (3)$$

where the subscripts 1 and 2 refer to the respective solvent phases. Substituting suitable expressions of μ,

$$\mu_1^o + RT \ln m_1 + RT \ln \gamma_1 = \mu_2^o + RT \ln m_2 + RT \ln \gamma_2 \quad (4)$$

where μ^o represents the chemical potential of the solute in a hypothetical ideal 1 molal solution, *m*, the solute concentration in molality and γ, the molal activity coefficient. The molal distribution coefficient,

$$D = \frac{m_2}{m_1} = \frac{\gamma_1}{\gamma_2} e^{-(\mu_2^o - \mu_1^o)/RT} \quad (5)$$

For a system in which the two solvents are completely immiscible under all circumstances the exponential term is a constant, *K*, so that

$$D = \frac{m_2}{m_1} = \frac{\gamma_1}{\gamma_2} K \quad (6)$$

Thus, *D* depends on the activity coefficients of the solute in each of the phases. When the activity coefficients approach unity, i.e., at low concentrations, *D* becomes constant. The distribution coefficient is related to the percentage extraction, E, by the equation

$$E = \frac{100D}{D + \frac{V_{aq}}{V_{org}}} \quad (7)$$

where V_{aq} and V_{org} are the volumes of the aqueous and organic phases, respectively. The separation factor, S.F., is given by

$$\text{S.F.} = D_1/D_2 \quad (8)$$

where D_1 and D_2 are the distribution coefficients for elements 1 and 2, respectively.

1.3.1. Synergistic solvent extraction

The phenomenon in which two extractants taken together extract a metal ion species with much higher efficiency as compared to the normal additive effect of these extractants (separately) is called 'synergism'. The converse of this effect is called 'antagonism'.

An increase in the hydrophobic character of the extracted metal complex is observed in the synergistic extraction of mixed complexes. Three different mechanisms are postulated [Choppin and Morgenstern 2000]. The first one involves the opening of one or more of the chelate rings and occupation by the adduct molecule(s) of the vacated metal coordination site(s). In the second mechanism, the metal ion is not coordinately saturated by the ligand and hence, it retains residual water in the coordination sphere, which can be replaced by the adduct molecules. The third mechanism involves an expansion of the coordination sphere of the metal ion to allow bonding of the adduct molecules.

1.3.2. Measure of synergism

The synergistic coefficient (S.C.) may be described by

$$\text{S.C.} = \log \frac{D_{(1,2)}}{D_1 + D_2}$$

where D_1, D_2 and $D_{(1,2)}$ are the distribution coefficients of a metal ion with two extractants taken separately and with the mixture of the two extractants, respectively. When S.C. > 0, the extraction is synergistic. The cases where S.C. < 0 involve an antagonistic effect.

Chapter 2

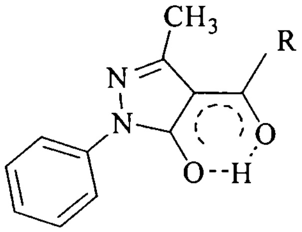
Literature Review

2.1. Synergistic Solvent Extraction of Trivalent Lanthanoids: Literature Review

The extraction of trivalent lanthanoids with mixtures of various β-diketones and adduct forming reagents has been extensively investigated and these data are well documented in reviews on "Synergistic extraction of lanthanides and actinides" [Mathur 1983; Bond et al. 2000].

2.1.1. Extraction of lanthanoids with 4-acyl-5-pyrazolones in the presence and absence of various neutral oxo-donors

1-Phenyl-3-methyl-4-acyl-5-pyrazolones, which are heterocyclic β-diketone ligands, have been widely used as extractants for many metal ions. These reagents are so called "hard bases", having coordinating oxygen atoms and are suitable especially for the extraction of "hard acids" such as lanthanoids. The nature of the substituent in the 4-position of pyrazolone ring causes significant variations in the electronic, steric and solubility parameters of the ligand, thereby affecting complexation and extraction behaviour. Further, these ligands were found to have longer distances between the two donating oxygens (bite size) as compared to the conventional β-diketones, such as acetylacetone and HTTA, according to the estimation by molecular orbital calculations.



R =

CH_3	HPMAP
$C(CH_3)_3$	HPMPP
Ph	HPMBP
CF_3	HPMTFP

Recently, the relationship between the bite size of the 4-acyl-5-pyrazolones and the selectivity in the extraction of lanthanoids has been investigated and reported that the O---O distance is one of the most significant factors that governs the selectivity in the complexation of 4-acyl-5-pyrazolones with metal ions [Umetani et al. 2000].

2.1.1.a. *Extraction of Ln^{3+} ions with 4-acyl-5-pyrazolones:*

The extraction equilibrium of trivalent lanthanoids with 4-acyl-5-pyrazolones (HP) has been well studied by many investigators and simple metal chelate formation has been reported [Roy and Nag 1977; Umetani et al. 1980; Sasaki and Freiser 1983; Sasayama et al. 1983; Umetani and Freiser 1987; Mukai et al. 1990; Saleh et al. 1990; Sujatha et al. 1994; Luxmi Varma et al. 1996; Thakur et al. 1996; Sujatha et al. 1996; Mukai et al. 1997; Umetani et al. 2000; Mukai et al. 2003].

$$Ln^{3+}_{aq} + 3\,HP_{org} \overset{K_{ex,0}}{\rightleftharpoons} LnP_{3\,org} + 3\,H^{+}_{aq}$$

On the other hand, the formation of self-adducts have been noticed in the extraction of Ln^{3+} ions with HPMTFP and HPMBP [Dukov and Genov 1986; Dukov and Genov 1986a; Mathur and Khopkar 1987; Mathur and Khopkar 1988; Dukov and Genov 1988; Dukov 1992; Santhi et al. 1994; Reddy et al. 1995; Dukov and Jordanov 1996; Dukov and Jordanov 1996a;

Dukov 1997; Dukov and Jordanov 1998; Jordanov et al. 2002; Jia et al. 2003].

$$\mathrm{Ln^{3+}_{aq}} + 4\,\mathrm{HP_{org}} \overset{K_{\mathrm{ex},0}}{\rightleftharpoons} \mathrm{LnP_3.HP_{org}} + 3\,\mathrm{H^{+}_{aq}}$$

where HP = HPMTFP. The equilibrium constants of $\mathrm{Ln^{3+}}$ ions with various 4-acyl-5-pyrazolones were found to increase monotonically with decreasing ionic radii of $\mathrm{Ln^{3+}}$ ions [Sasaki and Freiser 1983; Umetani and Freiser 1987; Dukov and Genov 1988; Saleh et al. 1990; Dukov 1992; Santhi et al. 1994; Sujatha et al. 1994; Reddy et al. 1995; Dukov and Jordanov 1996; Luxmi Varma et al. 1996; Thakur et al. 1996; Sujatha et al. 1996; Umetani et al. 2000; Jordanov et al. 2002]. Further, a linear relationship between log K_{ex} and pK_{a} values of various 4-acyl-5-pyrazolones in the extraction of $\mathrm{Ln^{3+}}$ ions has also been observed [Umetani et al. 1980; Sasayama et al. 1983; Mukai et al. 1990; Saleh et al. 1990; Mukai et al. 1997; Umetani et al. 2000; Mukai et al. 2003].

2.1.1.b. Extraction of $\mathrm{Ln^{3+}}$ ions with mixture of 4-acyl-5-pyrazolone and crown ethers:

The synergistic extraction of $\mathrm{Eu^{3+}}$ ion with mixtures of HPMTFP and crown ether, DC18C6 or B15C5 has been investigated [Mathur and Khopkar 1988] in chloroform and the extraction equilibrium has been reported as:

$$\mathrm{Eu^{3+}_{aq}} + 4\,\mathrm{HP_{org}} + \mathrm{DC18C6_{org}} \overset{K_{\mathrm{syn},1}}{\rightleftharpoons} \mathrm{EuP_3.HP.DC18C6_{org}} + 3\,\mathrm{H^{+}_{aq}}$$

$$\mathrm{Eu^{3+}_{aq}} + 3\,\mathrm{HP_{org}} + n\,\mathrm{B15C5_{org}} \overset{K_{\mathrm{syn},n}}{\rightleftharpoons} \mathrm{EuP_3.}n\mathrm{B15C5_{org}} + 3\,\mathrm{H^{+}_{aq}}$$

where HP = HPMTFP and $n = 1$ or 2. The high stability of the synergistic complexes has been attributed to the attachment of more than one oxygen atom of crown ether with the metal chelates.

Partitioning of Pr^{3+}, Gd^{3+} and Yb^{3+} by B15C5 and HPMBP in CCl_4, C_6H_6 or $CHCl_3$ is reported and the number of B15C5 molecules in the extracted complexes is shown to vary with the diluent [Dukov 1992]. Slope analyses indicate that $Ln(PMBP)_3$.B15C5 is extracted into $CHCl_3$ or C_6H_6, while a mixture of mono and bis B15C5 adducts is observed in CCl_4.

The extraction of Ln^{3+} ions with HPMTFP in the presence of various crown ethers, 18C6, DB18C6, 15C5 or B15C5 into $CHCl_3$ has been investigated and found significant synergistic enhancement in the extraction of these metal ions (10-100 fold in the case of Nd^{3+}; 2-40 fold in the case of Eu^{3+} and 1-20 fold in the case of Tm^{3+}) [Thakur et al. 1996]. The synergistic equilibrium constants of Ln^{3+} ions are found to increase monotonically with decrease in ionic radii of these metal ions. The organic phase stability constants of the synergistically extracted species with various crown ethers follow the order: 18C6 > 15C5 > B15C5 > DB18C6, which is also the basicity sequence of these CEs. The sharp decrease in the complexation from 18C6 to DB18C6 for these trivalent metal ions mostly reflects the increasing steric effects as well as decreasing basicity.

2.1.1.c. Extraction of Ln^{3+} ions with mixture of 4-acyl-5-pyrazolones and neutral organophosphorus extractants:

The synergistic extraction of Ln^{3+} ion with HPMBP from nitrate solutions in the presence of various neutral organophosphorus extractants such as TBP and TOPO has been well studied and these data are covered in a review on synergism of trivalent lanthanides and actinides [Mathur 1983]. The synergistic species extracted into the organic phase have been established as $Ln(PMBP)_3.(TBP)_2$, $Ln(PMBP)_3.(TOPO)_2$ and $Ln(PMBP)_2.NO_3(TOPO)_2$.

Mixed-ligand chelate extraction of Ln^{3+} ions with HPMTFP in the presence of various phosphine oxides, TOPO, CMPO and MBDPO from perchlorate solutions into chloroform has been studied [Umetani and Freiser 1987]. Ln^{3+} ions are found to be extracted as $Ln(PMTFP)_3.(TOPO)_2$, $Ln(PMTFP)_3.CMPO$, respectively. On the other hand, with mixtures of HPMTFP and MBDPO, the extracted species are found to be $Ln(PMTFP)_3.MBDPO$ or $Ln(PMTFP)_2.(ClO_4)\ (MBDPO)_2$. The synergistic equilibrium constants of these systems do not increase monotonically with increase in atomic number, but have a maximum at Eu^{3+} or Ho^{3+}. The stability constants of these mixed-ligand complexes decrease monotonically with increase in atomic number. Generally, in mixed-ligand extraction system of lanthanoids, the decrease of the adduct formation constants could be explained by a diminution of the co-ordination power of the lanthanoid ion resulting from a stable chelate, with a consequently less stable adduct formation. In addition, the Ln^{3+} ion, to which three molecules of chelating agents have already been co-ordinated, allows space for the adduct forming reagent in proportion to its ionic radius, so that steric hindrance for adduct formation increases with atomic number. Hence, when the equilibrium constant of the adduct formation reaction decreases rapidly, the reversal of the extractability, i.e., the extraction constant, takes place. Although, addition of an adduct-forming reagent can bring a decrease of the separation factor, it is notable that addition of TOPO or MBDPO improves the separation of the heavier lanthanoids by virtue of a surprising increase in the extractability of lighter metals to a greater extent than that of the heavier ones.

The synergistic extraction of Ln^{3+} ions with 4-acyl-5-pyrazolones in the presence of sterically hindered branched chain extractant, B2EHSO, TPhPO or bifunctional organophosphorus extractants, CMPO and CMP has been investigated and significant enhancement in the extraction efficiency has been reported (10-100 fold) [Luxmi Varma et al. 1996; Sujatha et al. 1996; Reddy et al. 1995; Santhi et al. 1994]. The synergistic extraction equilibria of Ln^{3+} ions with various 4-acyl-5-pyrazolones in the presence of B2EHSO has been reported as:

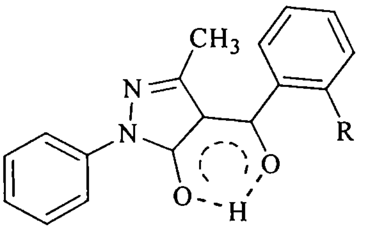
$$Ln^{3+}_{aq} + 3\ HP_{org} + n\ B2EHSO_{org} \xrightleftharpoons{K_{syn,n}} LnP_3.nB2EHSO_{org} + 3\ H^{+}_{aq}$$

where HP = HPMBP, HPMAP and HPMTFP and n = 0, 1 and 2. On the other hand, in the presence of bifunctional organophosphorus extractants, the synergistic equilibrium has been reported as:

$$Ln^{3+}_{aq} + 3\ HP_{org} + S_{org} \xrightleftharpoons{K_{syn}} LnP_3.S_{org} + 3\ H^{+}_{aq}$$

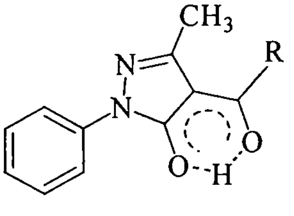
where S = CMPO or CMP. The addition of a B2EHSO improves the selectivity among these lanthanoids. However, the addition of bifunctional organophosphorus extractants decreases the selectivity. The IR spectral data indicates that CMP acts as a bidentate ligand in these mixed-ligand complexes [Luxmi Varma et al. 1996]. The equilibrium constants of the synergistic complexes have been deduced by non-linear regression analysis and are found to increase monotonically with decreasing ionic radii of these metal ions. The adduct formation constants of these mixed-ligand complexes decrease with decrease in ionic radii of these metal ions.

Steric effects of ortho substituents of 1-phenyl-3-methyl-4-aroyl-5-pyrazolones on the synergistic extraction of Ln^{3+} ions with TOPO have been studied. Obvious steric hindrance by ortho substituent was observed in the extraction reactions especially in the adduct formation reactions. The steric hindrance is determined by three factors: bulkiness of the substituents, proximity of the neutral ligand to the metal chelate and the crowdedness of the ligands around the central metal ion [Mukai et al. 1990; Mukai et al. 1997; Mukai et al. 2003].



R =
H
2 - CH_3
2 - OCH_3
2 - CF_3
2 - F
2 - Cl
2 - Br

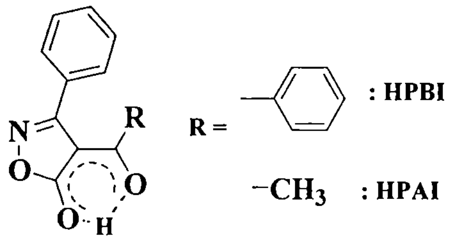
The substituent effect of several 1-phenyl-3-methyl-4-acyl-5-pyrazolones on the adduct formation between Eu^{3+} chelate and TOPO in C_6H_6 has been studied by liquid-liquid extraction [Sasayama et al. 1983]. The Eu-acylpyrazolonates react with TOPO to form adduct of the EuR_3L type for an aliphatic group and EuR_3L_2 type for an aromatic and trifluoromethyl groups. The stability of adducts increases in the order: aliphatic < aromatic < trifluoromethyl. A steric effect of the terminal group on adduct formation was observed for 2-, 3- and 4- methyl substituted benzoyl pyrazolonates of Eu^{3+} ion.



R =
Phenyl
2 - chlorophenyl
2,4 - dichlorophenyl
4 - chlorophenyl
2 - methylphenyl
3 - methylphenyl
4 - methylphenyl
Trifluoromethyl
Cyclohexyl
2 - naphthyl
n-Heptyl
Methyl

2.1.2. *Extraction of lanthanoids with 4-acyl-5-isoxazolones in the presence and absence of various neutral oxo-donors*

Preliminary studies show that 4-acyl-5-isoxazolones (acyl = acetyl and benzoyl) are potential extractants for f-elements [Jyothi and Rao 1988; Jyothi and Rao 1989; Jyothi and Rao 1990]. Among 4-acyl-5-isoxazolones, HPBI has come to occupy a special place in the solvent extraction of metal ions due to its lower pK_a value (1.23).



The extraction behaviour of trivalent lanthanoid ions (Ln^{3+}) into chloroform from perchlorate solutions with HPBI has been investigated [Le et al. 1993]. The results have demonstrated the formation of simple metal chelates.

$$Ln^{3+}_{aq} + 3\ HPBI_{org} \overset{K_{ex,0}}{\rightleftharpoons} Ln(PBI)_{3\,org} + 3\ H^{+}_{aq}$$

The extraction of lanthanoids increases with increasing atomic number (log $K_{ex,\,La}$ = -1.77; log $K_{ex,\,Pr}$ = -1.20; log $K_{ex,\,Eu}$ = -0.39; log $K_{ex,\,Ho}$ = -0.36; log $K_{ex,\,Yb}$ = -0.30). The equilibrium constants of the simple metal chelates of Ln^{3+} ions with HPBI (log $K_{ex,\,Eu}$ = -0.39) are found to be much higher than that with HTTA (log $K_{ex,\,Eu}$ = -7.66) and 4-acylpyrazolones (log $K_{ex,\,Eu}$ with HPMTFP = -3.78; log $K_{ex,\,Eu}$ = -5.33 with HPMBP). Synergistic effects have been observed in the extraction of Ln^{3+} ions in the presence of adduct forming reagent like TOPO. The synergistic extraction equilibrium of Ln^{3+} ions with HPBI in the presence of TOPO has been reported as:

$$Ln^{3+}_{aq} + 3HPBI_{org} + mTOPO_{org} \xrightleftharpoons{K_{Syn,m}} Ln(PBI)_3.mTOPO_{org} + 3H^{+}_{aq}$$

where m = 0, 1 and 2. The synergistic equilibrium constants were found to increase monotonically with increase in atomic number up to Eu^{3+} ion and thereafter show a decreasing trend unlike that of simple metal chelates.

The synergistic extraction of Ln^{3+} ions with HPBI in the presence of various crown ethers such as 18C6, 15C5, B15C5 or DB18C6 has been studied. The addition of CE to the metal chelate system not only enhances the extraction efficiency (10^2) but also improves the selectivity among these metal ions. The equilibrium constants of the synergistically extracted complexes are found to increase monotonically with decreasing ionic radii of Ln^{3+} ions. Further, it also improves the selectivity among Nd-Eu pairs. The complexation strength of Ln^{3+} ions with various CEs follows the order: 18C6 > 15C5 > B15C5 > DB18C6, which is in accordance with the basicity of crown ethers [Reddy et al. 1997].

An attempt has also been made to use various 4-acyl-5-isoxazolone derivatives in the presence of TBP for the extraction of Ln^{3+} ions and reported the extracted species as $LnX_3.2TBP$ where X denotes the anion of 4-acyl-5-isoxazolone [Odashima et al. 1995].

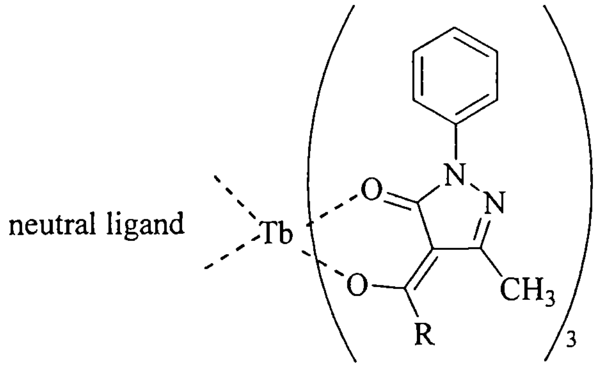
2.2. Luminescence of Organolanthanoid Complexes: Literature Review

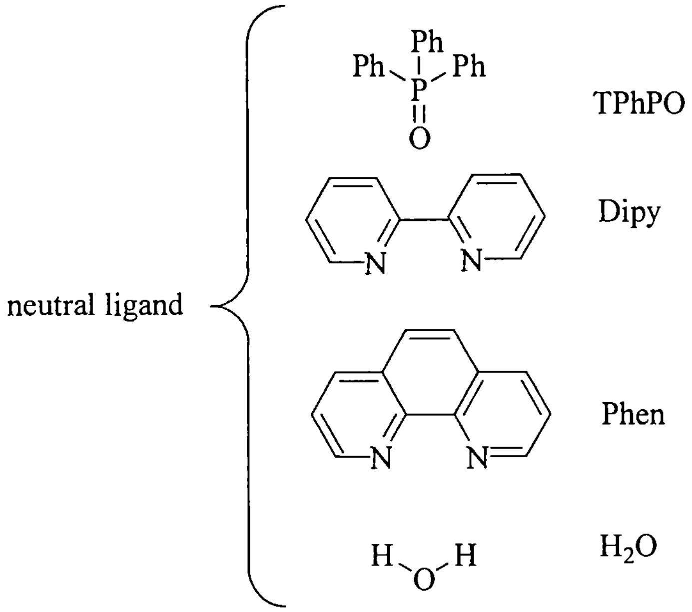
Advances in the development of efficient light conversion molecular devices (LCMD) based on lanthanoid complexes are brought out in a recent review article [de Sa et al. 2000]. A critical review on the use of organolanthanoid metal complexes as emitting layers in electroluminescent devices is also available [Kido and Okamoto 2002].

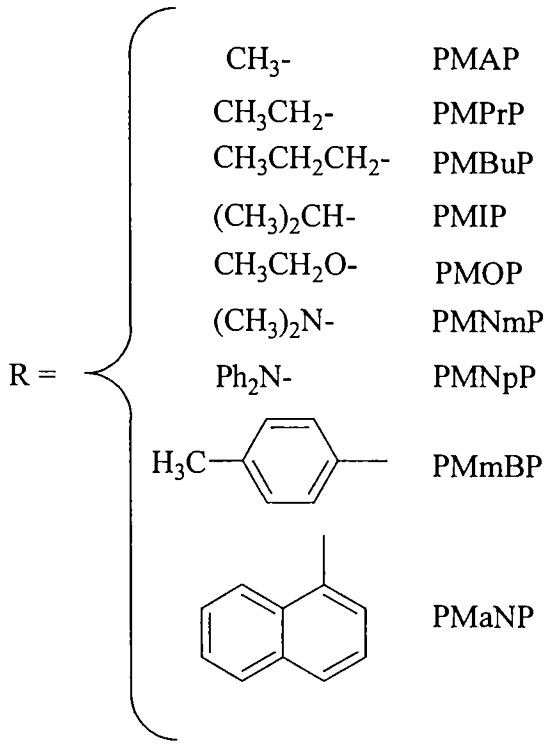
Molecular lanthanoid chelates containing 4-acylpyrazol-5-onate ligands have been successfully used in the production of emission layers in organic electroluminescent devices [Kido and Okamoto 2002; Gao et al. 1998].

The photoluminescence (PL) and electroluminescence (EL) properties of PMIP complexes of Lu^{3+} ion in the presence of TPhPO, bipy and phen have been investigated. The PL intensity of complex containing TPhPO is about 100 times higher than that of complexes containing bipy and Phen as adduct forming reagents. Blue light originating from $Lu(PMIP)_3.2TPhPO$, with a luminescence of 119 cd m^{-2} was obtained by constructing a configured device. Although the PL intensity of complexes containing bipy and Phen was weaker than that of $Lu(PMIP)_3.2TPhPO$ complex, they displayed a better EL performance because of formation of the exciplex. Further, the above results indicate that not only complexes with high PL intensities can be used as emitters in OLEDs, but also that those showing weak or no PL have potential applications if they can form exciplexes with a high EL efficiencies [Xin et al. 2003].

Photoluminescence and electroluminescence of a series of terbium complexes based on 1-phenyl-3-methyl-4-acyl-pyrazolone-5 were investigated [Gao et al. 1999]. It is clear from the results that when the substituent at the 4th position changes from a strong electron attracting group as in PMFP-Tb-TPhPO to an electron donating group as in PMOP-Tb-TPhPO, the quantum efficiency of the complex increases remarkably. The neutral ligands such as TPhPO, Phen, dipyridine, water also affect the photoluminescence and electroluminescence of terbium complexes. A photochemical explanation for the influence of the acyl group and the neutral ligand on the photoluminescence was proposed in relation to ligand-to-metal energy transfer. The electroluminescence of terbium complexes having a neutral ligand comes from both the light emitting layer and the hole transport layer while the electroluminescence of the terbium complex without a neutral ligand is pure green coming solely from the light emitting layer. It therefore demonstrates that the former has higher electron transport ability than the latter.

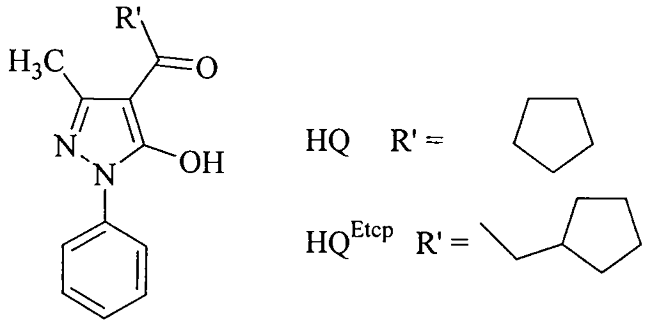






Structure of the terbium pyrazolonate complex with various neutral ligands

Recently, the synthesis and characterization of new lanthanoid complexes of the formula $[M(Q)_3(H_2O)(EtOH)]$, $NBu_4[M(Q)_4]$ and $[M(Q)_3(L)]$ (M= Eu or Tb; HQ = 1-phenyl-3-methyl-4-R-pyrazol-5-one; R = cyclopentylcarbonyl and cyclopentylpropionyl; L = 1,10-phenanthroline (phen) or 4,7-diphenyl-1,10-phenanthroline (bathophen)) are reported [Pettinari et al. 2004a]. Luminescence studies have been performed and the data suggested a strong influence of the nature of the acyl moiety in Q ligands and of phenyl groups in bathophen on luminescence properties.



Structure of the proligands HQ^{cp} and HQ^{Etcp}.

A series of ternary mixed-ligand 4-acyl-5-pyrazolone lanthanoid complexes: $LnQ_3.2H_2O$ (where $Ln^{3+} = Tb^{3+}$ or Gd^{3+} and Q = 1-phenyl-3-methyl-4-acyl-pyrazolone-5 where acyl = propionyl, acetyl, isobutyryl, neovaleryl or benzoyl) have been synthesized and characterized by FT-IR, UV-spectra and TG-DTA analysis [Zhou et al. 1997]. Room temperature phosphorescence was observed from the Gd^{3+} complexes by excitation of the sample with the fourth harmonic frequency of Nd:YAG laser beam (λ = 266 nm) and the triplet energies of the pyrazolone ligands were evaluated. Both the fluorescence intensity and fluorescence lifetime of terbium complexes depend on the structure of the ligands. The crystal structure of $[Tb(PMPP)_3.2H_2O].EtOH$ was determined by X-ray diffraction and the complex was found to be mononuclear. Tb^{3+} ion is coordinated to 8 oxygen atoms (six of which are from the 3 bidentate pyrazolone ligands and the other 2 are from the two coordinated water molecules) to form a square antiprism coordination polyhedron. It has been concluded from the above study that the substitution of the benzoyl group with an acyl group may decrease the electron conjugate system to yield a ligand with a higher triplet energy level, so that ligand-to-metal energy transfer may proceed much more easily.

The time resolved emission spectra and lifetimes of a series of lanthanoid-acylpyrazolone complexes were measured under 266 nm laser excitation. The phosphorescence spectra of the triplet states of the Gd^{3+} complexes were observed at room temperature. The relative efficiencies of intramolecular energy transfer from the triplet state of different ligands to the $^5D_4$ level of Tb^{3+} ion have been quantitatively calculated on the basis of the exchange-interaction theory. The properties and functions of ligand-localized excited singlet and triplet states have been discussed and identified the triplet energy level as one of the key parameters in intramolecular energy transfer. The illumination efficiency of the Tb^{3+} complex is associated with two factors: one is the lifetimes of the singlet and triplet states of the ligand and the $^5D_4$ level of Tb^{3+} ion and the other is the intersystem-crossing rate of the ligand and the energy transfer rate from triplet state to the $^5D_4$ level [Ying et al. 1996].

Influence of ligands on the photoluminescent properties of Eu^{3+} ion in Eu-β-diketonates/poly(methylmethacrylate) doped systems have been studied. The three kinds of Eu-β-diketonates, $Eu(DBM)_3$, $Eu(BA)_3$ and $Eu(TTA)_3$ were doped in PMMA matrix. Eu^{3+} ions in the doped $Eu(DBM)_3$/PMMA systems have two distinct symmetric sites and the emission band changes greatly with the compositions. The results highlight that the interaction between the chelate molecules and between the chelate and PMMA are different for $Eu(DBM)_3$, $Eu(BA)_3$ and $Eu(TTA)_3$. For $Eu(DBM)_3$, the carbonyl groups coordinate to the Eu^{3+} ion resulting in the variation of the first coordination sphere around the Eu^{3+} ion, leading to the great change in the photoluminescence properties. On the other hand, crystallites formed in the doped systems due to the stronger interaction between the chelates, may be the π-π interactions between the phenyl groups, causing the inhomogeneous broadening of the emission bands. For

$Eu(BA)_3$ and $Eu(TTA)_3$, these two chelates dispersed well in PMMA due to the interaction between $-CH_3$ groups in PMMA and $-CH_3$ and $-CF_3$ groups in the chelate, the emission bands are narrower than those of the corresponding $Eu(DBM)_3$ sample, and the first coordination sphere around Eu^{3+} ion keeps, resulting in similar photoluminescent properties [Liu et al. 2004].

Oxadiazole-functionalised Eu^{3+} dibenzomethanate and oxadiazole functionalised Tb^{3+} (DBM) complexes have been used as emitting layers in OLEDs [Wang et al. 2001; Liang et al. 2003]

A novel Eu^{3+} complex, tris(dibenzoylmethanato)(2-4'-triphenylamino)imidazo [4,5-f]1,10-phenanthroline-europium(III), $Eu(DBM)_3(TPIP)$, was synthesized by integrating light-emitting-centre, hole-transporting triphenylamine and electron-transporting phenanthroline fragments into one molecule and utilized as emitting layer in the electroluminescence devices [Sun et al. 2003; Bian et al. 2004].

[$Eu(DBM)_3$.HPBM], [$Eu(DBM)_3$.Phen], [$Eu(DBM)_3$.bath] and [$Eu(DBM)_3$.EPBM] were prepared and used as emitting materials in organic electroluminescent materials [Liu et al. 1997; Hong et al. 1997; Huang et al. 2001].

Synthesis, characterization and photoluminescent properties of the $Eu(ppa)_3.2H_2O$ and $Eu(ppa)_3$.Phen have been reported. The study reports a new complex of Eu^{3+} ion with a β-diketone with a phenyl group attached to the centre of the coordination ring, which represents an efficient antenna molecule for the transfer of the absorbed energy to lanthanoid ion. The ternary complex, $Eu(ppa)_3$.Phen synthesized present a strong luminescence, with the characteristic very sharp bands of the transitions $^5D_0 \rightarrow {}^7F_J$ (J = 0-4) of Eu^{3+} (band widths of $^5D_0 \rightarrow {}^7F_2$ at 610.6 nm = 15 cm^{-1} and

$^5D_0 \rightarrow {}^7F_0$ at 578.8 nm = 12 cm^{-1}), becoming a promising candidate as luminescent material for photoluminescence applications [Ribeiro et al. 2004].

Adducts of the type $Ln(NTA)_3.L$ (Ln = Eu^{3+}, Gd^{3+}; L = DAB, DMSO, Phen, bipyrimidine, bipy, H_2O) have been prepared and characterized by elemental analyses, thermogravimetric analyses, IR and Raman spectroscopy and photoluminescence spectroscopy. It has been found that the $^5D_0$ quantum efficiency for these complexes vary considerably depending on the nature of L, decreasing in the order L = DMSO (62%), phen (40%), bipyrimidine (39%), H_2O (29%) and DAB (2-3%). The low $^5D_0$ quantum efficiencies for the DAB adducts can be reliably assigned to a non-radiative decay through the LMCT state of Eu^{3+} ion, which is at rather low energies in these diimine compounds [Fernandes et al. 2004; Carlos et al. 2003].

The excitation spectra of $Eu(TTFA)_3.5Mphen$ in solid state and in solution show strong sensitization of Eu^{3+} emission. The efficiency of the ligand-to-metal energy transfer is confirmed by very pronounced emission from $^5D_1$ energy level of Eu^{3+} ion. The strong temperature dependence of the luminescent decay times, suggests the presence of thermally activated energy back transfer from Eu^{3+} energy levels to the ligand triplet state and perhaps LMCT states take part in this process. Considerably lower decay times in alcohol solutions suggest efficient quenching of the Eu^{3+} red emission by OH modes [Gawryszewska et al. 2004].

Luminescent properties of supramolecules of 2-thenoyltrifluoroacetonate of Eu^{3+} ion and crown ethers as ligands have been investigated. The emission spectrum of the DB18C6 system shows only one peak for the $^5D_0 \rightarrow {}^7F_0$ transition indicating the presence of a single chemical environment around the Eu^{3+} ion. In contrast, 18C6 system presents two sites of symmetry for the Eu^{3+} ion. The above results suggest that Eu^{3+} supramolecules are promising photochemically stable compounds to be used as luminescent probes [Felinto et al. 2003].

Structure, photophysics and magnetism of Eu mixed complex, $[Eu(HFAA)_3 .bipy.H_2O]$ in the solid state and in solution have been investigated and important characteristics of this material has been correlated with donor-acceptor properties of the substituents in ligands. X-ray single crystal study shows that Eu^{3+} ion is coordinated by six oxygen atoms of HFAA, 2 N-atoms of 2,2'-bipyridine molecule and one molecule of water. The emission properties of the complex were strongly dependent on the energy of the excitation beam and on temperature. Strong dependence of emission intensity and composition of the spectra in the range of the $^5D_0 \rightarrow {}^7F_{1,2}$ transitions indicate the possible role of 2,2'-bipyridine molecules in intra- and inter-molecular energy transfer. Magnetic data obtained down to 1.7K showed the existence of some discrepancies between the spectroscopically determined $^7F_0 \rightarrow {}^7F_1$ splitting and that obtained from the magnetic data [Thompson et al. 2002].

$Eu(MHD)_3$.o-phen has been prepared and characterized by means of a luminescence spectrum and by complete structure determination by X-ray diffraction. The β-diketonate ligand is unsymmetrical with a methyl group at one end and an isobutyl group at the other. The luminescence spectrum is typical for low-symmetry complexes of this type with a single sharp $^5D_0 \rightarrow {}^7F_0$ transition at 579.9 nm accompanied by a weak shoulder. The $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions are completely resolved with weak additional transitions that are most likely vibronic in origin. The X-ray structure shows a single eight-coordinate coordination geometry that approximates a square antiprism [Thompson and Berry 2001].

The photophysical properties of Eu^{3+}, Gd^{3+} and Tb^{3+} complexes with 2-hydroxy-2,4,6-cycloheptatrien-1-one have been investigated. The results show that the ligand triplet states are at lower energies than the Eu^{3+} and Tb^{3+} emitting states, thus quenching the luminescence from these ions by non-radiative relaxation to the ground state [Santos et al. 1997].

The influence of the donor-acceptor properties and of the size of the ligands on the spectroscopic characteristics of a series of $Eu(DPM)_3$.Phen compounds was investigated. The dependencies of the Stark splitting of the Eu^{3+} energy levels, the efficiency of the excitation of Eu^{3+} ion through the ligand bands, vibration frequencies, and patterns of vibronic sidebands with variation of the phenanthroline substituent were examined. Crystal field parameters were calculated. It was shown that the steric factors are significant in determining the structure of the compound. The same intensity distribution patterns of vibronic sidebands of the $^7F_0 \rightarrow {}^5D_2$ transition in excitation spectra of different β-diketonates were demonstrated. $Eu(DPM)_3$.Phen compounds containing phenyl derivatives of phenanthroline, exhibit the highest luminescence [Tsaryuk et al. 2000; Malta et al. 1996].

The synthesis, characterization and photophysical properties of $Tm(ppa)_3.2H_2O$ complex have been reported. Its characterization has been carried out by EDTA titration and TGA analysis, which indicates the presence of the tris-β-diketonate complex with two water molecules completing the metal coordination sphere. The photophysical analyses of the $Tm(ppa)_3.2H_2O$ complex were carried out at room and liquid nitrogen temperatures (77K). The excitation and absorption spectra showed a broad band centered at 335 nm, which is ascribed to the complex since ppa absorbance maximum is centered at 295 nm. The emission spectra presented the characteristic bands of Tm^{3+} due to the $^1G_4 \rightarrow {}^3H_6$ (478 nm), $^1G_4 \rightarrow {}^3F_4$ (650 nm), $^1G_4 \rightarrow {}^3H_5$ (770 nm) and $^3H_4 \rightarrow {}^3H_6$ (790 nm) transitions [Serra et al. 1998].

The solid state photophysical properties (luminescence spectra, quantum yield and decay times) of the complexes $Ln(bzac)_3.L$ ($Ln = Eu^{3+}$ or Gd^{3+}; $L = H_2O$, Phen, PhenNO) were investigated down to 77K and compared to those of the related complexes $Eu(btfa)_3.L$. Quantum yield values were enhanced by PhenNO molecule. This can be ascribed to a decrease in the non-radiative $^5D_0$ relaxation rates. Further, the quantum yields are larger for the btfa complexes, probably due to the presence of the electron withdrawing CF_3 groups [Junior et al. 1997].

Syntheses, luminescence and quantum yields of Eu^{3+} mixed complexes with 4,4,4-trifluoro-1-phenyl-1,3-butanedione and PhenNO or H_2O have been described. The more pronounced temperature dependence of the quantum yield (q) and the larger difference between the q values upon ligands and the direct Eu^{3+} excitation for the hydrated compounds show that there are other quenching processes operative, besides the expected multiphonon relaxation via the water vibrations. The results clearly show that the substitution of the water molecules by phenNO leads to greatly enhanced q values (30% vs. 66% upon ligand excitation at 300K) and longer $^5D_0$ life times (380 μs vs. 670 μs, respectively). This can be ascribed to a more efficient ligand-to-metal energy transfer and to less efficient non-radiative $^5D_0$ relaxation processes [de Mello Donega et al. 1996; de Mello Donega et al. 1997].

The synthesis, characterization and spectroscopic properties of the complex $Eu(TTA)_3.2DBSO$ have been described. Experimental and theoretical results on ligand field parameters, 4f-4f intensities and intramolecular energy transfer processes are described. The characteristic emission spectrum of the Eu^{3+} ion shows a very high intensity for the hypersensitive $^5D_0 \longrightarrow {}^7F_2$ transition, pointing to a highly polarizable chemical environment around the Eu^{3+} ion. Lifetime measurements confirm that the Eu^{3+} luminescence has a higher efficiency than in the case of the hydrated compound. The theoretical model developed was proved to be very useful in predicting coordination geometries and electronic structure of the organic part of rare earth coordination compounds. Lifetime measurements confirm that the Eu^{3+} luminescence has a higher efficiency than in the case of hydrated compounds [Malta et al. 1997].

Organic-inorganic hybrids, named di-ureasils and described by polyether based chains grafted to both ends to a siliceous backbone through urea cross linkages, were used as hosts for incorporation of the well-known coordination complex of the Eu^{3+} ions described by the formula $[Eu(TTA)_3.2H_2O]$. These materials enhanced the quantum efficiency for photoemission of Eu^{3+} ions. The enhancement can be explained by the coordination ability of the organic counterpart of the host structure which is strong enough to displace water molecules in $[Eu(TTA)_3(H_2O)_2]$ from the lanthanoid neighbourhood after the incorporation process. High intensity of Eu^{3+} ion emission was observed with a low non-radiative decay rate under ultraviolet excitation. The quantum efficiency calculated from the decay of $^5D_0$ emission was 74%, which is in the same range of values previously obtained for the most efficient Eu^{3+} coordination compounds. Thus this approach makes the compounds introduced potentially interesting for application in luminescent devices [Molina et al. 2003].

Fluorescence lifetimes and energy transfer of rare earth β-diketone complexes (EuL_3Phen) (L = acac, TFA, HFAA and TTA) in organized molecular films have been investigated. Both the fluorescence lifetime and the fluorescence intensity of the lanthanoid complexes have been found to vary with the β-diketone ligand and were found to be longer in Langmuir-Blodgett (LB) films than that in solution. These investigation results help in further understanding the intra- and inter-molecular energy transfer processes of lanthanoid complexes in organized molecular films [Zhang et al. 1997; Zhang et al. 1997a; Zhang et al. 2000].

Chapter 3

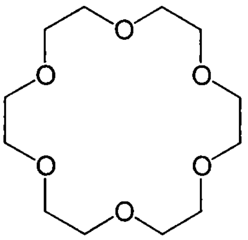
Investigations on the Interactions of Structurally Related Crown Ethers with 3-Phenyl-4-aroyl-5-isoxazolone Complexes of Trivalent Lanthanoids

Although there have been many studies on the synergistic extraction of trivalent lanthanoids using oxo-donors as adduct forming reagents in the presence of 1,3-β-diketones, improvement in the selectivity among these metal ions has been hardly achieved [Mathur 1983; Bond et al. 2000]. However, a remarkable increase in the extractability and selectivity has been reported in the extraction of trivalent lanthanoids with 18C6 or DC18C6 in the presence of HTTA [Kitatsuji et al. 1995] or benzoyltrifluoroacetone [Reddy et al. 1998]. This has been attributed to the characteristic ion-pair extraction of the lighter lanthanoids with 1,2-dichloroethane containing HTTA or Hbtfa and 18C6 or DC18C6, in which the cationic complex, $Ln(TTA)_2.CE^+$ or $Ln(btfa)_2.CE^+$ was formed and extracted. Also, this has been interpreted on the basis of the size-fitting effect in the complex formation of the lighter lanthanoids with CE.

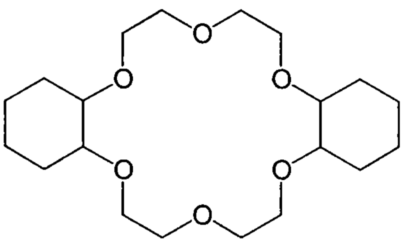
Macrocyclic crown ethers (CE) have unique complexation properties for metal ions, i.e., the size selectivity originates from the correct fit of a metal ion into the cavity of the crown ether. This property of crown ethers renders them attractive as size selective extractants for the extraction separation of a series of metals such as alkali, alkaline earths and possibly lanthanoids.

The extraction of trivalent lanthanoids with mixtures of crown ethers and 1,3-β–diketones involves a variety of geometric (cavity size and steric repulsion between extractants), enthalpic (donor basicity) and entropic effects (cation dehydration) [Bond et al. 2000; Mathur and

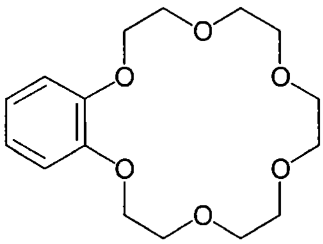
Choppin 1993]. The crown ethers do exhibit synergistic behaviour but the fit of the cation and crown cavity size does not seem to be a significant factor in some of these 1,3-β–diketone complexes.



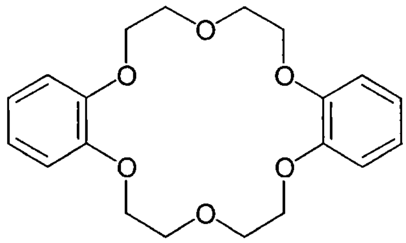
18-crown-6



Dicyclohexano-18-crown-6



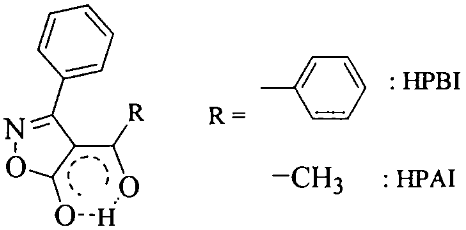
Benzo-18-crown-6



Dibenzo-18-crown-6

Further, it has also been reported that these metal ions may interact with only a few of the potential donor oxygens and steric effects are probably significant in establishing this number. These factors prompted us to investigate the nature of the interactions of structurally related crown ethers with heterocyclic lipophilic ketone, namely, 3-phenyl-4-aroyl-5-isoxazolone complexes of lanthanoids.

Among 3-phenyl-4-acyl-5-isoxazolones (**1**), HPBI has come to occupy a special place in the solvent extraction of metal ions due to its lower pK_a value [Le et al. 1993; Reddy et al. 1995a; Torkestani et al. 1996; Sahu et al. 2000]. The lower pK_a value of HPBI (1.23) is due to the electron delocalization induced by the isoxazolone moiety. This property makes 3-phenyl-4-acyl-5-isoxazolone an interesting class of β-diketones with potential application as reagent in the extraction separation of metal ions complexing from strong acid media [Mohapatra and Manchanda 1993; Manchanda et al. 1996; Sahu et al. 1999; Reddy and Meera 2001].



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In the solvent extraction separation of metal ions, fluorinated substituents have often been introduced in extractant molecule. The acidity of the extractant is, thus, enhanced by the strong electron withdrawing nature of the fluorinated substituent, and thus the metal ions are extractable from more strongly acidic solutions. Hence, in the present study, various para-substituted 4-aroyl derivatives of 3-phenyl-5-isoxazolones, namely, 3-phenyl-4-(4-fluorobenzoyl)-5-isoxazolone (HFBPI) and 3-phenyl-4-(4-toluoyl)-5-isoxazolone (HTPI), by introducing both electron withdrawing (-F) and electron donating (-CH_3) groups, have been synthesized and utilized to study their effects on the extraction behaviour of Ln^{3+} ions in the presence and absence of various crown ethers.

3.1. Experimental

3.1.1. Apparatus

A well-type NaI(Tl) Gamma Scintillation Counter supplied by Nucleonix Systems, India, was used for the measurement of the gamma activities of ^{147}Nd, ^{152,154}Eu and ^{170}Tm isotopes. Carbon, H and N analyses were performed with a Perkin-Elmer Series 2 Elemental Analyser 2400. A Nicolet Impact 400D IR Spectrophotometer using potassium bromide pellet, was used to obtain IR spectral data and a Bruker 300 MHz NMR spectrometer was used to obtain ^{1}H NMR spectra of the extractants and extracted complexes in $CDCl_3$ and $CDCl_3$-DMSO-d_6 or acetone-d_6 media, respectively. An Orion 720A Ion Analyzer (Beverly, USA) was used for pH measurements. Semi empirical molecular orbital calculations were carried out using Titan Version 1 from wave function Inc., 18401, Von Karman, Suite 370, Irvine, CA 92612 [Stewart 1989]. All the computer programs were written in FORTRAN 77 and executed on a Pentium PC (HCL, India).

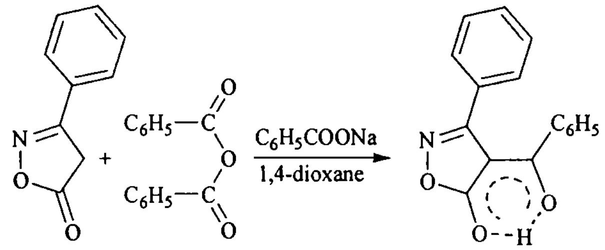
3.1.2. Chemicals

Radio isotopes ^{147}Nd ($t_{1/2}$ = 10.98d), ^{152,154}Eu ($t_{1/2}$ = 13.33y) and ^{170}Tm ($t_{1/2}$ = 128.6d) were supplied by the Board of Radiation and Isotope Technology (BRIT), India. Crown ethers; 18C6, DC18C6, B18C6, DB18C6, $Eu(NO_3)_3.6H_2O$, 3-phenyl-5-isoxazolone, benzoic anhydride, sodium benzoate and various acid chlorides were obtained from Aldrich Chemical Company.

Stock solutions of Nd^{3+}, Eu^{3+} and Tm^{3+} ions were prepared by dissolving appropriate amounts of Nd_2O_3, Eu_2O_3 and Tm_2O_3 (Rare Earth Products, Cheshire, U.K., 99.99 %) in concentrated nitric acid and made up to the required volume with distilled water. The stock solutions were standardized by titrating against standard solution of EDTA at pH = 5.0 acetate buffer with xylenol orange indicator [Reddy et al. 1989]. Initial lanthanoid ion concentration was maintained at 1.0×10^{-6} mol dm^{-3} for all the extraction studies. Ionic strength was maintained at 1.0 mol dm^{-3} using sodium nitrate.

Syntheses of ligands

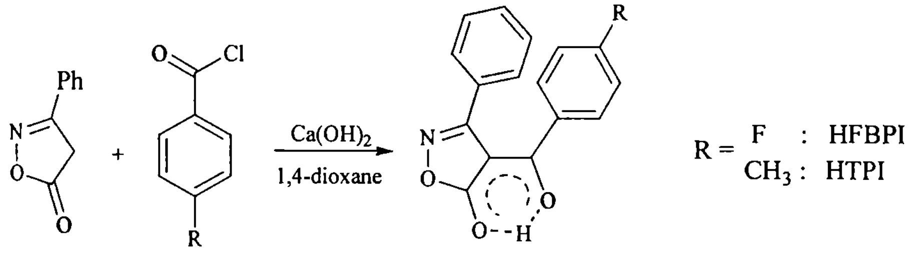
3-Phenyl-4-benzoyl-5-isoxazolone: HPBI was synthesized by the benzoylation of 3-phenyl-5-isoxazolone [Korte and Storiko 1961] (**Scheme 3.1**). Stoichiometric amounts of 3-phenyl-5-isoxazolone, benzoic anhydride and sodium benzoate were refluxed in dry 1,4-dioxane for 3 hrs. The reaction mixture was cooled and filtered. The filtrate was diluted with distilled water and acidified with HCl. The precipitate was filtered, dried and recrystallized from ethyl acetate.



Scheme 3.1

3-Phenyl-4-aroyl-5-isoxazolones: HFBPI and HTPI were synthesized from 3-phenyl-5-isoxazolone and corresponding acid chlorides [Korte and Storiko 1961] (**Scheme 3.2**). The crude products were filtered, dried and recrystallized from ethyl acetate. The synthesized 3-phenyl-4-aroyl-5-

isoxazolones were identified by elemental analyses, IR and ^{1}H NMR spectral data. All other chemicals used were of analytical reagent grade.



Scheme 3.2

HPBI : M.P. 146^0C; ^{1}H NMR data: δ 6.94-8.06 (m, 10H, phenyl); IR (KBr) data (υ cm^{-1}) : 3052, 1699, 1613, 1489, 831; Elemental analysis: calculated for $C_{16}H_{11}NO_3$, C 72.45; H 4.15; N 5.28; Found: C 72.27; H 4.18; N 5.17 %; HTPI : M.P. = 145^0C; ^{1}H NMR data: δ 6.93-7.37 (m, 9H, phenyl); 2.31 (3H, methyl); IR data (υ cm^{-1}): 2600, 1699, 1613, 1600, 830; Elemental analysis: calculated for $C_{17}H_{13}NO_3$, C 73.12; H 4.66; N 5.02; Found: C 73.52; H 4.73; N 5.31 %; HFBPI : M.P. = 149^0C; ^{1}H NMR data: δ 6.80-7.40 (m, 9H, phenyl); IR data (υ cm^{-1}) : 2600, 1702, 1620, 1583; Elemental analysis: calculated for $C_{16}H_{10}NO_3F$, C 67.84; H 3.53; N 4.95; Found: C 67.56; H 4.08; N 4.95 %. In the ^{1}H NMR spectra of HPBI, HTPI and HFPBI (Figs. 3.1-3.3), peaks observed at δ 5.90, δ 4.08 and δ 3.57, respectively, correspond to the enolic –OH in these compounds, which were found to have exchanged on addition of D_2O. Thus, confirming the existence of these compounds in the enolic form. The absence of a peak at δ 3.8 corresponding to the methylene proton at the fourth position of the isoxazolone ring, further confirms the existence of various 3-phenyl-4-aroyl-5-isoxazolones quantitatively in the enolic form.

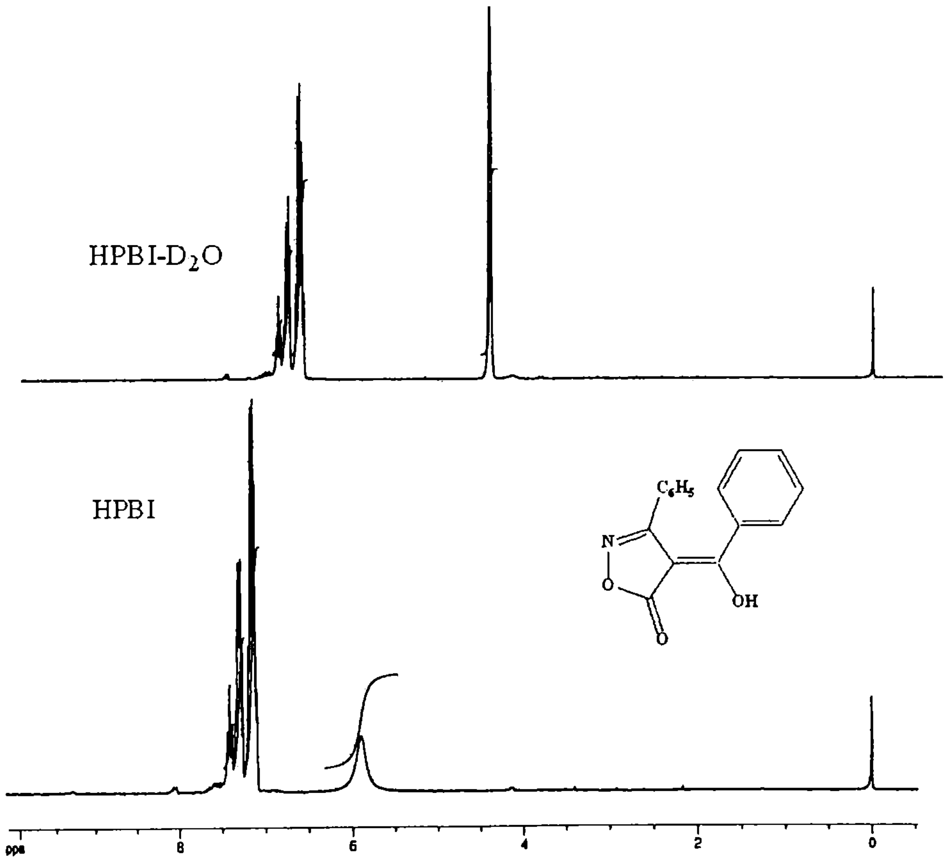


Fig. 3.1. ^{1}H NMR spectrum of HPBI.

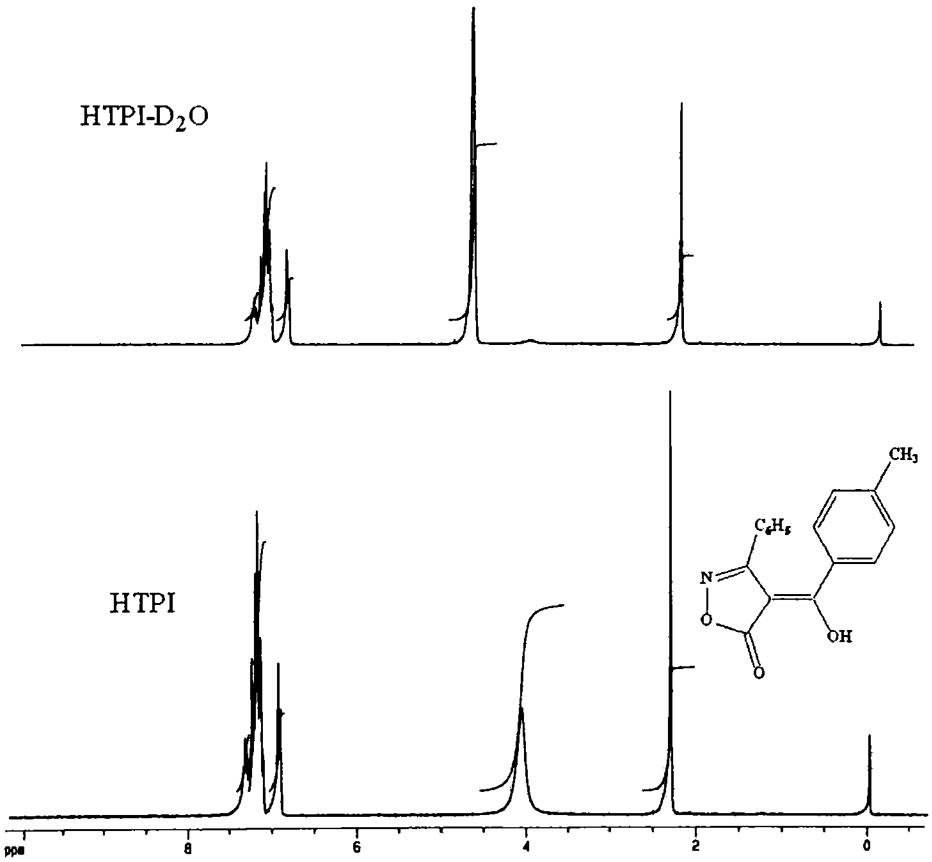


Fig. 3.2. ^{1}H NMR spectrum of HTPI.

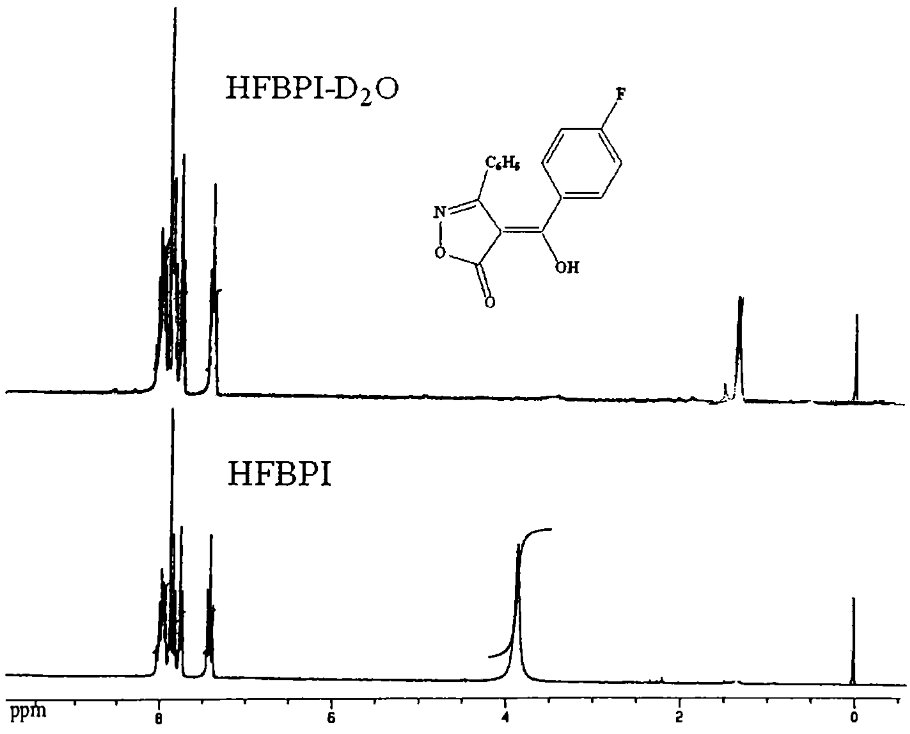


Fig. 3.3. ^{1}H NMR spectrum of HFBPI.

3.1.3. Solvent extraction and analytical procedure

Equal volumes of aqueous (1.0 mol dm^{-3} sodium nitrate of pH = 2.0 containing 1.0 × 10^{-6} mol dm^{-3} Ln^{3+} ions spiked with the respective tracers of trivalent lanthanoids) and organic phases were equilibrated for 60 min in a small stoppered glass centrifuge tube using a mechanical shaker at 303 ± 1 K. Preliminary experiments showed that the extraction equilibrium was attained within 40 min. The solutions were then allowed to settle, centrifuged, separated and assayed radiometrically using a NaI(Tl) gamma scintillation counter. The distribution ratio, D, of Ln^{3+} ion was determined as the ratio of the radioactivity of nuclide present in the organic phase to that in the aqueous phase. All the experiments were performed in duplicate and the general agreement with distribution ratio values obtained was within ± 5%.

3.1.4. Preparation of metal complexes

The metal complexes were prepared by the following procedure: Aqueous NaOH (3mmol) was added slowly to an ethanol solution containing 3mmol 3-phenyl-4-aroyl-5-isoxazolone with stirring giving a clear light yellow solution. Aqueous solution of 1mmol $Eu(NO_3)_3.6H_2O$ was added slowly to the above solution with constant stirring at room temperature. The resultant mixture was continually stirred for about 10h. The white precipitate obtained was collected and washed thoroughly with ethanol, water and ethanol, respectively, stored in a desiccator and dried over fused $CaCl_2$ [Yang and Yang 1995].

The ternary complex of HFBPI–crown ether with Eu^{3+} ion was synthesized as follows: Stoichiometric amounts of europium nitrate solution were added to a well stirred solution of HFBPI in ethyl acetate and the resultant mixture was stirred for 1 h. To this, crown ether dissolved in ethyl acetate was added and the resultant mixture was refluxed for 5 h in order to ensure completion of the reaction. The precipitates formed were filtered, recrystallized in ethyl acetate and dried in a desiccator over fused $CaCl_2$. The complexes were characterized by IR and ^1H NMR spectral data. The metal ions in the complex were determined by the following method. A definite quantity of the complex was decomposed with a small amount of concentrated HNO_3 solution by heating and the excess acid was evaporated off. The residue was diluted with distilled water and the lanthanoid ion concentration was determined spectrophotometrically by Arsenazo 1 method [Snell 1978].

3.2. Results and Discussion

3.2.1. *Extraction of trivalent lanthanoids with 3-phenyl-4-aroyl-5-isoxazolones*

The extraction behaviour of Nd^{3+}, Eu^{3+} and Tm^{3+} ions from 1.0 mol dm^{-3} sodium nitrate solution of pH = 2.0 with HFBPI alone in chloroform has been investigated as a function of the extractant concentration (HFBPI = 0.006–0.03 mol dm^{-3}) and the results are depicted in Fig. 3.4. For comparison extraction studies have also been performed with HPBI (0.01-0.04 mol dm^{-3}) and HTPI (0.01–0.06 mol dm^{-3}) and the results are given in Figs. 3.5 and 3.6. The relevant log-log plots (Figs. 3.4-3.6) gave straight lines with slopes of three for all the trivalent lanthanoids, indicating the extraction of simple metal chelates, $Ln(FBPI)_3$, $Ln(TPI)_3$ and $Ln(PBI)_3$ with HFBPI, HTPI and HPBI, respectively. These, in conjunction with slopes of three observed with pH variation experiments (pH = 1.5-2.0) at constant HFBPI (0.02 mol dm^{-3}) or HPBI (0.02 mol dm^{-3}) or HTPI (0.02 mol dm^{-3}) concentration, confirm the extraction of simple metal chelates (Figs. 3.7-3.9). Similar simple metal chelate formation for the extraction of trivalent lanthanoids from perchlorate solutions into chloroform with HPBI has also been reported elsewhere [Le et al. 1993; Reddy et al. 1997; Sahu et al. 1999]. The above results indicate that three moles of 3-phenyl-4-aroyl-5-isoxazolone react with one mole of Ln^{3+} ion, releasing three moles of H^+ ions.

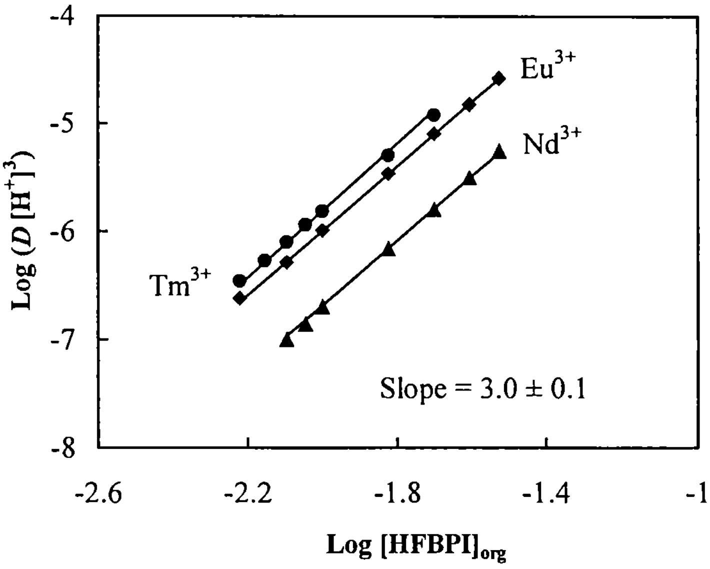


Fig. 3.4. Effect of HFBPI concentration on the extraction of Nd^{3+}, Eu^{3+} and Tm^{3+} ions. Aqueous phase = 1.0 mol dm^{-3} $NaNO_3$ of pH = 2.0 + Ln^{3+} = 1.0 × 10^{-6} mol dm^{-3}.

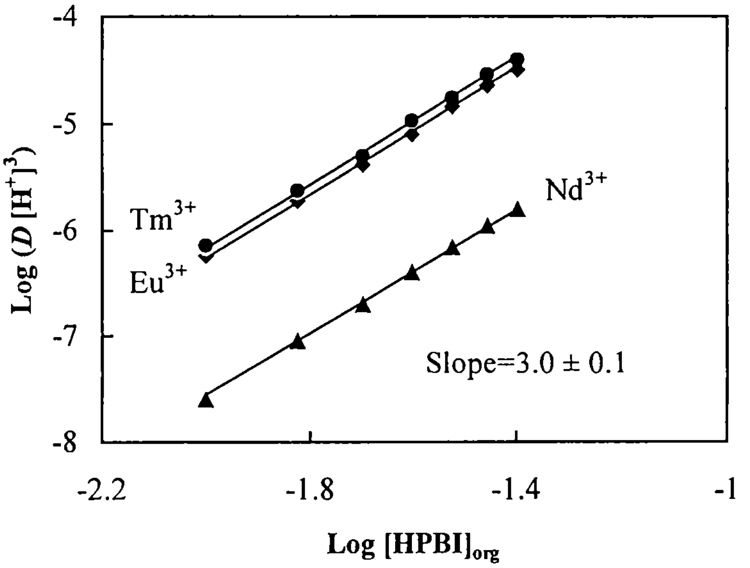


Fig. 3.5. Effect of HPBI concentration on the extraction of Nd^{3+}, Eu^{3+} and Tm^{3+} ions. Aqueous phase = 1.0 mol dm^{-3} $NaNO_3$ of pH = 2.0 + Ln^{3+} = 1.0 × 10^{-6} mol dm^{-3}.

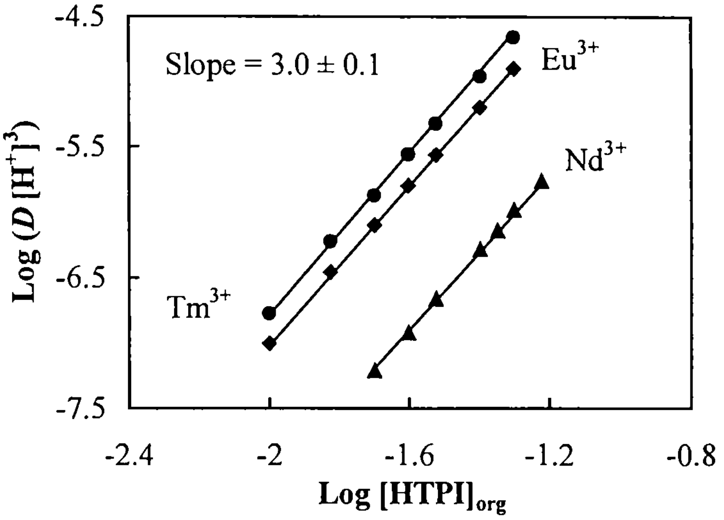


Fig. 3.6. Effect of HTPI concentration on the extraction of Nd^{3+}, Eu^{3+} and Tm^{3+} ions. Aqueous phase = 1.0 mol dm^{-3} $NaNO_3$ of pH = 2.0 + Ln^{3+} = 1.0 × 10^{-6} mol dm^{-3}.

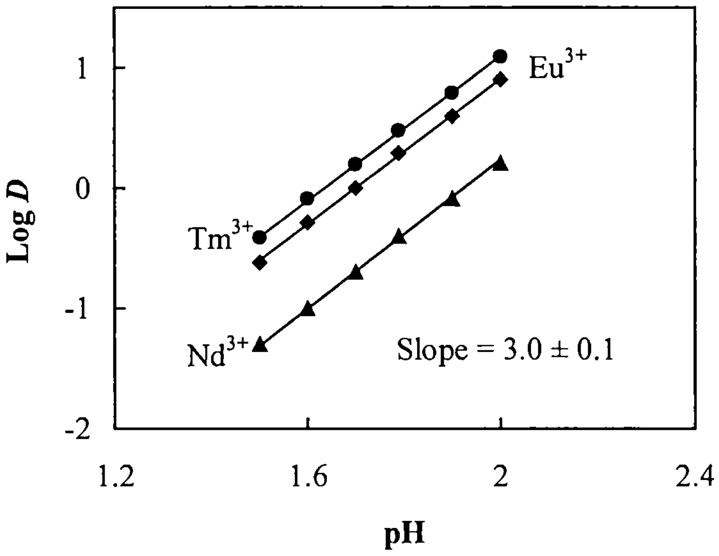


Fig. 3.7. Effect of pH on the extraction of Nd^{3+}, Eu^{3+} and Tm^{3+} ions. Aqueous phase = 1.0 mol dm^{-3} $NaNO_3$ + Ln^{3+} = 1.0 × 10^{-6} mol dm^{-3}, [HFBPI] = 0.02 mol dm^{-3}.

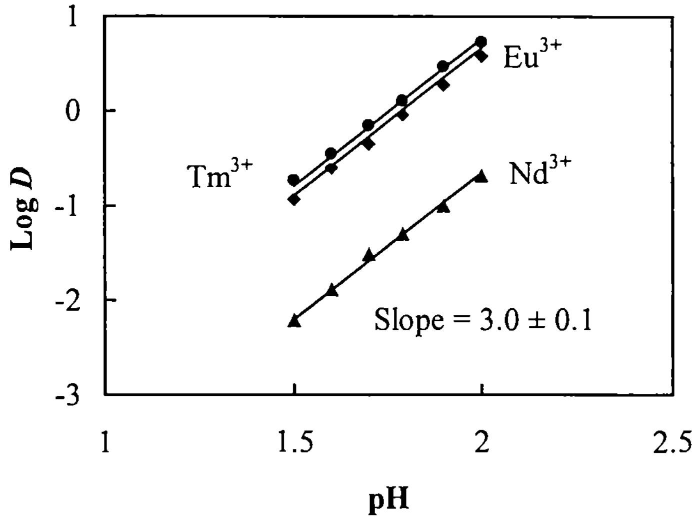


Fig. 3.8. Effect of pH on the extraction of Nd^{3+}, Eu^{3+} and Tm^{3+} ions. Aqueous phase = 1.0 mol dm^{-3} NaNO$_3$ + Ln^{3+} = 1.0 × 10^{-6} mol dm^{-3}, [HPBI] = 0.02 mol dm^{-3}.

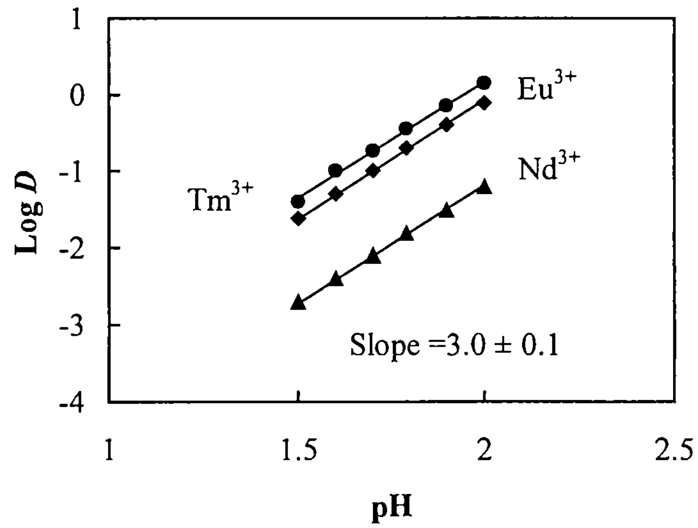


Fig. 3.9. Effect of pH on the extraction of Nd^{3+}, Eu^{3+} and Tm^{3+} ions. Aqueous phase = 1.0 mol dm^{-3} NaNO$_3$ + Ln^{3+} = 1.0 × 10^{-6} mol dm^{-3}, [HTPI] = 0.02 mol dm^{-3}.

Based on the preceding studies, the extraction equilibria of Nd^{3+}, Eu^{3+} and Tm^{3+} ions with chelating extractants, HX (HFBPI, HTPI or HPBI) alone may be expressed as:

$$Ln^{3+}_{aq} + 3\,HX_{org} \overset{K_{ex,0}}{\rightleftharpoons} LnX_{3\,org} + 3\,H^{+}_{aq} \qquad (1)$$

where $K_{ex,0}$ denotes the equilibrium constant.

$$K_{ex,0} = \frac{[LnX_3]_{org}\,[H^+]^3_{aq}}{[Ln^{3+}]_{aq}\,[HX]^3_{org}} \qquad (2)$$

Then the distribution ratio, D, from Eqs. (1) and (2) can be expressed as

$$D = \frac{K_{ex,0}[HX]^3{}_{org}}{[H^+]^3{}_{aq}} \qquad (3)$$

The equilibrium constants for the above complexes were determined by a non-linear regression analysis as described below and are given in Table 1.

(1) Assume values for $K_{ex,0}$

(2) Value of D under the given conditions are calculated from Eq. (3) and compared with the experimental values

(3) The value of equilibrium constant which leads to a minimum root mean square fractional error, y

$$y = \sqrt{\frac{1}{N}\sum_{i=1}^{N}\left\{\frac{D_{cal,i} - D_{exp,i}}{D_{exp,i}}\right\}^2} \qquad (4)$$

for all the experimental data, is taken as the equilibrium constant for the system under consideration. The equilibrium constants thus calculated refer only to concentration quotients, calculated on the assumption that the activity coefficients of the species involved do not change significantly under the experimental conditions. The partition coefficients of 4-aroyl-5-isoxazolones (log $K_{D,\mathrm{HPBI}}$ = 2.88 in chloroform-water system) [Le et al. 1993] in organic solvents are generally very high. Hence, no correction is required for the partitioning of ligands into the aqueous phase.

It is clear from Table 3.1 that the log equilibrium constants of these Ln^{3+} ions with various 4-aroyl-5-isoxazolones increase with decreasing ionic radii of the Ln^{3+} ions. Since the ionic radii of Ln^{3+} ions become smaller, with increase in atomic number, the charge density also increases. Consequently, the Ln^{3+} ions are well extracted with increase in atomic number. Thus, the strength of the electrostatic interaction between the extractant anion and the lanthanoid cation increases as the size of the latter decreases [Preston and du Preez 1990]. Comparing the equilibrium constants of various 3-phenyl-4-aroyl-5-isoxazolones for the extraction of lanthanoids from nitrate solutions (Table 3.1) with their pK_a [Odashima et al. 1995] values, it can be concluded that log equilibrium constant value increases as pK_a value decreases. The results demonstrate that the extraction efficiency of Ln^{3+} ions follows the order: HFBPI > HPBI > HTPI. It is interesting to note that the substitution of fluorine in the 4th position of the benzoyl moiety in HPBI molecule significantly improves the extraction efficiency of these metal ions. On the other hand, the substitution of an electron-releasing group like methyl ($-CH_3$) diminishes the extraction efficiency.

The extraction efficiency of various 4-aroyl-5-isoxazolones ($\mathrm{Log}K_{\mathrm{ex,HFPBI}} = 0$, $\mathrm{Log}K_{\mathrm{ex,\ HPBI}} = -0.27$, $\mathrm{Log}K_{\mathrm{ex,\ HTPI}} = -1.01$) is found to be significantly higher than that of 4-acylpyrazolones ($\mathrm{Log}K_{\mathrm{ex,\ HPMTFP}} = -3.78$, $\mathrm{Log}K_{\mathrm{ex,\ HPMBP}} = -5.33$) by comparing the equilibrium constant values of Eu^{3+} ion with these reagents.

Table 3.1. Two phase equilibrium constants of Nd^{3+}, Eu^{3+} and Tm^{3+}-4-aroyl-3-phenyl-5-isoxazolones -chloroform systems.

Extractant	pK_a	O---O distance Å	Log Equilibrium constant		
			Nd^{3+}	Eu^{3+}	Tm^{3+}
HFBPI	0.65	2.72	-0.69 ± 0.01	0.00 ± 0.02	0.19 ± 0.02
HPBI	1.23	2.72	-1.59 ± 0.01	-0.27 ± 0.02	-0.17 ± 0.02
HTPI	1.48	2.72	-2.11 ± 0.02	-1.01 ± 0.01	-0.75 ± 0.01

Table 3.2 gives the separation factors (S.F.) between these Ln^{3+} ions defined as the ratio of respective equilibrium constants with various 4-aroyl-5-isoxazolones. It is clear from the results that the selectivity among Ln^{3+} ions with various 4-aroyl-5-isoxazolones follows the order: HPBI > HTPI > HFBPI. This trend clearly highlights that the separation of lanthanoids becomes poorer as the extractability increases. Further, these results also strongly suggest the relationship between the selectivity and pK_a value of the ligand. The separation factors observed with various 4-aroyl-5-isoxazolones, especially, between Eu and Nd pair, are comparable with that obtained in the presence of EHEHPA (Eu/Nd = 3.94) [Bautista 1995] and D2EHPA (Eu/Nd = 12.5) [Pierce and Peck 1963; Reddy 1995b], which are widely used as extractants in the Rare Earth Industry.

Recently, the O---O distance has been identified as one of the most significant factors that governs the selectivity in the complexation of β-diketones with metal ions [Umetani et al. 2000]. Hence in the present study, the O----O distances in the para-substituted 4-aroyl-5-isoxazolones have been determined by semi-empirical PM3 molecular orbital calculation taking into account the hydrogen bond (Table 3.1) (Fig. 3.10). From the O-

--O distances (bite size) it is clear that para substitution in 3-phenyl-4-aroyl-5-isoxazolones ultimately does not induce any steric repulsion between the 3-phenyl group and the 4-aroyl group, thus unaffecting the O---O distance. The larger O---O distance in 4-aroyl-5-isoxazolones would decrease the stability of the intramolecular H-bonding resulting in a great enhancement of acidity. Thus, it is clear from the present study that the log K_{ex} values of lanthanoids with various para-substituted 3-phenyl-4-aroyl-5-isoxazolone vary in accordance with the substituent on the benzoyl moiety of isoxazolone, which ultimately reflects on the acidity of the ligand (pK_a).

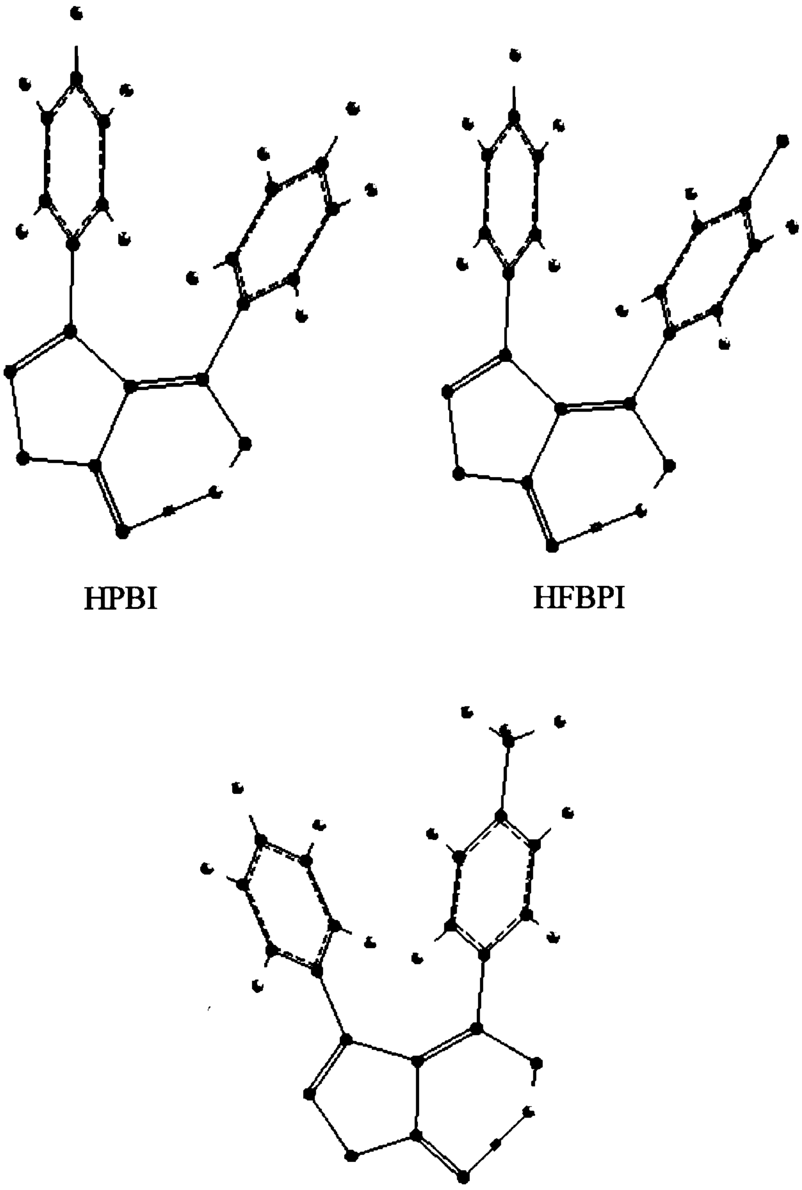
Table 3.2. Separation factors between Nd^{3+}, Eu^{3+} and Tm^{3+} ions with 4-aroyl-5-isoxazolone systems.

Extraction system	Separation Factor (S.F.)	
	Eu / Nd	Tm / Eu
HPBI	20.80	1.24
HFBPI	4.88	1.55
HTPI	12.66	1.80
EHEHPA	3.94	24.00
D2EHPA	12.50	161.00

3.2.2. Solid complexes of Eu^{3+} ion with various 4-aroyl-5-isoxazolones and their characterization

Elemental analyses of complexes

The analytical data presented in Table 3.3 show that Eu^{3+} ion has reacted with 4-aroyl-5-isoxazolones in the metal:ligand mole ratio of 1:3.



HPBI

HFBPI

HTPI

Fig. 3.10. Keto-enol structures of 4-aroyl-5-isoxazolones suggested by PM3 molecular modeling.

Table 3.3. Elemental analyses of the binary complexes of Eu^{3+} ion with 3-phenyl-4-aroyl-5-isoxazolones.

Compound	% Carbon	% Hydrogen	% Nitrogen	% Europium
	Found (Calcd.)	Found (Calcd.)	Found (Calcd.)	Found (Calcd.)
HPBI	72.27 (72.45)	4.18 (4.15)	5.17 (5.28)	
HFBPI	67.56 (67.84)	4.08 (3.53)	4.95 (4.95)	
HTPI	73.52 (73.12)	4.73 (4.66)	5.31 (5.02)	
$Eu(PBI)_3.2\ H_2O$	58.42 (58.78)	3.88 (3.47)	4.49 (4.28)	15.47 (15.51)
$Eu(FBPI)_3.3\ H_2O$	54.29 (55.70)	3.28 (3.0)	4.06 (4.06)	14.62 (14.44)
$Eu(TPI)_3.3\ H_2O$	58.63 (59.88)	4.27 (3.91)	4.40 (4.11)	14.52 (14.61)

IR spectra of binary complexes

The IR spectra of the Eu^{3+} binary complexes show a broad absorption in the region 3000-3500 cm^{-1} indicating the presence of water of hydration in the complex [Figs. 3.11-3.13]. The existence of hydrated lanthanoid-β-diketonate complexes is well documented [Pettinari et al. 2004; Mathur and Choppin 1993; Zhou et al. 1997; Ying et al. 1996]. The carbonyl stretching frequency has been shifted from 1702, 1699 and 1706 cm^{-1} in the free HFBPI, HPBI and HTPI, respectively, to 1646, 1620 and 1640 cm^{-1} in Eu-FBPI, Eu-PBI and Eu-TPI complexes indicating the involvement of carbonyl oxygen in complex formation.

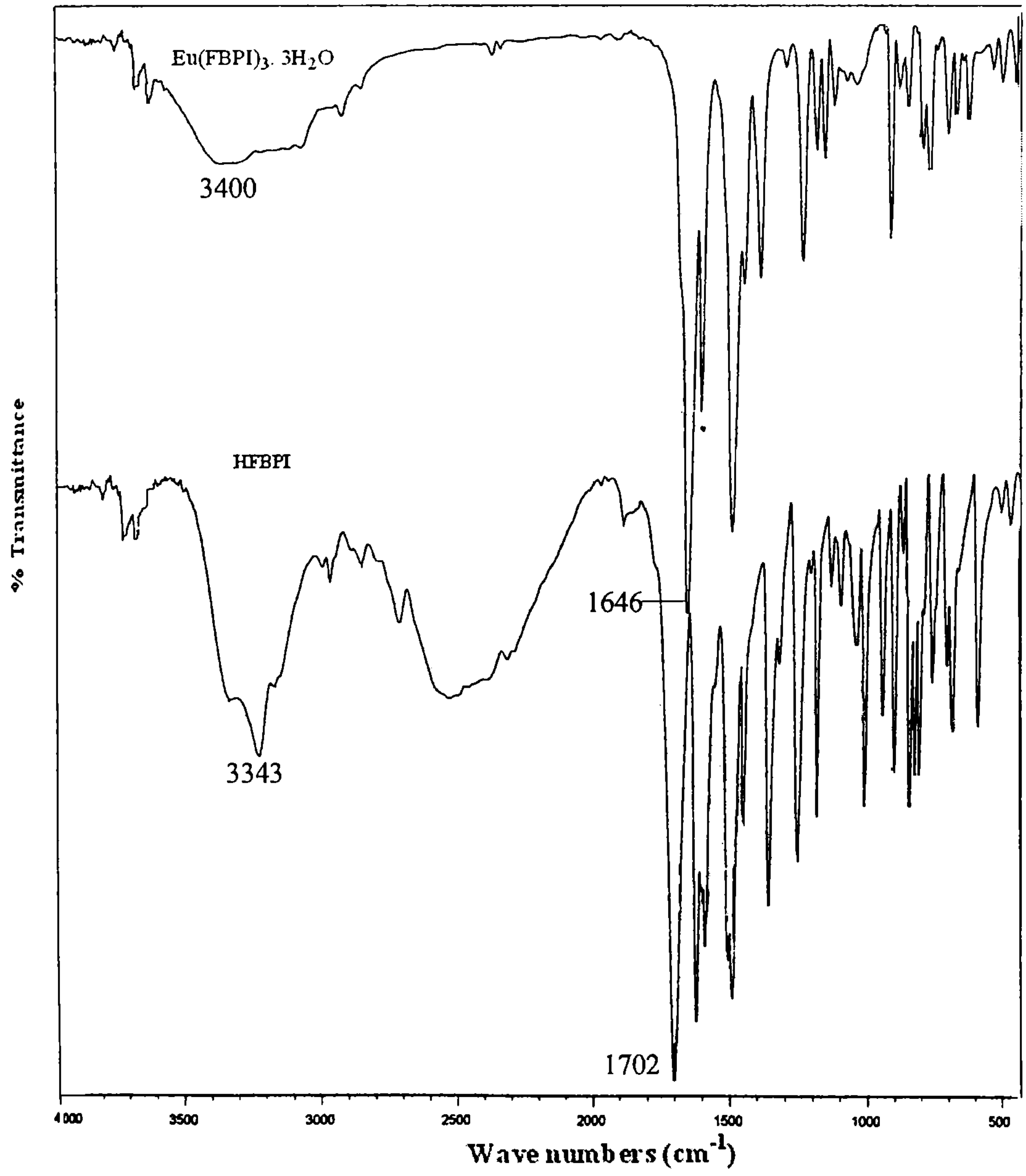


Fig. 3.11. IR spectrum of Eu^{3+}-HFBPI binary complex (KBr).

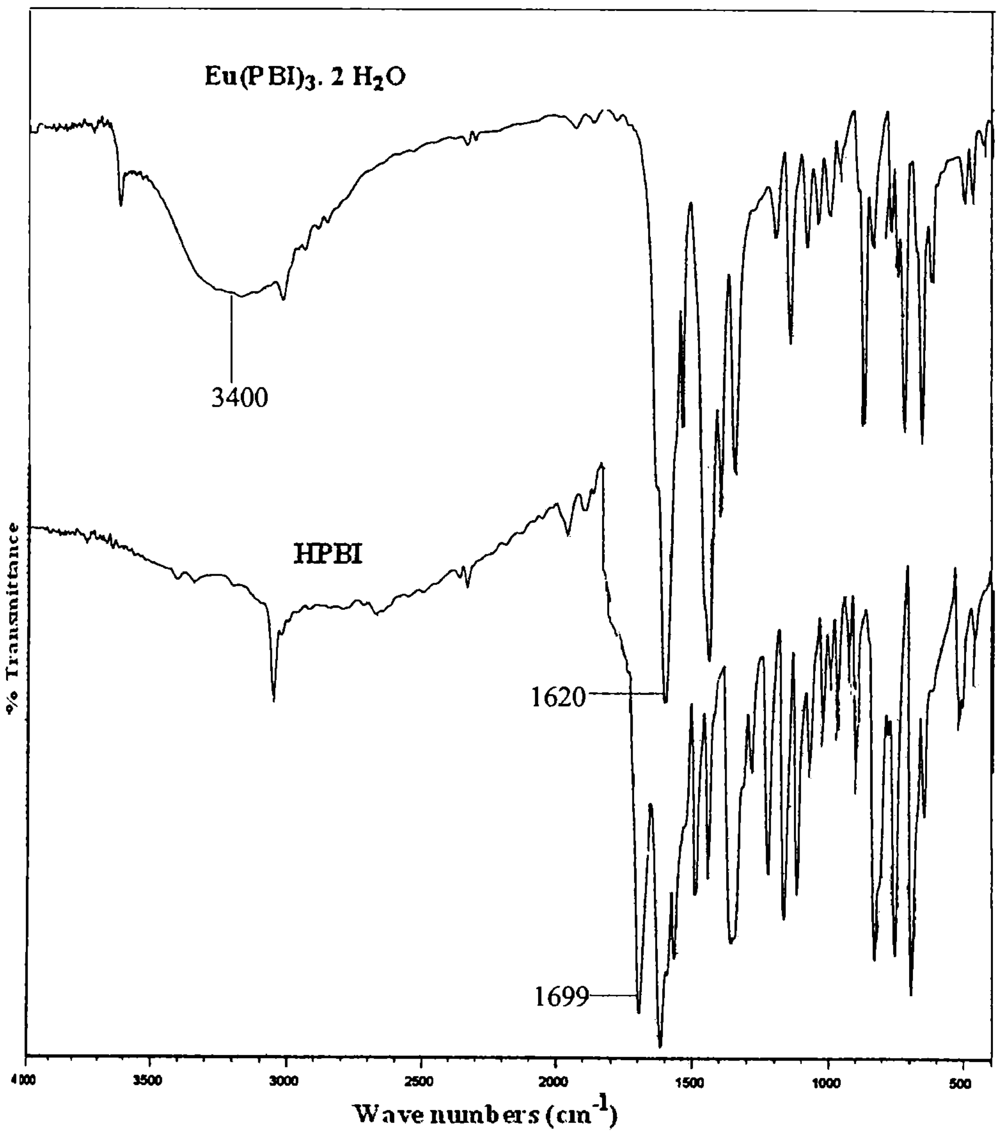


Fig. 3.12. IR spectrum of Eu^{3+}-HPBI binary complex (KBr).

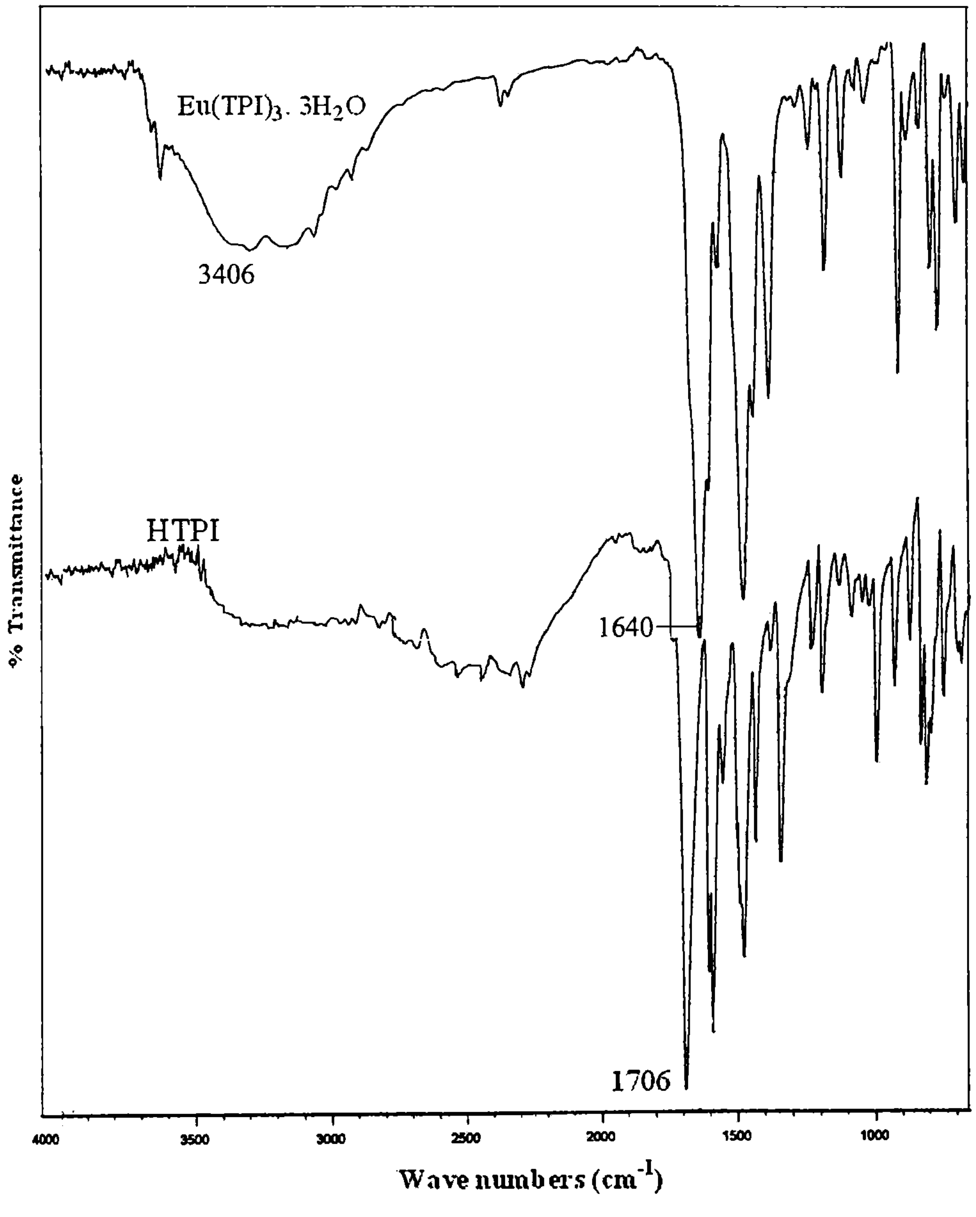


Fig. 3.13. IR spectrum of Eu^{3+}-HTPI binary complex (KBr).

^{1}H NMR spectra of binary complexes

The ^{1}H NMR spectra of the Eu^{3+} binary complexes showed all expected signals for 4-aroyl-5-isoxazolone protons. The integration of the bands was in accordance with the formulae proposed. A clear indication of the complex formation of 4-aroyl-5-isoxazolone derivatives is given by the absence of the enolic –OH peaks, present in the free ligands. Signals for water protons were also noticed in all the complexes. The signals of phenyl protons have always been shifted to up fields upon coordination with the metal ion in all the complexes (Figs. 3.14-3.16). The signal of $-CH_3$ group in HTPI complex has also been shifted to up field upon coordination with Eu^{3+} ion (Table 3.4).

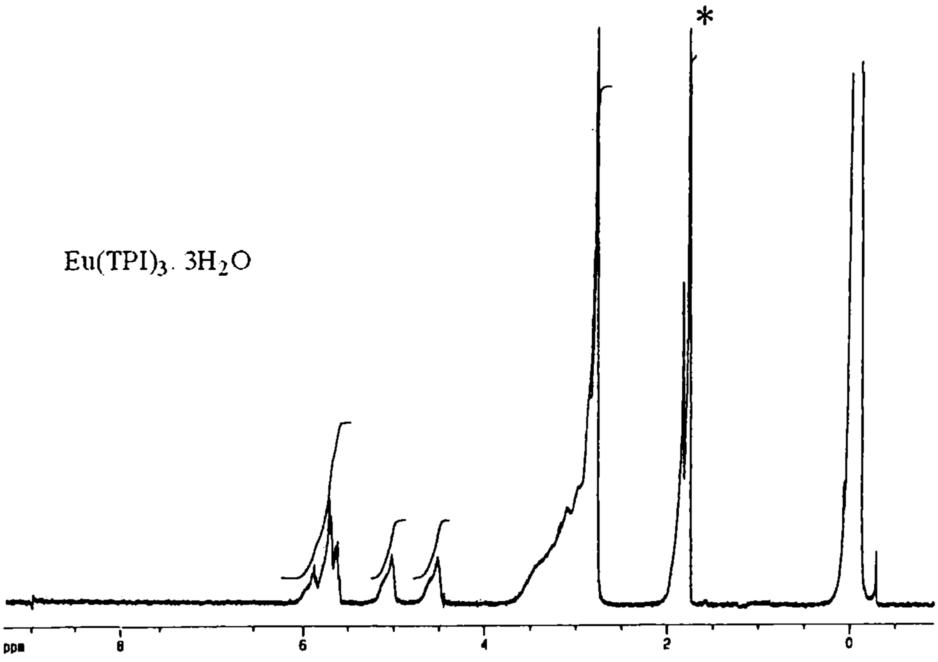


Fig. 3.14. ^{1}H NMR spectrum of $Eu(TPI)_3.3H_2O$ (acetone-d_6*).

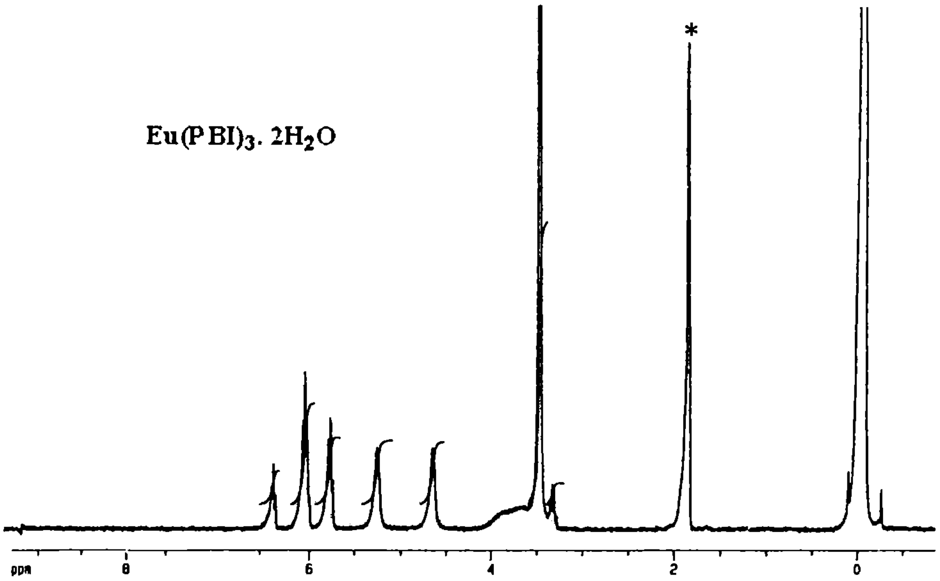


Fig. 3.15. ^1H NMR spectrum of $Eu(PBI)_3.2H_2O$ (acetone-d_6*).

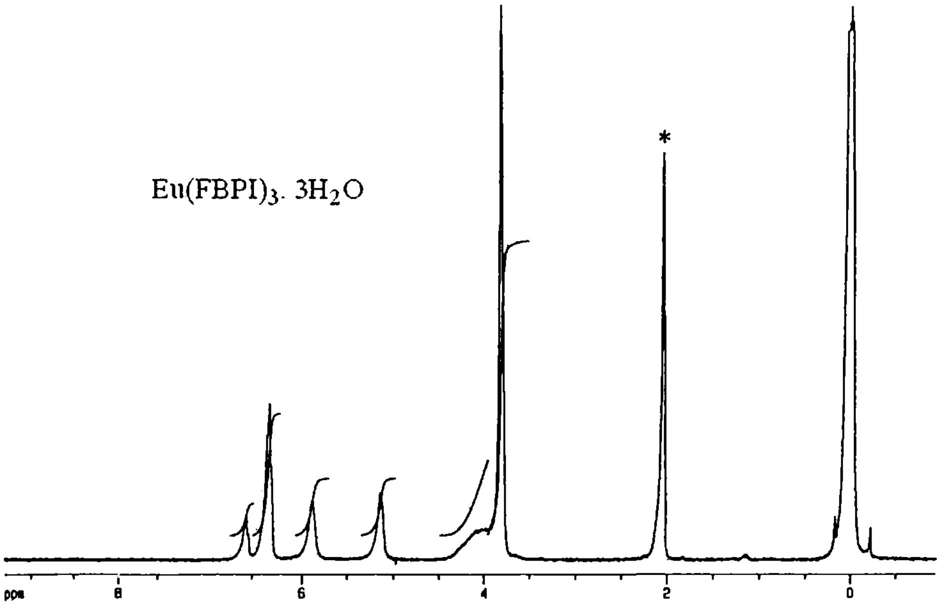


Fig. 3.16. ^1H NMR spectrum of $Eu(FBPI)_3.3H_2O$ (acetone-d_6*).

Table 3.4. ^{1}H NMR spectral data of free ligands and binary complexes of Eu^{3+} ion.

Compound	Phenyl protons	$-CH_3$ protons
HPBI	6.94-9.29	---
HTPI	6.93-7.36	2.31
HFBPI	6.80-7.40	---
$Eu(PBI)_3.\ 2H_2O$	5.07-6.97	---
$Eu(TPI)_3.\ 3H_2O$	4.99-6.57	2.13
$Eu(FBPI)_3.\ 3H_2O$	5.15-6.62	---

From the results of the extraction data, elemental analyses and IR spectral data, it is clear that Eu^{3+} ion is interacting with three molecules of 4-aroyl-5-isoxazolones, releasing three H^+ ions. In $Eu(PBI)_3.\ 2H_2O$, the eight oxygen atoms form square-antiprism coordination polyhedra around the central Eu^{3+} ion as observed in the X-ray crystal data of 1-phenyl-3-methyl-4-propionyl-5-pyrazolonate complex of Tb^{3+} ion [Zhou et al. 1997; Vicentini et al. 2000]. In $Eu(FBPI)_3.\ 3H_2O$ and $Eu(TPI)_3.\ 3H_2O$, the nine oxygen atoms form tri-capped trigonal prismatic geometry around the Eu^{3+} ion. The proposed structure of the extracted complex is shown in Fig. 3.17.

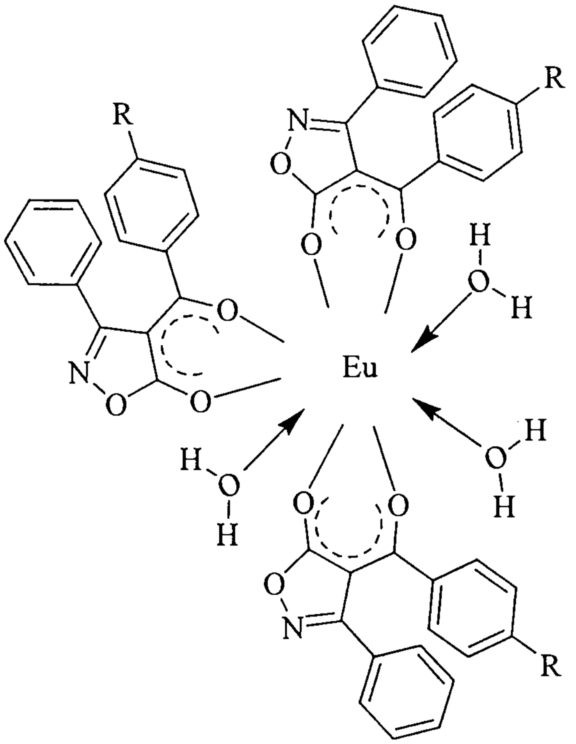


Fig. 3.17. Proposed structure of $Eu(FBPI)_3 . 3H_2O$ or $Eu(TPI)_3 . 3H_2O$, ($R = F$ or CH_3).

3.2.3. *Extraction of Ln^{3+} ions with mixtures of HFBPI and structurally related crown ethers*

The extraction equilibria of Ln^{3+} ions with a chelating agent, HFBPI (HX) in the presence of CE can be expressed as

$$Ln^{3+}_{aq} + 3\,HX_{org} + m\,CE_{org} \xrightleftharpoons{K_{Syn,m}} LnX_3.mCE_{org} + 3\,H^{+}_{aq} \qquad (4)$$

where $m = 0$ or 1. Then distribution ratio, $D_{Syn,m}$ from Eqs. (3) & (4) can be written as

$$D_{Syn,m} = \frac{[HX]^3_{org}}{[H^+]^3_{aq}} \{K_{ex,0} + K_{Syn,1}\,[CE]_{org}\} \tag{5}$$

$$\text{where } [CE] = [CE]_{initial} / (1 + \frac{1}{K_D}) \tag{6}$$

The equilibrium concentration of 18C6 was calculated using the partition coefficient (log $K_{D,18C6}$ = 0.8) taken from the literature [Sahu et al. 2000]. Since the partition coefficients of DC18C6 and DB18C6 (log $K_{D,DB18C6}$ = 3.8; log $K_{D,DC18C6}$ = 3.52) are known to be quite large, no correction is necessary for the partitioning of CEs into the aqueous phase. It is assumed that this is also true for B18C6. The interaction between the chelating agent and a neutral oxo-donor in chloroform are, in general, weaker when the diluent itself has strong interaction with the oxo-donor [Sekine et al. 1983; Torkestani et al. 2000]. Hence, it is assumed that there is negligible interaction between HFBPI and CEs in chloroform. The adduct formation reaction in the organic phase and the stability constant, β_l, is given by

$$LnX_{3\,org} + CE_{org} \overset{\beta_l}{\rightleftharpoons} LnX_3\,.\,CE_{org} \tag{7}$$

$$\beta_l = K_{syn,1} / K_{ex,0} \tag{8}$$

For confirming the above extraction equilibria, the extraction of Nd^{3+}, Eu^{3+} and Tm^{3+} ions from 1.0 mol dm^{-3} $NaNO_3$ solution of pH = 2.0 with mixture of HFBPI and various crown ethers into chloroform has been investigated. HFBPI has been chosen for synergistic extraction studies in view of its high extraction efficiency. It was found that the extraction of these metal ions into chloroform with CE alone was negligible under the present experimental conditions. However, with mixtures of HFBPI and CEs a very high synergistic enhancement factor of the order of 10^2 (Synergistic enhancement factor = $D_{syn,m}/(D_{\text{HFBPI}} + D_{\text{CE}})$, where $D_{syn,m}$ = distribution ratio with HFBPI + CE; D_{HFBPI} = distribution ratio with HFBPI alone and D_{CE} = distribution ratio with CE alone) has been observed in the extraction of these metal ions (Table 3.5). It is clear from Table 3.5 that the synergistic enhancement factors of these Ln^{3+} ions increase with increasing concentration of the CE in the order DC18C6 > 18C6 > B18C6 > DB18C6. This may be due to a difference in the extent of complexation of various CEs with lanthanoid chelates in the synergistic extraction systems. The extent of complexation essentially depends on relative sizes of the cation and the crown cavity, number of oxygen atoms in the polyether ring, coplanarity of the oxygen atoms, symmetrical placement of oxygen atoms, basicity of the oxygen atoms, steric hindrance in the polyether ring and electrical charge on the metal ion [Pedersen 1967].

The effect of HFBPI concentration (0.001-0.005 mol dm^{-3}) on the extraction efficiency of Ln^{3+} ions has been investigated in the presence of various structurally related CEs (0.002 mol dm^{-3}) from 1.0 mol dm^{-3} sodium nitrate solution of pH = 2.0. It is clear from the plots (Figs. 3.18-3.21) of log $\{D_{syn,m}[H^+]^3/(1+[CE](K_{\text{syn},1}/K_{\text{HFBPI}}))\}$ (rearrangement of Eq. (5)) vs. log $[\text{HFBPI}]_{\text{org}}$ that at constant CE concentration only three HFBPI moieties are attached to the synergistic species in all the systems studied here. The extraction efficiency of Ln^{3+} ions from 1.0 mol dm^{-3} sodium nitrate solution of pH = 2.0 has been studied as a function of CE concentration; 18C6 (0.002-0.02 mol dm^{-3}), B18C6 (0.001-0.006 mol dm^{-3}), DB18C6 (0.002-0.02 mol dm^{-3}) or DC18C6 (0.001-0.006 mol dm^{-3}) in the presence of HFBPI (0.002 mol dm^{-3}) and the results are shown in Figs.

3.22-3.25. The plots of log $\{(D_{syn,m}[H^+]^3/[HFBPI]^3)\text{-}K_{HFBPI}\}$ vs. log $[CE]_{org}$ at constant HFBPI concentration gave slopes of unity for all the metal ions, indicating the participation of only one CE molecule in the synergistic extracted species. These, in conjunction with the slopes of three observed with pH variation (1.5-2.0) experiments with a mixture of constant HFBPI (0.002 mol dm^{-3}) and CE (0.002 mol dm^{-3}) concentrations (Figs. 3.26-3.29) confirm the extraction of $Ln(FBPI)_3.CE$ complexes. Similar types of complexes have been noticed by many investigators in the extraction of Ln^{3+} ion with 1,3-β-diketones like HTTA and 4-acylpyrazolones in the presence of various CEs [Bond et al. 2000].

Table 3.5. Synergistic enhancement factors of Ln^{3+} ions with HFBPI in the presence of crown ethers (CEs).

Crown Ether	Concn. of HFBPI (mol dm^{-3})	Concn. of CE (mol dm^{-3})	Synergistic Enhancement Factors		
			Nd^{3+}	Eu^{3+}	Tm^{3+}
DC18C6	2×10^{-3}	2×10^{-3}	1.56×10^2	1.25×10^2	1.41×10^2
	2×10^{-3}	4×10^{-3}	3.13×10^2	2.50×10^2	2.82×10^2
	2×10^{-3}	6×10^{-3}	4.69×10^2	3.75×10^2	4.43×10^2
18C6	2×10^{-3}	6×10^{-3}	1.56×10^2	1.25×10^2	1.47×10^2
	2×10^{-3}	8×10^{-3}	2.06×10^2	1.65×10^2	1.94×10^2
	2×10^{-3}	1×10^{-2}	2.63×10^2	2.08×10^2	2.42×10^2
B18C6	2×10^{-3}	2×10^{-3}	0.38×10^2	0.31×10^2	0.33×10^2
	2×10^{-3}	4×10^{-3}	0.75×10^2	0.61×10^2	0.65×10^2
	2×10^{-3}	5×10^{-3}	0.94×10^2	0.79×10^2	0.81×10^2
DB18C6	2×10^{-3}	4×10^{-3}	0.25×10^2	0.25×10^2	0.27×10^2
	2×10^{-3}	8×10^{-3}	0.49×10^2	0.50×10^2	0.56×10^2
	2×10^{-3}	1×10^{-2}	0.61×10^2	0.63×10^2	0.71×10^2

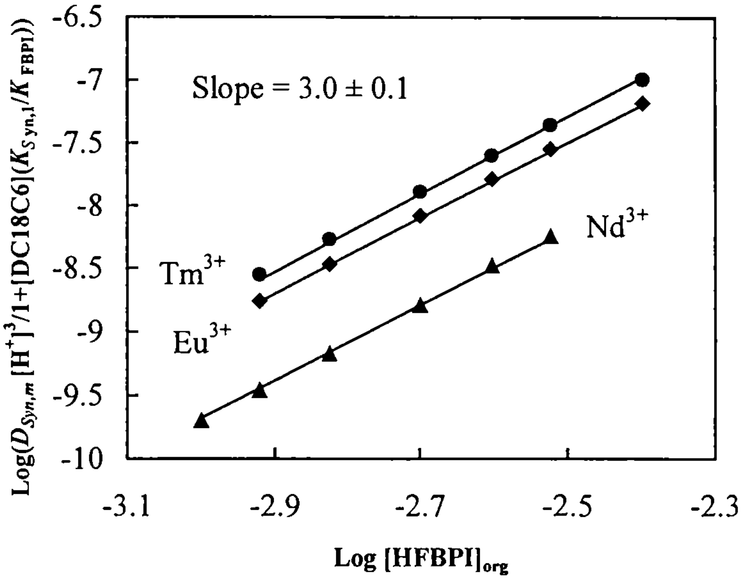


Fig. 3.18. Effect of HFBPI concentration on the extraction of Nd^{3+}, Eu^{3+} and Tm^{3+} ions at constant DC18C6 concentration (0.002 mol dm^{-3}). Aqueous phase = 1.0 mol dm^{-3} $NaNO_3$ of pH = 2.0 + Ln^{3+} = 1.0×10^{-6} mol dm^{-3}.

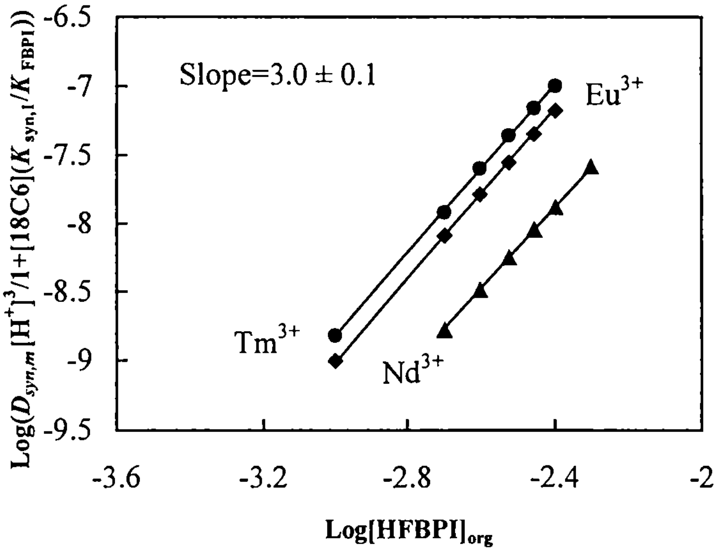


Fig. 3.19. Effect of HFBPI concentration on the extraction of Nd^{3+}, Eu^{3+} and Tm^{3+} ions at constant 18C6 concentration (0.002 mol dm^{-3}). Aqueous phase = 1.0 mol dm^{-3} $NaNO_3$ of pH = 2.0 + Ln^{3+} = 1.0×10^{-6} mol dm^{-3}.

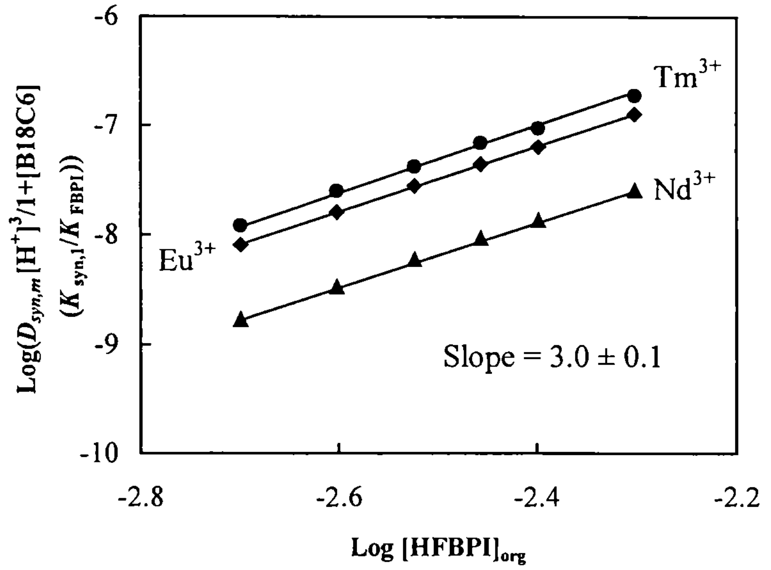


Fig. 3.20. Effect of HFBPI concentration on the extraction of Nd^{3+}, Eu^{3+} and Tm^{3+} ions at constant B18C6 concentration (0.002 mol dm^{-3}). Aqueous phase = 1.0 mol dm^{-3} $NaNO_3$ of pH = 2.0 + Ln^{3+} = 1.0 × 10^{-6} mol dm^{-3}.

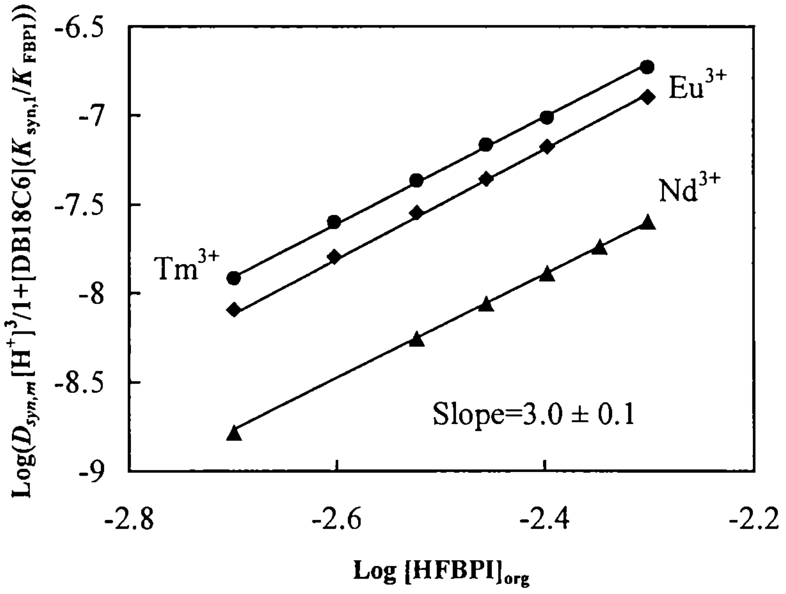


Fig. 3.21. Effect of HFBPI concentration on the extraction of Nd^{3+}, Eu^{3+} and Tm^{3+} ions at constant DB18C6 concentration (0.002 mol dm^{-3}).

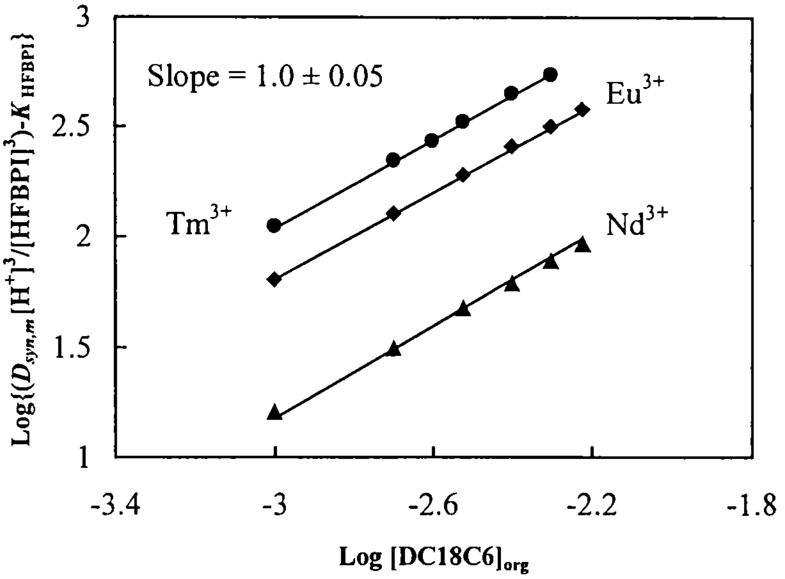


Fig. 3.22. Effect of DC18C6 concentration on the extraction of Nd^{3+}, Eu^{3+} and Tm^{3+} ions at constant HFBPI concentration (0.002 mol dm^{-3}).

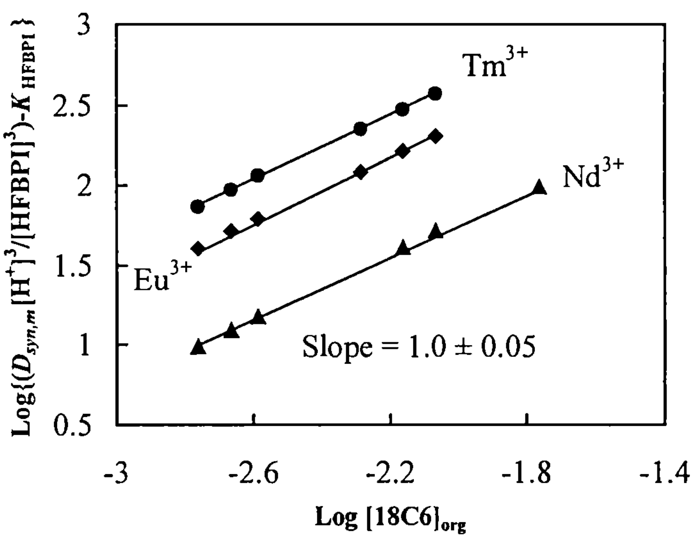


Fig. 3.23. Effect of 18C6 concentration on the extraction of Nd^{3+}, Eu^{3+} and Tm^{3+} ions at constant HFBPI concentration (0.002 mol dm^{-3}).

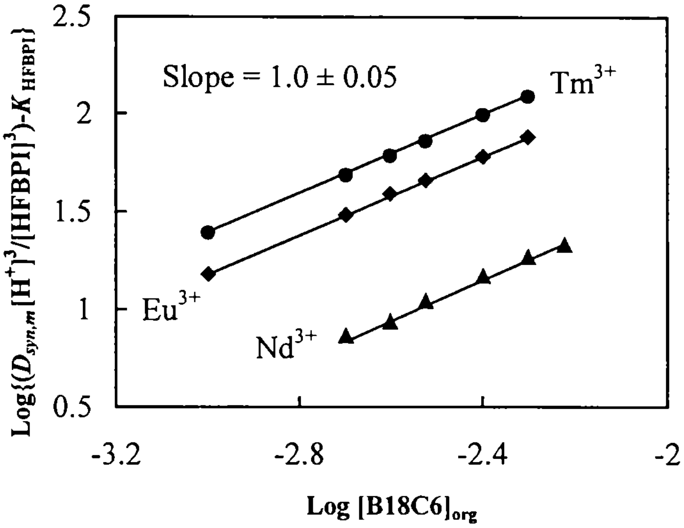


Fig. 3.24. Effect of B18C6 concentration on the extraction of Nd^{3+}, Eu^{3+} and Tm^{3+} ions at constant HFBPI concentration (0.002 mol dm^{-3}).

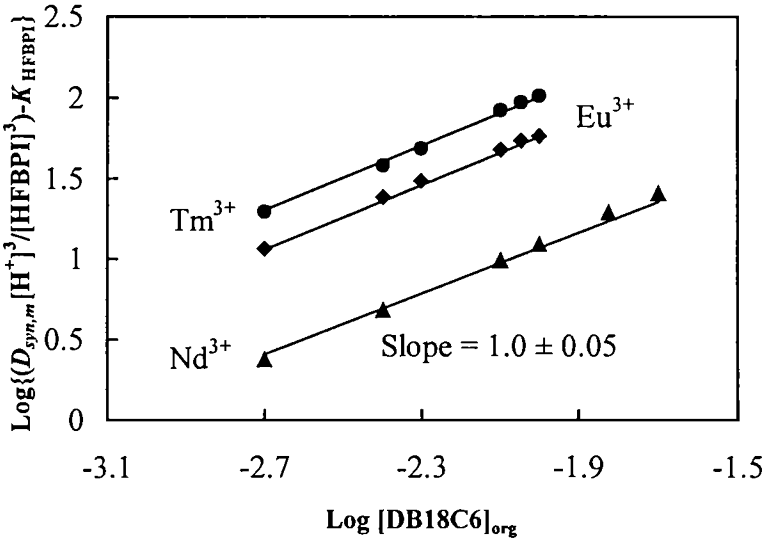


Fig. 3.25. Effect of DB18C6 concentration on the extraction of Nd^{3+}, Eu^{3+} and Tm^{3+} ions at constant HFBPI concentration (0.002 mol dm^{-3}).

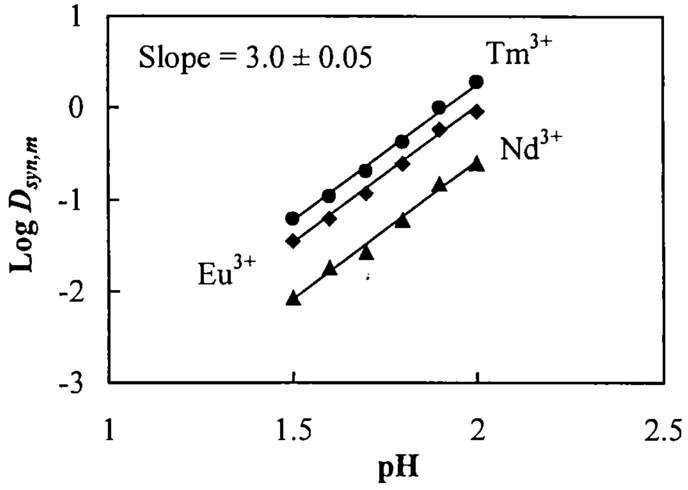


Fig. 3.26. Effect of pH on the extraction of Nd^{3+}, Eu^{3+} and Tm^{3+} ions. Aqueous phase = 1.0 mol dm^{-3} $NaNO_3$ + Ln^{3+} = 1.0 × 10^{-6} mol dm^{-3}, [HFBPI] = 0.002 mol dm^{-3}, [DC18C6] = 0.002 mol dm^{-3}.

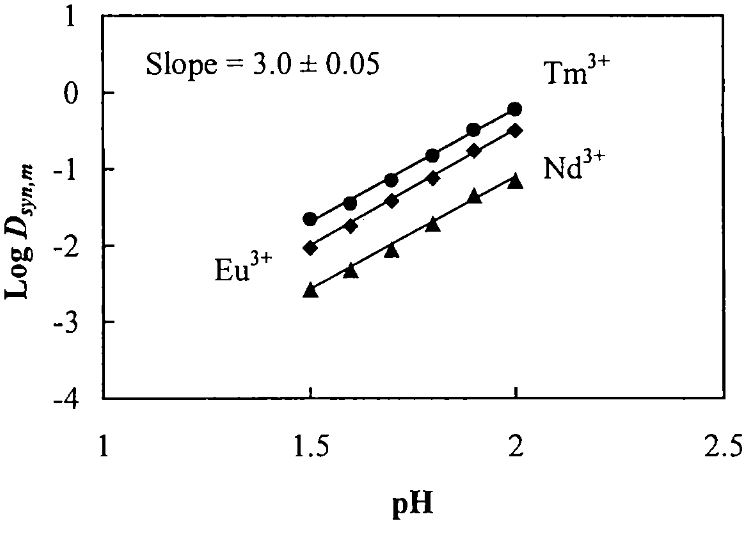


Fig. 3.27. Effect of pH on the extraction of Nd^{3+}, Eu^{3+} and Tm^{3+} ions. Aqueous phase = 1.0 mol dm^{-3} $NaNO_3$ + Ln^{3+} = 1.0 × 10^{-6} mol dm^{-3}, [HFBPI] = 0.002 mol dm^{-3}, [18C6] = 0.002 mol dm^{-3}.

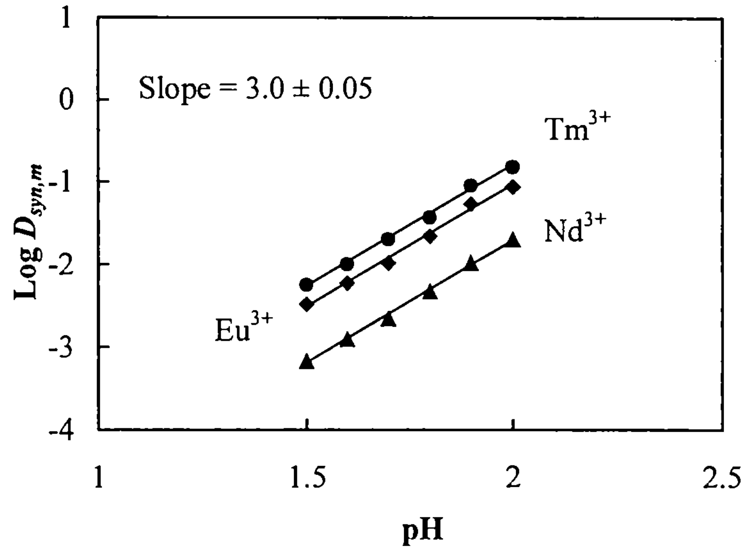


Fig. 3.28. Effect of pH on the extraction of Nd^{3+}, Eu^{3+} and Tm^{3+} ions. Aqueous phase = 1.0 mol dm^{-3} $NaNO_3$ + Ln^{3+} = 1.0 × 10^{-6} mol dm^{-3}, [HFBPI] = 0.002 mol dm^{-3}, [DB18C6] = 0.002 mol dm^{-3}.

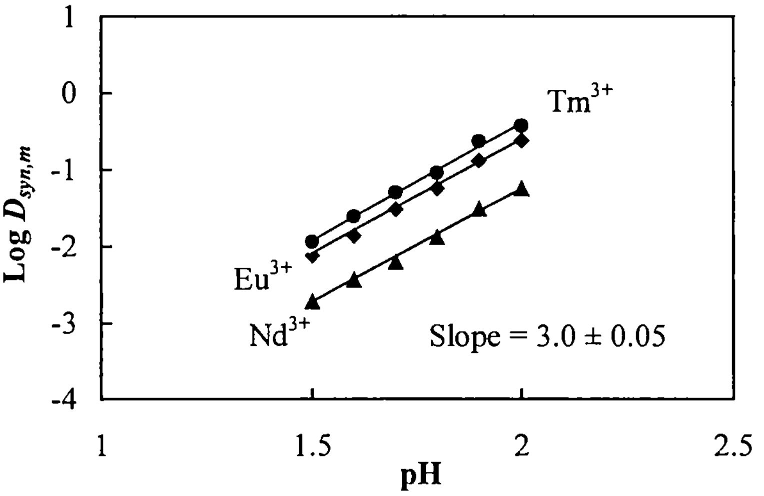


Fig. 3.29. Effect of pH on the extraction of Nd^{3+}, Eu^{3+} and Tm^{3+} ions. Aqueous phase = 1.0 mol dm^{-3} $NaNO_3$ + Ln^{3+} = 1.0 × 10^{-6} mol dm^{-3}, [HFBPI] = 0.002 mol dm^{-3}, [B18C6] = 0.002 mol dm^{-3}.

The equilibrium constants of the above synergistic complexes of these metal ions were deduced by a non-linear regression analysis and are given in Table 3.6. It is evident from Table 3.6 that the synergistic constant ($K_{syn,1}$) increases with decreasing ionic radii of these metal ions, for all the systems studied here. In polar diluents, this can be attributed to the increasing coulombic interactions with charge density of the Ln^{3+} ions [Manchanda et al. 1988].

Table 3.6. Two phase equilibrium constants of Nd^{3+}, Eu^{3+} and Tm^{3+}-HFBPI-CE-chloroform systems.

Extraction System	Log Synergistic constant (log $K_{syn,1}$)		
	Nd^{3+}	Eu^{3+}	Tm^{3+}
HFBPI + DC18C6	4.20 ± 0.02	4.80 ± 0.02	5.04 ± 0.02
HFBPI + 18C6	3.75 ± 0.02	4.36 ± 0.02	4.64 ± 0.02
HFBPI + B18C6	3.54 ± 0.02	4.18 ± 0.02	4.40 ± 0.01
HFBPI + DB18C6	3.08 ± 0.02	3.76 ± 0.02	4.00 ± 0.02

The increase in the extractability of lanthanoid complexes from Nd^{3+} to Tm^{3+} ion can be due to the increase in electrostatic interactions between the cation and the ligand with decrease in ionic radii. The stability constants, β_1, for the organic phase synergistic reaction of Ln^{3+}–HFBPI chelate with various CEs were calculated according to Eq. (8) and are given in Table 3.7. The complexation strength of trivalent lanthanoids with various CEs follows the order: DC18C6 > 18C6 > B18C6 > DB18C6. The sharp decrease in the complexation from 18C6 to B18C6 and to DB18C6 mostly reflects increasing steric effects and decreasing basicity. This seems reasonable, since the extensive thermodynamic studies on cation-crown ether complexation have shown that the cation binding ability of the CE containing benzo groups is lower than that for the parent CE, and have demonstrated that the diminished complex stability is due to the decreased electron density of donor oxygens produced by the electron withdrawing aromatic ring [Liu et al. 2000]. The cyclohexano group has a less dramatic effect on the stability of the complex and on cation selectivity [Izatt et al. 1985]. Aliphatic substituents in the ligands do not alter the binding properties to any measurable extent as observed in our present study. The higher extractability of these Ln^{3+} ions with DC18C6 or 18C6 can also be explained on the basis of size fitting effect of these CEs. The DC18C6 and 18C6, with cavity sizes of 2.6-3.2 Å, complex more strongly with metal ions such as lanthanoids having ionic diameters (2.06-1.72 Å) close to the cavity size. On the other hand, the theory of cavity ion fit leads to the assumption that lanthanoids are too small to be stabilized by the size effect of DB18C6 (4.0 Å) [Izatt et al. 1985; Liu et al. 2000].

Table 3.7. Organic phase synergistic stability constants of Nd^{3+}, Eu^{3+} and Tm^{3+}-HFBPI-CE-chloroform systems.

Extraction System	Log Stability Constant (log β_l)		
	Nd^{3+}	Eu^{3+}	Tm^{3+}
HFBPI + DC18C6	4.89 ± 0.02	4.80 ± 0.02	4.84 ± 0.02
HFBPI + 18C6	4.44 ± 0.02	4.36 ± 0.02	4.45 ± 0.02
HFBPI + B18C6	4.23 ± 0.02	4.18 ± 0.02	4.21 ± 0.01
HFBPI + DB18C6	3.77 ± 0.02	3.76 ± 0.02	3.81 ± 0.02

It is clear from Table 3.7 that the stability constants of these Ln^{3+} ions with various CEs do not follow a simple pattern with decrease in ionic radii of these metal ions unlike that of synergistic constants. The unusual behaviour observed in the present investigations of CEs with Ln^{3+} ions in the presence of HFBPI may be due to a variety of geometric (cavity size and steric repulsion between the extractant classes), enthalpic (donor basicity) and entropic (cation dehydration) effects [Bond et al. 2000].

3.2.4. IR and ^1H NMR spectral data of Eu-FBPI-CE complexes

The IR spectra of the Eu^{3+} ternary complexes (Figs. 3.30-3.32) show a broad absorption in the region 3000-3500 cm^{-1}, indicating the presence of water molecule in the complex. The presence of water molecules has also been reported elsewhere in the complexes of Eu^{3+} ion such as in $[Eu(TTA)_3(H_2O)_2(18C6)_2]$ and $[Eu(TTA)_2(H_2O)_2(DB18C6)_2]$ [Felinto et al. 2003]. The stretching frequencies of the C=O group of HFBPI have been shifted from 1702 cm^{-1} to $\upsilon_{C=O}$: 1646 (Eu-FBPI-DC18C6), 1640 (Eu-FBPI-18C6) and 1660 (Eu-FBPI-DB18C6) cm^{-1}, which suggests that the carbonyl group is involved in the complex formation. The IR bands of C-O-C and Ph-C-O stretching vibrations in CE ligands show a significant shift to lower frequencies or diminution in intensity on complexation with the metal ion. The C-O-C vibrations at 1096, 1116 and 1136 cm^{-1} of DC18C6, 18C6 and DB18C6, respectively appear at 1089, 1116 and 1129 cm^{-1} in the respective complexes with less intensity. This suggests the involvement of oxygen of the CE in complex formation.

Table 3.8 shows the ^1H NMR chemical shifts of free HFBPI, 18C6, DC18C6, DB18C6 and complexes of these ligands with Eu^{3+} ion. For DC18C6 alone, in the ^1H NMR spectra, the CE protons were observed as a singlet at 3.67ppm, and the CH_2 protons of the cyclohexane were observed as a multiplet at 1.88-1.29ppm [Pedersen 1967].

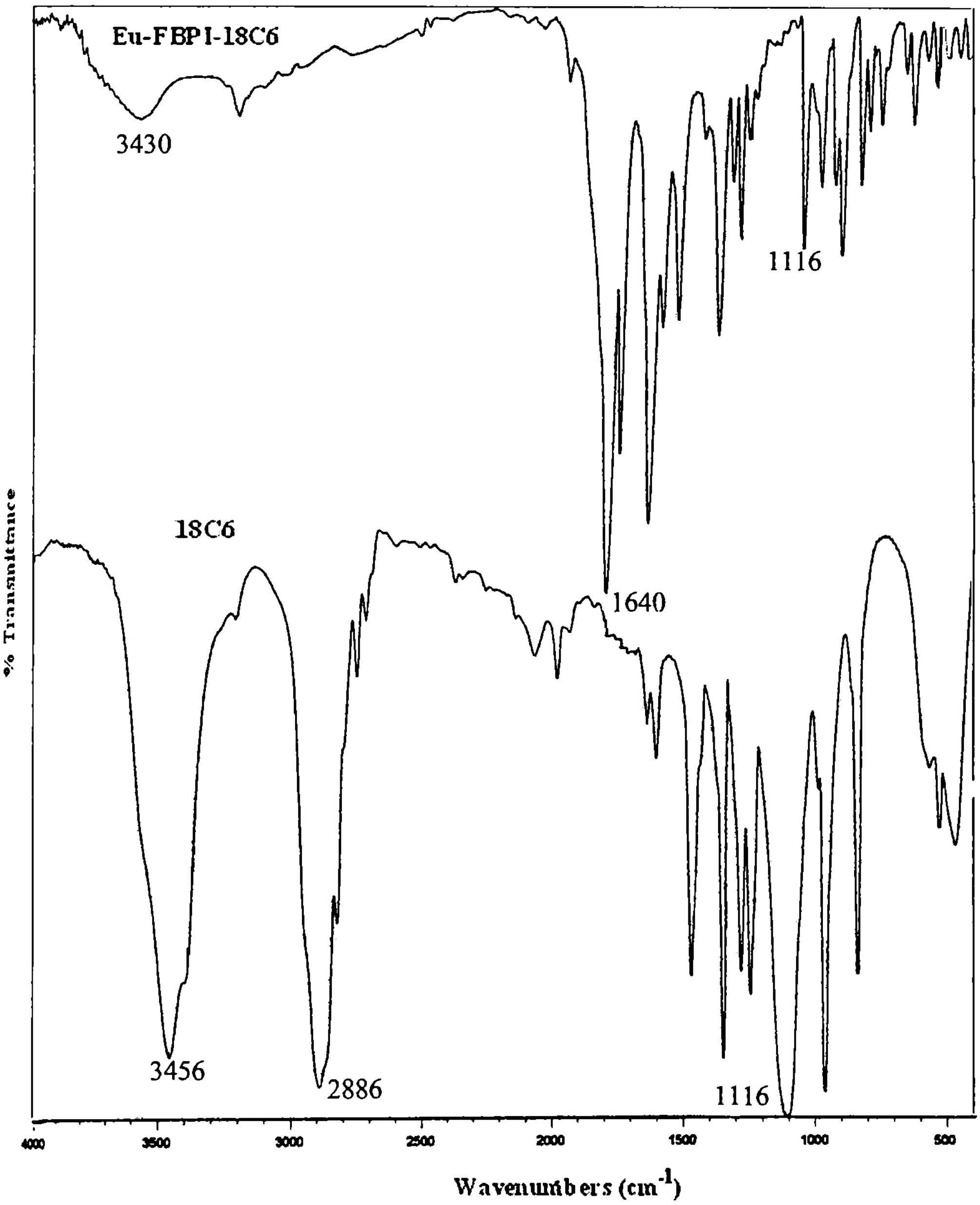


Fig. 3.30. IR spectrum of ternary complex of Eu^{3+} ion with HFBPI and 18C6 (KBr).

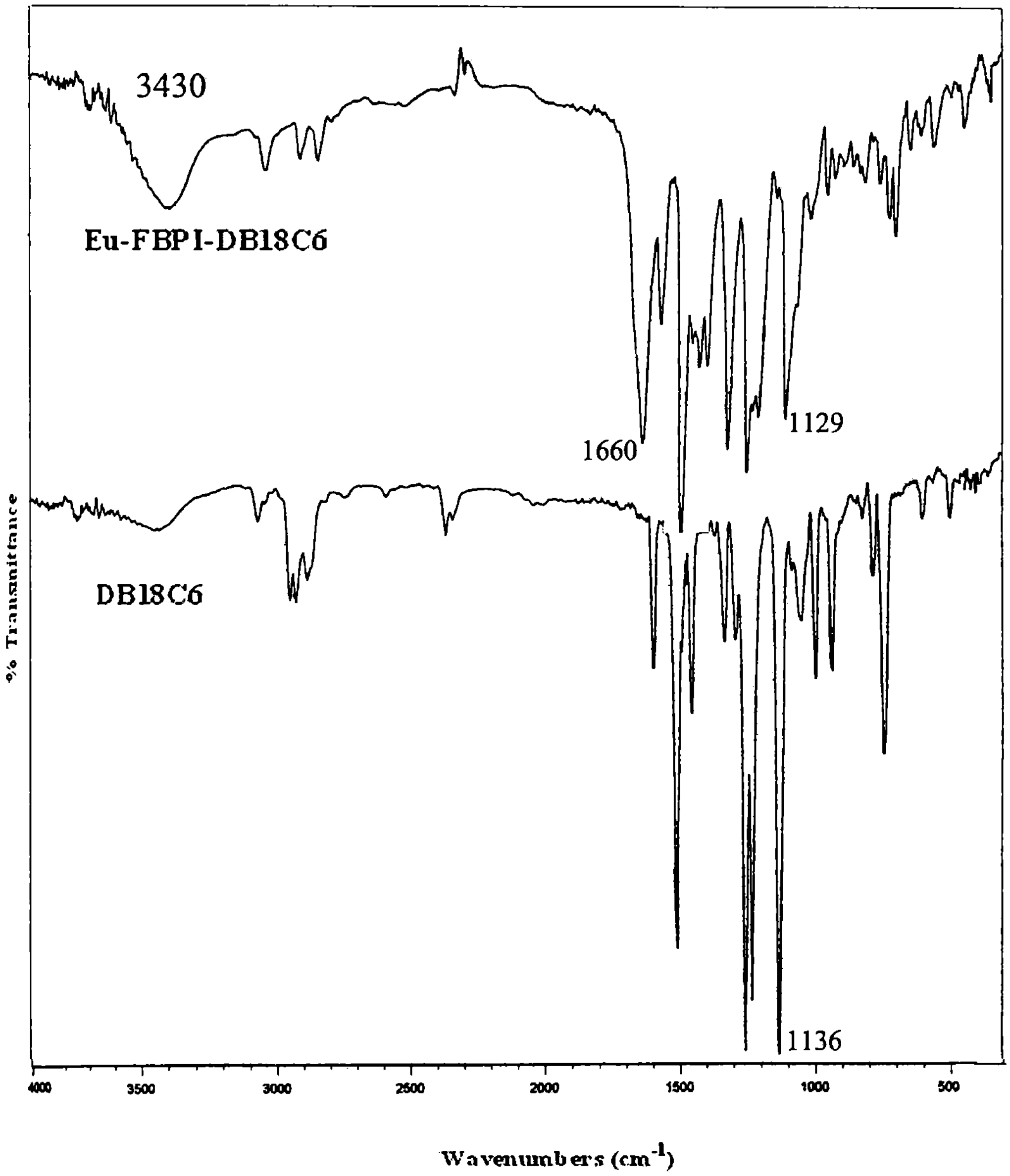


Fig. 3.31. IR spectrum of ternary complex of Eu^{3+} ion with HFBPI and DB18C6 (KBr).

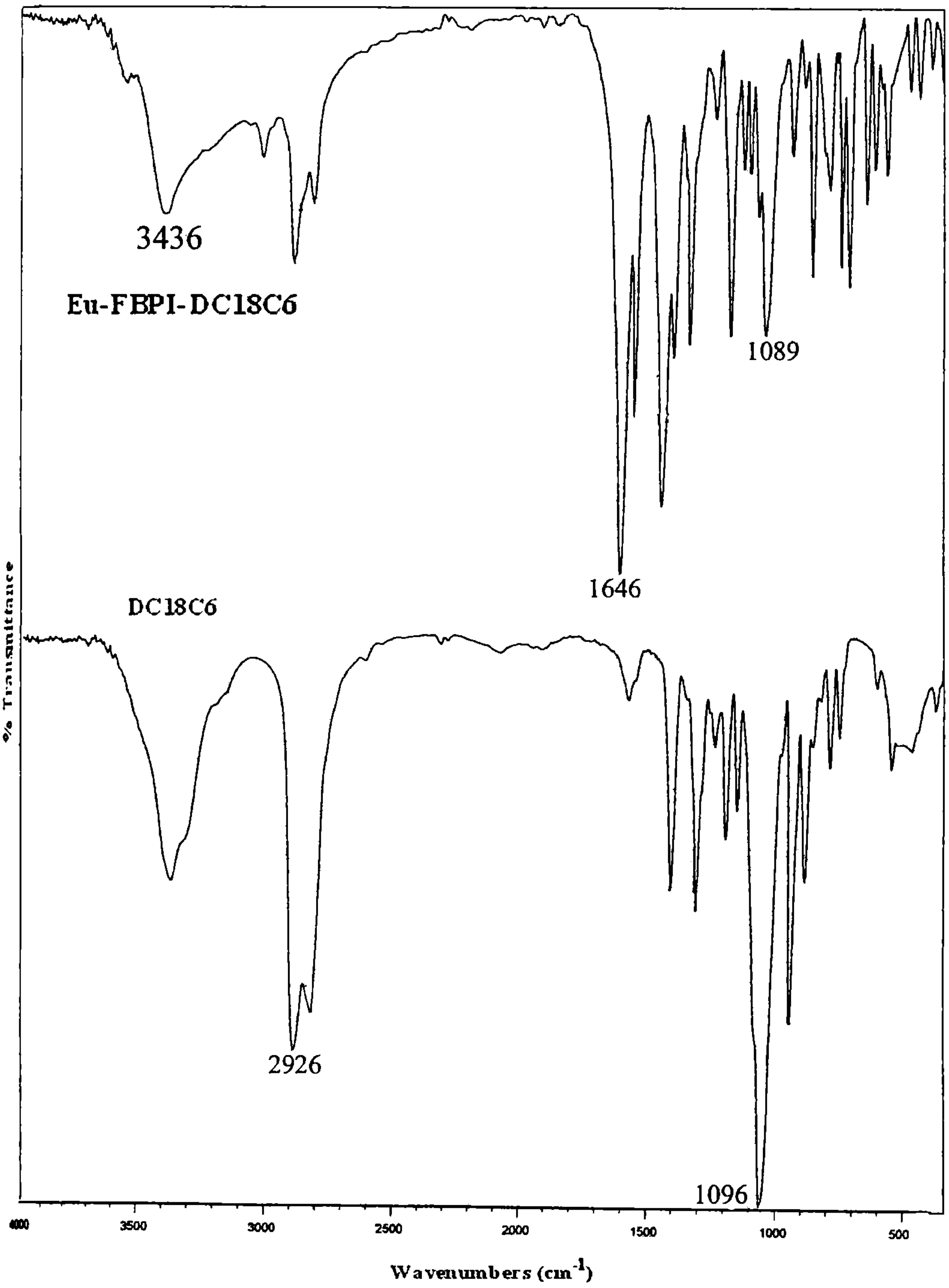


Fig. 3.32. IR spectrum of ternary complex of Eu^{3+} ion with HFBPI and DC18C6 (KBr).

In the complex, the CE protons were observed at 3.50 ppm and 2.70 ppm (up field) of equal intensity, indicating non-uniform interactions of ethereal oxygens of DC18C6 with Eu^{3+} ion. On the other hand, CH_2 protons of cyclohexane were observed as a multiplet at 1.19-1.97 ppm. For 18C6 alone, a singlet is observed at 3.68 ppm. In the complex, Eu-FBPI-18C6, two singlets were observed at 3.86 ppm and 3.84 ppm (down field) confirming non-uniform interactions of ethereal oxygens of 18C6 with Eu^{3+} ion. The CE protons observed at 4.03 ppm and 4.17 ppm in the free ligand, DB18C6, are observed at 4.04, 4.17 and 4.24 ppm in the complex, Eu-FBPI-DB18C6, indicating non-uniform interactions of ethereal oxygens of DB18C6 with Eu^{3+} ion (Figs. 3.33-3.35). It can be concluded from the ^1H NMR studies that lanthanoids may not interact uniformly with all the potential donor oxygens of CEs. This is in good agreement with the earlier reports of the extraction of lanthanoids with 2-thenoyltrifluoroacetonate (HTTA) complexes in the presence of CEs [Mathur and Choppin 1993].

Table 3.9 gives the separation factors (S.F.) between these trivalent metal ions, defined as the ratio of the respective equilibrium constants in the HPBI, HFBPI, HTPI and HFBPI + CE systems. It is clear from the table that the addition of a CE to the metal chelate system enhances the extraction efficiency significantly, but, at the same time, it diminishes the selectivity among these trivalent metal ions. Better selectivity has been well documented in the case of lanthanoids with HTTA or Hbtfa in the presence of CEs due to ion pair extraction of lighter lanthanoids. However, in the present study, no such behaviour has been observed. Thus the decrease in selectivity in the present system may be due to the formation of simple metal chelate in the presence of CEs.

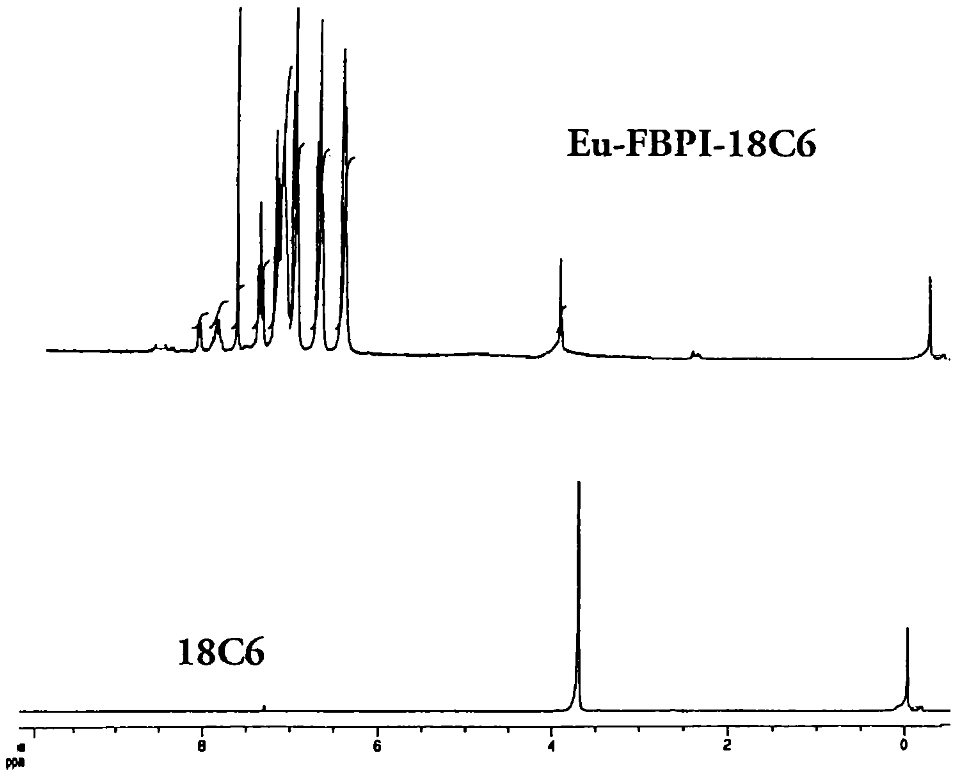


Fig. 3.33. ^{1}H NMR spectrum of Eu^{3+}-HFBPI-18C6 ternary complex ($CDCl_3$-DMSO-d_6).

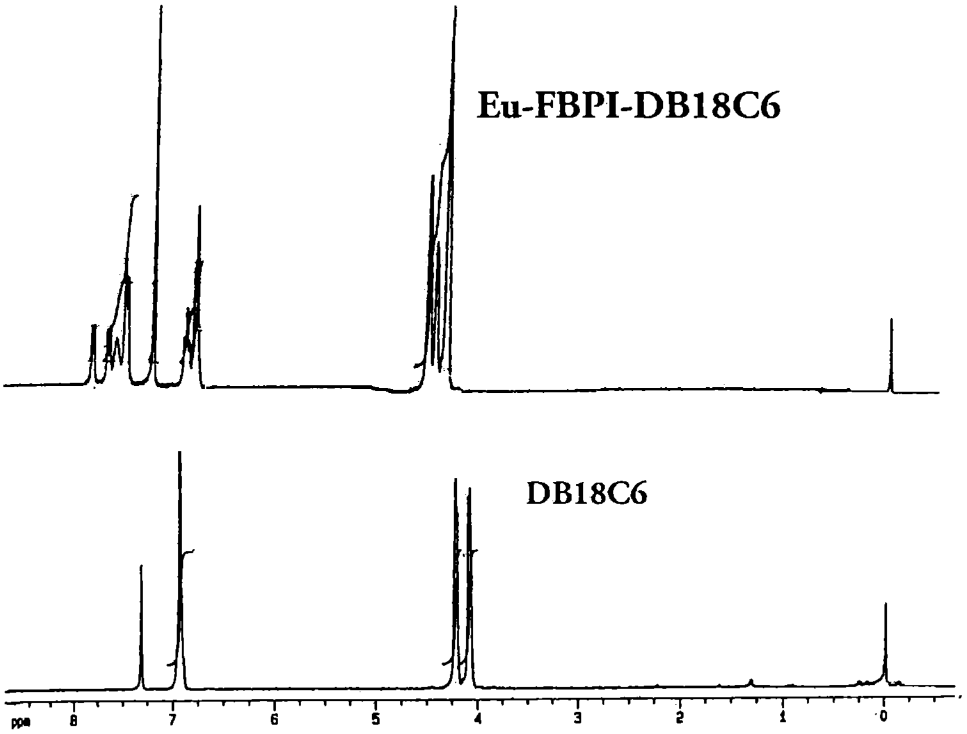


Fig. 3.34. ^{1}H NMR spectrum of Eu^{3+}-HFBPI-DB18C6 ternary complex ($CDCl_3$-DMSO-d_6).

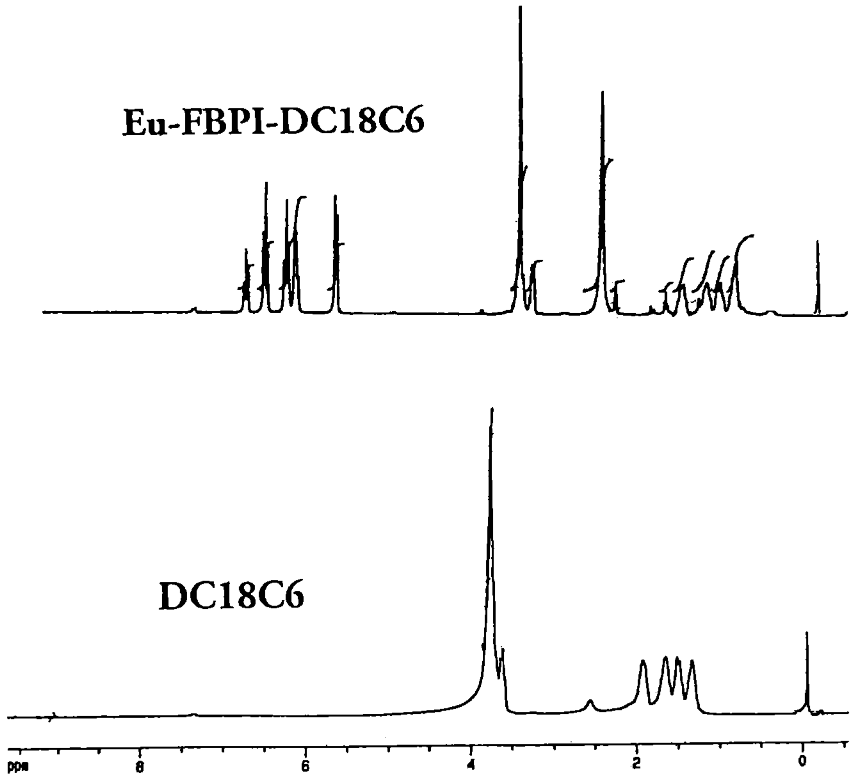


Fig. 3.35. ^{1}H NMR spectrum of Eu^{3+}-HFBPI-DC18C6 ternary complex (CDCl$_3$-DMSO-d$_6$).

Table 3.8. ^{1}H NMR spectral data of free ligands and metal-chelate-CE complexes.

Compound	Phenyl protons (ppm)	Crown ether protons (ppm)
18C6	---	3.68
DC18C6	---	3.67, 1.88-1.29*
DB18C6	6.87	4.03, 4.17
HFBPI	6.80-7.39	---
$Eu(FBPI)_3.18C6$	6.16-8.11	3.86, 3.84
$Eu(FBPI)_3.DC18C6$	5.7-6.76	3.50, 2.70, 1.19-1.97*
$Eu(FBPI)_3.DB18C6$	6.88-8.09	4.04, 4.17, 4.24

*-cyclohexyl -CH_2 protons

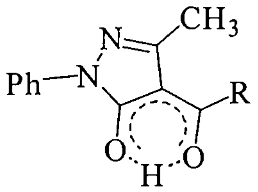
Table 3.9. Separation factors between Nd^{3+}, Eu^{3+} and Tm^{3+} ions with HPBI, HFBPI, HTPI and HFBPI + CE systems.

Extraction system	Separation Factor (S.F.)	
	Eu/Nd	Tm/Eu
HPBI	20.80	1.24
HFBPI	4.88	1.55
HTPI	12.66	1.80
HFBPI + DC18C6	3.97	1.74
HFBPI + 18C6	4.07	1.92
HFBPI + B18C6	4.30	1.66
HFBPI + DB18C6	4.78	1.75

Chapter 4

Synergistic Solvent Extraction of Trivalent Lanthanoids with Mixtures of 1-Phenyl-3-methyl-4-pivaloyl-5-pyrazolone and Structurally Related Crown Ethers

1-Phenyl-3-methyl-4-acyl-5-pyrazolones (1) form an interesting class of β-diketones capable of extracting metal ions, particularly the "hard" metal ions, such as lanthanoids from relatively strong acidic solutions due to their lower pK_a values (2.56-4.01) as compared to the familiar β-diketone, 2-thenoyltrifluoroacetone (HTTA; pK_a = 6.25) [Umetani and Freiser 1987; Reddy et al. 2000; Umetani et al. 2000; Jordanov et al. 2002]. The nature of the substituent in the 4-position of pyrazolone ring causes significant variations in the electronic, steric, and solubility parameters of the ligand, thereby affecting complexation and extraction behaviour of metal ions.



R	
CH_3	HPMAP
$C(CH_3)_3$	HPMPP
Ph	HPMBP
CF_3	HPMTFP

1

Further, these ligands were found to have longer distances between the two donating oxygens (bite size) as compared to the conventional β-diketones, such as acetylacetone and HTTA, according to estimation by molecular orbital calculations (Table 4.1) [Umetani et al. 2000]. Recently the relationship between the bite size and the selectivity in the extraction of Ln^{3+} ions has been investigated and reported that the O---O distance is one of the most significant factors that governs the selectivity in the complexation of β-diketones with metal ions. Our investigations in the previous chapter show that the para substitution by an electron withdrawing (-F) or electron-donating ($-CH_3$) group on the benzoyl moiety of HPBI was unable to narrow the distance between the two donating oxygen atoms. Hence, if we can modify the structure of the β-diketone by introducing bulky groups to create a steric effect, this distance, may intentionally be controlled, and consequently the extractability and / or the selectivity can be improved. These factors prompted us to synthesize 1–phenyl–3-methyl–4–pivaloyl–5–pyrazolone (HPMPP) by introducing a bulky group (pivaloyl) at the 4-position of the pyrazolone ring to create a steric effect and consequently, reducing the bite size that may enhance the selectivity among the Ln^{3+} ions.

Table 4.1. Bite size of some of the β-diketones determined by semi-empirical MNDO/H molecular orbital calculation.

β-Diketone	O---O distance (bite size), Å
HPMTFP	2.66
HPMBP	2.65
HPMAP	2.60
HPMPP	2.48
HTTA	2.50

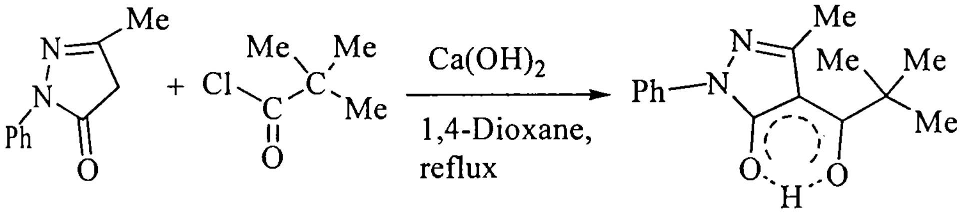
This chapter incorporates the results of the investigations carried out on the extraction of Ln^{3+} ions with HPMPP in the presence and absence of various macrocyclic crown ethers.

4.1. Experimental

4.1.1. Chemicals

Synthesis of 1–phenyl–3–methyl–4–pivaloyl–5–pyrazolone (HPMPP)

HPMPP was synthesized by the acylation of 1–phenyl–3-methyl–5–pyrazolone with pivaloyl chloride as described in **Scheme 4.1** [Jensen 1959].



Scheme 4.1

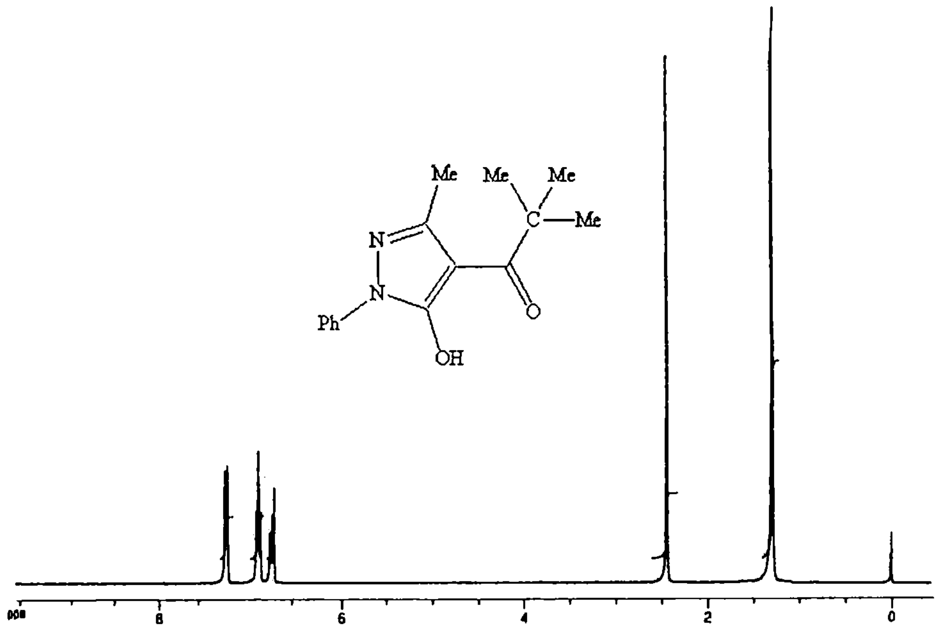


Fig. 4.1. ^{1}H NMR spectrum of HPMPP.

Purity of the synthesized ligand was established by elemental analyses, IR and ^1H NMR (Fig. 4.1) spectral data. Recrystallization from ethyl acetate-hexane mixture gave pale yellow crystals, M.P. 93-94^{0}C. Elemental analysis: Calc. for $C_{15}H_{18}N_2O_2$: C, 69.74; H, 7.02; N, 10.84. Found: C, 69.65; H, 6.82; N, 10.96%. ^1H NMR data ($CDCl_3$): δ 1.38 (9H, s, pivaloyl CH_3), 2.61 (3H, s, CH_3 of the ring), 7.22-7.32 (1H, t, Ar-*p*-H), 7.38-7.48 (2H, t, Ar-*m*-H), 7.77-7.87 (2H, d, Ar-*o*-H) (Fig. 4.1). No enolic proton peak is observed in the ^1H NMR of HPMPP, although it exists quantitatively in the enolic form in organic solvents, which can be assured by the lack of a peak for the methyne proton at the 4th position. IR data: $\upsilon(cm^{-1})$: 2820-3118, 1646, 1620, 1545, 1500, 1387, 1328, 1116, 957, 844, 738, 692. The methods of preparation of stock solutions of metal ions and apparatus used are the same as described in Chapter 3. Initial metal ion concentration was maintained at 1.0×10^{-4} mol dm^{-3} for all the extraction studies. Sodium acetate (0.01 mol dm^{-3}) was used as the buffering component and the aqueous phase pH was adjusted to the desired value with HCl or NaOH solution. All other chemicals used were of analytical reagent grade.

4.1.2. Solvent extraction and analytical procedure

The solvent extraction and analytical procedure used for the determination of metal ions are the same as described in Chapter 3. Preliminary experiments showed that the extraction equilibrium was attained within 40 min.

4.1.3. *Preparation of metal complexes*

The procedure followed for the synthesis of Eu-PMPP and Eu-PMPP-DC18C6 complexes is the same as that described in Chapter 3.

4.2. Results and Discussion

4.2.1. *Extraction of Ln^{3+} ions with HPMPP*

The extraction behaviour of Nd^{3+}, Eu^{3+} and Tm^{3+} ions from 0.1 mol dm^{-3} perchlorate solution with HPMPP alone in chloroform as a function of the extractant concentration (0.005–0.05 mol dm^{-3}) and pH (4.90-5.95), respectively, has been investigated. The relevant log-log plots (Figs. 4.2-4.3) gave straight lines with slopes of three, indicating the extraction of simple metal chelates, $Ln(PMPP)_3$.

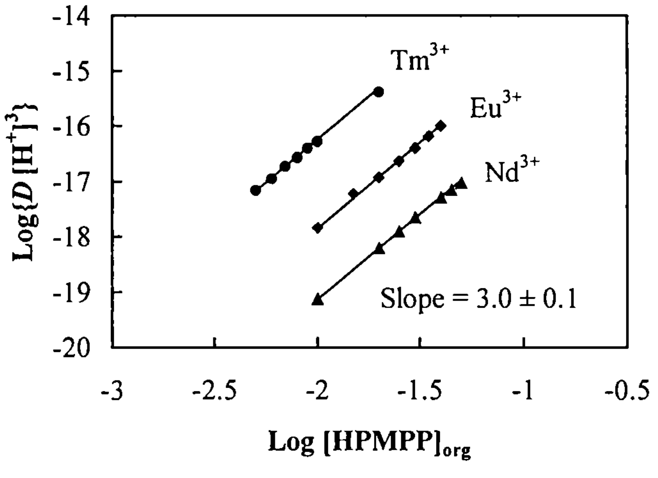


Fig. 4.2. Effect of HPMPP concentration on the extraction of Ln^{3+} ions. Aqueous phase = 0.1 mol dm^{-3} $NaClO_4$ + 0.01 mol dm^{-3} NaOAc + Ln^{3+} = 1×10^{-4} mol dm^{-3} of pH = 5.87.

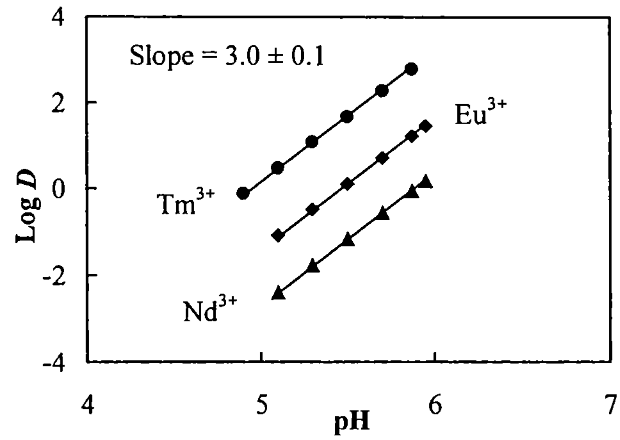


Fig. 4.3. Effect of pH on the extraction of Ln^{3+} ions at constant HPMPP concentration (0.03 mol dm^{-3}). Aqueous phase = 0.1 mol dm^{-3} $NaClO_4$ + 0.01 mol dm^{-3} NaOAc + Ln^{3+} = 1 × 10^{-4} mol dm^{-3}.

The formation of simple metal chelates, $Ln(PMTFP)_3$ for the extraction of Ln^{3+} ions with HPMTFP in chloroform has been well documented [Umetani and Freiser 1987; Thakur et al. 1996].

Based on the preceding studies, the extraction equilibria of Nd^{3+}, Eu^{3+} and Tm^{3+} ions with a chelating extractant, HPMPP alone may be expressed as:

$$Ln^{3+}_{aq} + 3\,HPMPP_{org} \overset{K_{HPMPP}}{\rightleftharpoons} Ln(PMPP)_{3\,org} + 3\,H^+_{aq} \quad (1)$$

where K_{HPMPP} denotes the equilibrium constant and is given by

$$K_{HPMPP} = \frac{[Ln(PMPP)_3]_{org}\,[H^+]^3_{aq}}{[Ln^{3+}]_{aq}\,[HPMPP]^3_{org}} \quad . \qquad (2)$$

Then the distribution ratio, D, can be expressed as:

$$D = \frac{K_{\mathrm{HPMPP}}\,[\mathrm{HPMPP}]^3_{\mathrm{org}}}{[\mathrm{H}^+]^3_{\mathrm{aq}}} \qquad (3)$$

The equilibrium constants of the above extracted complexes were determined by non-linear regression analysis (as described in chapter 3) and are given in Table 4.2. The equilibrium constants thus calculated refer only to concentration quotients, calculated on the assumption that the activity coefficients of the species involved do not change significantly under the present experimental conditions. It can be seen from Table 4.2 that the equilibrium constants (K_{HPMPP}) of these trivalent metal ions increase with decreasing ionic radii of the Ln^{3+} ion. A similar trend has been observed with other derivatives of 4-acylpyrazolones such as HPMAP [Sasaki and Freiser 1983], HPMTFP [Mathur and Khopkar 1987] and HPMBP [Santhi et al. 1994] in the extraction of Ln^{3+} ions. The equilibrium constants (Log K_{ex}) of various 4-acyl-5-pyrazolones for the extraction of Eu^{3+} ion have been correlated with their pK_a values [Sasaki and Freiser 1983; Mathur and Khopkar 1987] in Fig. 4.4 and it is clear that the Log K_{ex} value increases as pK_a value decreases.

Table 4.2. Two phase equilibrium constants of Ln^{3+}-HPMPP-crown ether-chloroform systems.

Extraction System	Log Equilibrium constant (log K_{HPMPP} or log $K_{\mathrm{Syn,1}}$)		
	Nd^{3+}	Eu^{3+}	Tm^{3+}
HPMPP	-13.09 ± 0.02	-11.82 ± 0.03	-10.25 ± 0.03
HPMPP + 18C6	-9.73 ± 0.02	-8.55 ± 0.02	-7.70 ± 0.01
HPMPP + DC18C6	-9.95 ± 0.02	-8.69 ± 0.03	-7.94 ± 0.01
HPMPP + DB18C6	-10.99 ± 0.03	-9.32 ± 0.02	-8.19 ± 0.01

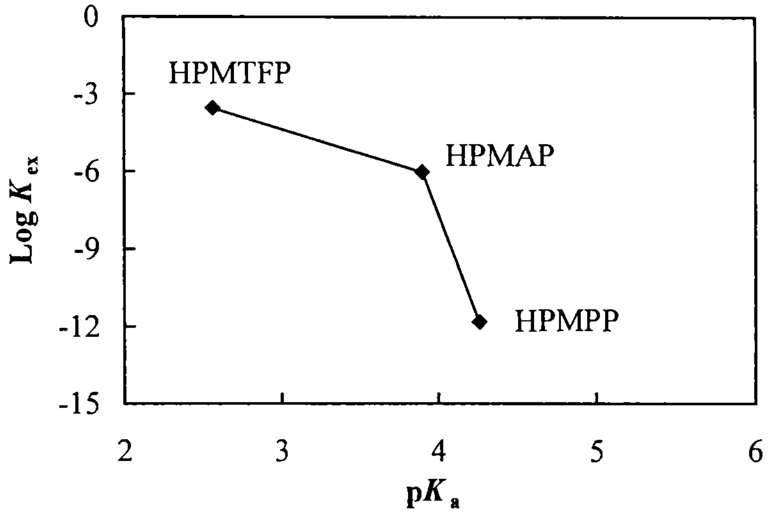


Fig. 4.4. Correlation between the pK_a values of 4-acylpyrazolones and the Log K_{ex} values of Eu^{3+} ion.

4.2.2. Solid complex of Eu^{3+} ion with HPMPP and its characterization

Solid complex of Eu^{3+} ion with HPMPP has been synthesized and characterized by IR and ^1H NMR spectral data.

IR spectral data of Eu-PMPP complex

IR spectrum of the Eu^{3+}-PMPP complex shows a broad absorption in the region 3000-3500 cm^{-1} indicating the presence of water of hydration in the complex. The presence of water molecules in the extracted β-diketone complexes of Ln^{3+} ion is well documented [Mathur and Choppin 1993]. The carbonyl stretching frequency has been shifted from 1620 in the free HPMPP to 1613 cm^{-1} in Eu^{3+}-PMPP complex indicating the involvement of carbonyl oxygen in complex formation (Fig. 4.5).

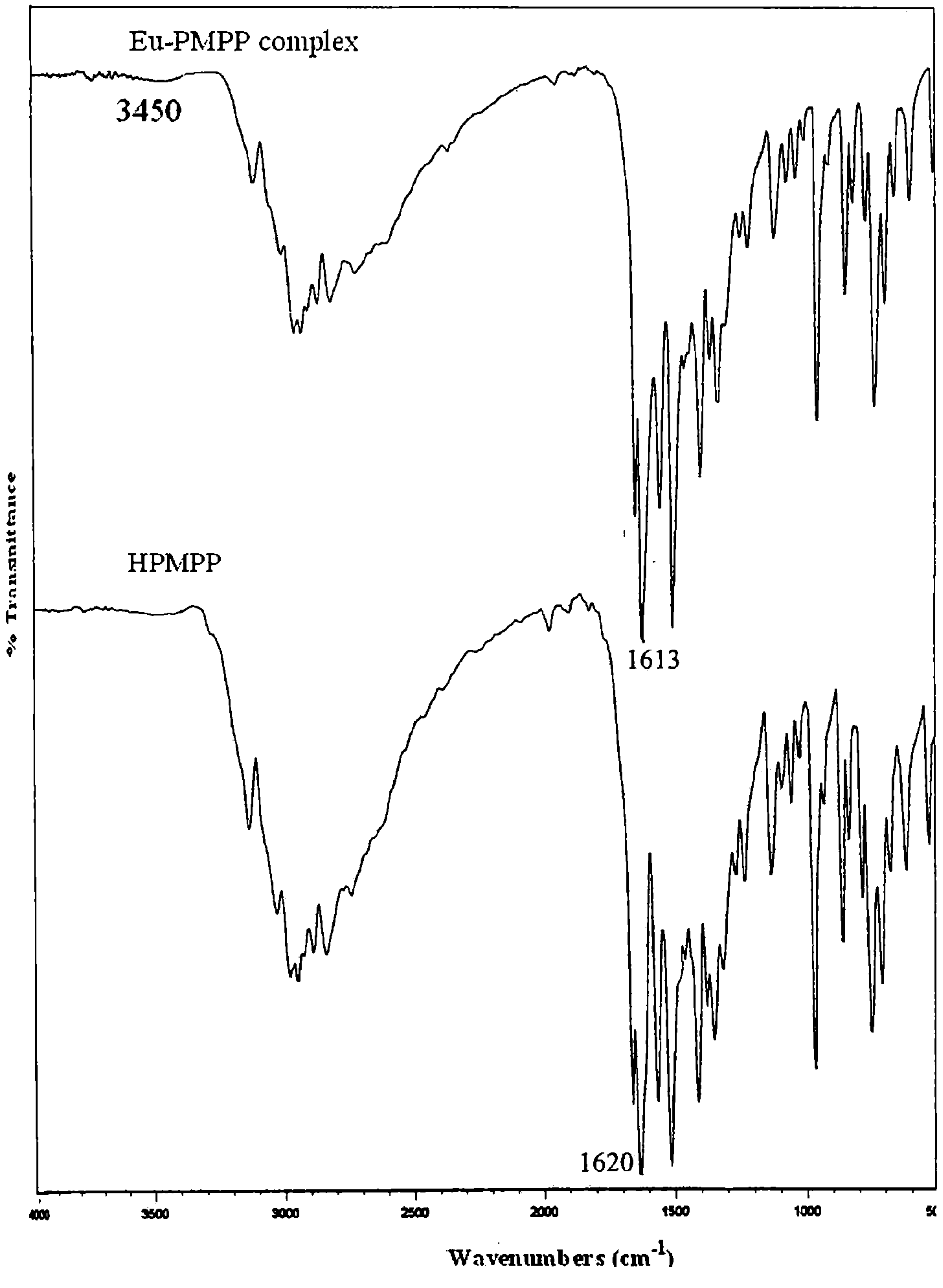


Fig. 4.5. IR spectrum of Eu^{3+}-HPMPP binary complex (KBr).

^1H NMR spectral data of Eu^{3+}-PMPP complex

The ^{1}H NMR spectrum of Eu^{3+}-PMPP complex showed all expected signals for HPMPP protons. The signals of phenyl protons (7.87-7.22 ppm) have always been shifted to up field (7.75-7.19 ppm) upon coordination with the metal ion (Fig. 4.6). The pivaloyl CH_3 groups and the CH_3 group of the pyrazolone ring have been shifted from 1.38 to 1.33 and 2.60 to 2.54 ppm, respectively, on complexation. Signals for water protons were also noticed in the ^{1}H NMR spectrum.

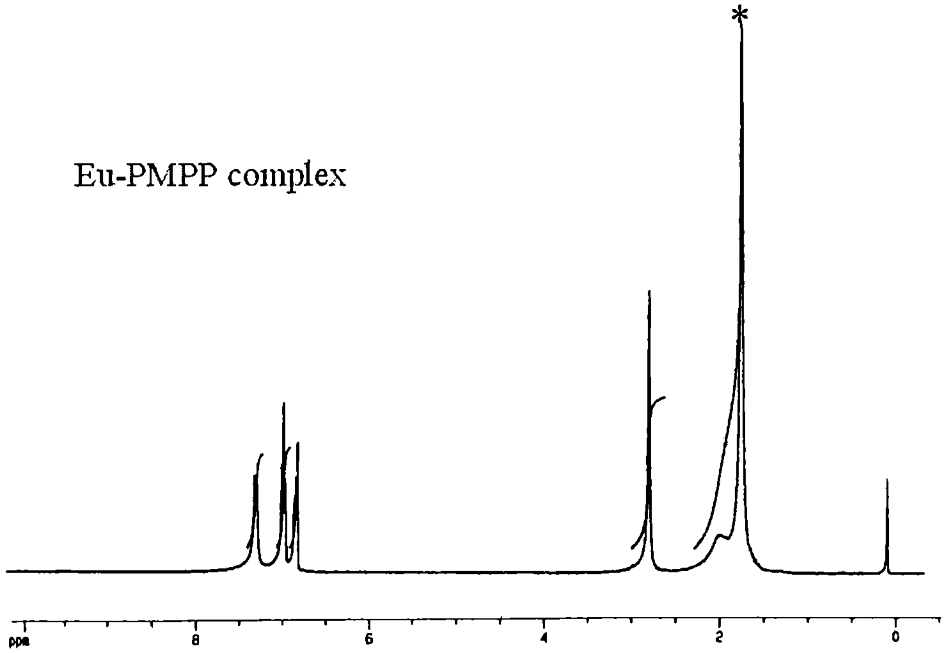


Fig. 4.6. ^{1}H NMR spectrum of Eu^{3+}-HPMPP binary complex (acetone-d_6*).

From the results of the extraction data, elemental analyses and IR spectral data, it is clear that Eu^{3+} ion is interacting with three molecules of HPMPP, releasing three H^+ ions. The proposed structure of the extracted complex is shown in Fig. 4.7.

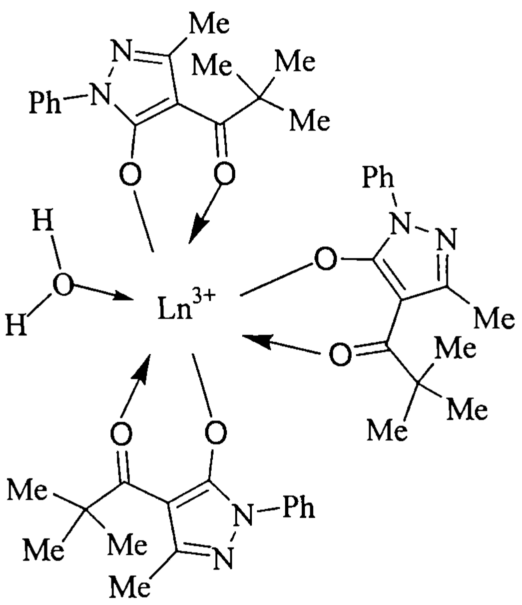


Fig. 4.7. Proposed structure of Eu^{3+}-HPMPP binary complex.

Table 4.3 gives the separation factors (S.F.) between Ln^{3+} ions defined as the ratio of the respective equilibrium constants with HPMPP. The S.F. values obtained especially between Eu and Nd pair with HPMPP is found to be significantly higher than that obtained with D2EHPA or EHEHPA, which are widely used as extractants in the Rare Earth Industry [Bautista 1995; Pierce and Peck 1963; Reddy 1995b].

Table 4.3. Separation factors between Nd^{3+}, Eu^{3+} and Tm^{3+} ions.

Extraction Systems	Separation Factors (S.F.)	
	Eu / Nd	Tm / Eu
HPMPP	19.00	37.00
HFBPI	4.88	1.55
HPBI	20.80	1.24
HTPI	12.66	1.80
EHEHPA	3.94	24.00
D2EHPA	12.50	161.00

Also the S.F. value with HPMPP is found to be higher than that obtained with 4-aroyl-5-isoxazolones (chapter 3). This indicates that the separation becomes poorer as the extractability increases. This would strongly suggest the relationship between the selectivity and the O---O distance of the β-diketones. The β-diketones with shorter O---O distances (HPMPP = 2.48 Å) were found to have better selectivity than those with longer O---O distances (HFBPI, HTPI and HPBI = 2.72 Å).

4.2.3. *Extraction of Ln^{3+} ions with mixtures of HPMPP and structurally related crown ethers*

The extraction equilibria of Ln^{3+} ions with a chelating agent, HPMPP in presence of crown ether (CE) can be expressed as:

$$Ln^{3+}_{aq} + 3\,HPMPP_{org} + m\,CE_{org} \overset{K_{Syn,m}}{\rightleftharpoons} Ln(PMPP)_3 \cdot mCE_{org} + 3H^{+}_{aq} \quad (4)$$

where m = 0 or 1. The distribution ratio, $D_{Syn,1}$ can be written as

$$D_{Syn,1} = \frac{[\,HPMPP\,]^{3}_{org}\,\{K_{HPMPP} + K_{syn,1}\,[\,CE\,]_{org}\}}{[\,H^{+}\,]^{3}_{aq}} \quad (5)$$

$$\text{where } [CE]_{org} = [CE]_{initial} / (1 + \frac{1}{K_D}) \quad (6)$$

The equilibrium concentration of 18C6 was calculated using the partition coefficient (log $K_{D,18C6}$ = 0.8) taken from the literature [Sahu et al. 2000]. Since the partition coefficients of DC18C6 and DB18C6 (log $K_{D,DB18C6}$ = 3.8; log $K_{D,DC18C6}$ = 3.52) are known to be quite large, no correction is necessary for the partitioning of CEs into the aqueous phase [Mohapatra and Manchanda 1991; Reddy et al. 1997]. The interaction between the chelating agent and a neutral oxo-donor in chloroform are, in general, weaker when the diluent itself has strong interaction with the oxo-donor [Sekine et al. 1983]. Hence, it is assumed that there is negligible interaction between HPMPP and crown ethers in chloroform. The adduct formation reaction in the organic phase and the stability constant, β_1, is given by

$$\mathrm{Ln(PMPP)_{3\,org}} + \mathrm{CE_{org}} \overset{\beta_1}{\rightleftharpoons} \mathrm{Ln(PMPP)_3.CE_{org}} \qquad (7)$$

$$\beta_1 = K_{\mathrm{Syn},1} \,/\, K_{\mathrm{HPMPP}} \qquad (8)$$

The extraction of Nd^{3+}, Eu^{3+} and Tm^{3+} ions from 0.1 mol dm^{-3} sodium perchlorate solution of pH = 5.87 with mixtures of HPMPP and 18C6, DC18C6, or DB18C6 in chloroform has been studied. It was found that the extraction of Ln^{3+} ions into chloroform was negligible with crown ether alone under the present experimental conditions. However, with mixtures of HPMPP (0.01 mol dm^{-3}) and crown ethers (0.005 mol dm^{-3}), considerable synergistic enhancement (Synergistic enhancement factor = $D_{Syn,1} / (D_{\mathrm{HPMPP}} + D_{\mathrm{CE}})$, where $D_{Syn,1}$ = distribution ratio with HPMPP + CE; D_{HPMPP} = distribution ratio with HPMPP alone and D_{CE} = distribution ratio with CE alone) in the extraction of these metal ions has been observed (Table 4.4). It is clear from Table 4.4 that the synergistic enhancement factor of a particular Ln^{3+} ion decreases from 18C6 to DB18C6, and this can be attributed to steric effects.

The effect of HPMPP concentration (0.004-0.04 mol dm^{-3}) on the extraction efficiency of Ln^{3+} ions has been investigated in the presence of various structurally related CEs (0.005 mol dm^{-3}) from 0.1 mol dm^{-3} sodium perchlorate solution of pH = 5.87. It is clear from the plots (Figs. 4.8-4.10) of log $\{D_{Syn,1}\,[H^+]^3 / (1 + (K_{\mathrm{Syn},1}/K_{\mathrm{HPMPP}})\,[CE]\,)\}$ (rearrangement of Eq. (5)) vs. log $[HPMPP]_{org}$ that at constant CE concentration only three HPMPP moieties are attached to the synergistic species in all the systems studied here. The extraction efficiency of Ln^{3+} ion from 0.1 mol dm^{-3} sodium perchlorate solution of pH = 5.87 has been studied as a function of CE concentration; 18C6 (0.006-0.04 mol dm^{-3}), DC18C6 (0.003-0.01 mol dm^{-3}) or DB18C6 (0.004-0.05 mol dm^{-3}) in the presence of constant concentration of HPMPP (0.01 mol dm^{-3}) and the results are given in Figs. 4.11-4.13. The plots of log $\{(D_{Syn,1}\ [H^+]^3 / [HPMPP]^3) - K_{HPMPP}\}$ vs. log $[CE]_{org}$ at constant HPMPP concentration gave slopes of unity for all the metal ions, indicating the participation of only one crown ether molecule in these synergistic extracted complexes. These, in conjunction with slopes of three (Figs. 4.14-4.16) observed with pH variation (4.9-5.95) experiments with a mixture of constant HPMPP (0.01 mol dm^{-3}) and CE (0.005 mol dm^{-3}) concentrations, indicated the extraction of the species $Ln(PMPP)_3.CE$. Synergistic complexes containing one molecule of crown ether have been reported [Thakur et al. 1996] for the extraction of Ln^{3+} ions with mixtures of HPMTFP and various crown ethers in chloroform.

The involvement of one molecule of benzo-15-crown-5 (B15C5) in the synergistic extraction of Ln^{3+} ions with HPMBP and B15C5 in chloroform has also been reported elsewhere [Dukov 1992]. The equilibrium constants of the synergistic complexes of these Ln^{3+} ions were deduced by a non-linear regression analysis and are given in Table 4.2. It can be clearly seen from Table 4.2 that the synergistic constant ($K_{Syn,1}$) increases with decreasing ionic radii of these metal ions for all the systems studied here. Similar trends have been noticed in the extraction of Ln^{3+} ions with mixtures of 4-acylpyrazolones and various CEs in chloroform [Dukov 1992; Thakur et al. 1996]. The increase in the extractability of lanthanoid complexes from Nd^{3+} to Tm^{3+} ion can be due to the increase in electrostatic interactions between the cation and the ligand with decrease in ionic radii. In polar diluents, this can be attributed to the increasing coulombic interactions with charge density of the lanthanoid ions [Manchanda et al. 1988].

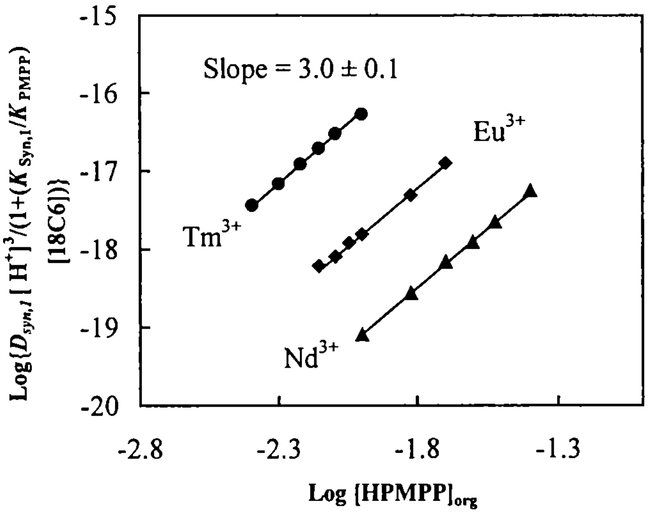


Fig. 4.8. Effect of HPMPP concentration on the extraction of Ln^{3+} ions at constant 18C6 concentration (0.005 mol dm^{-3}).

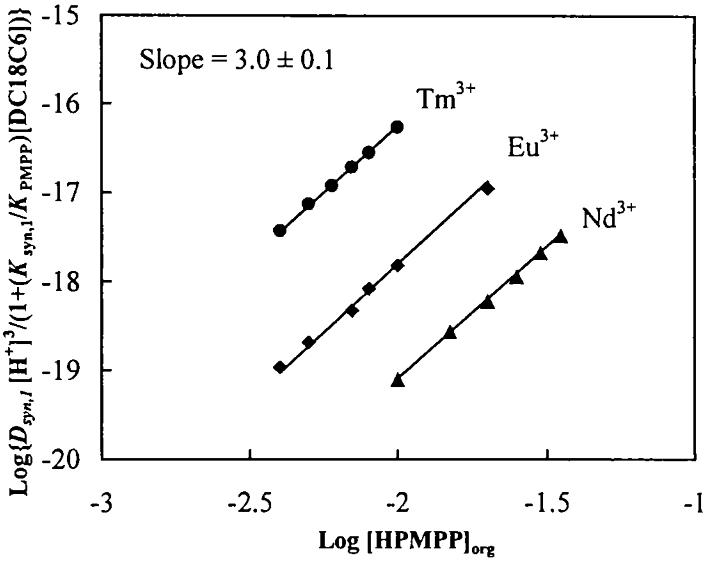


Fig. 4.9. Effect of HPMPP concentration on the extraction of Ln^{3+} ions at constant DC18C6 concentration (0.005 mol dm^{-3}).

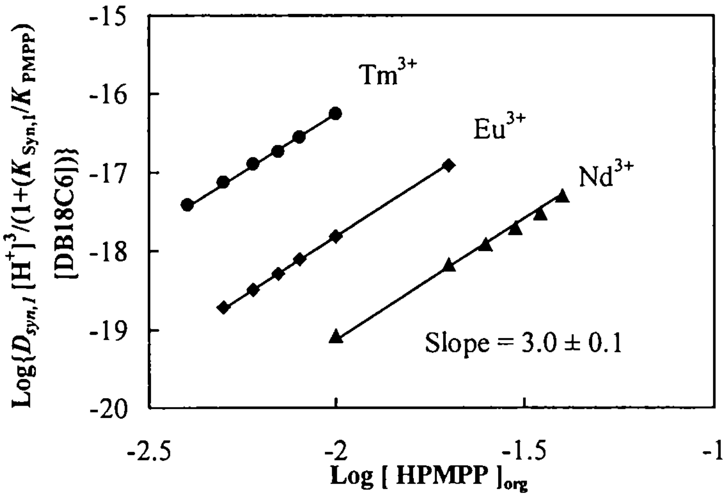


Fig. 4.10. Effect of HPMPP concentration on the extraction of Ln^{3+} ions at constant DB18C6 concentration (0.005 mol dm^{-3}).

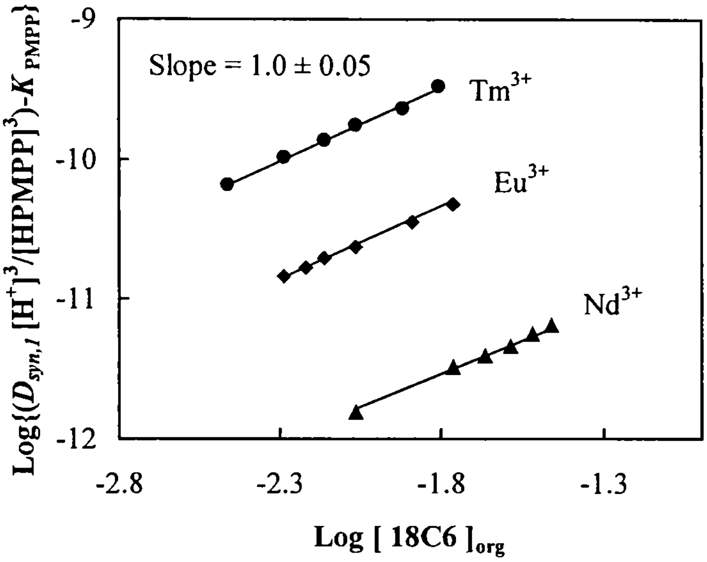


Fig. 4.11. Effect of 18C6 concentration on the extraction of Ln^{3+} ions at constant HPMPP concentration (0.01 mol dm^{-3}).

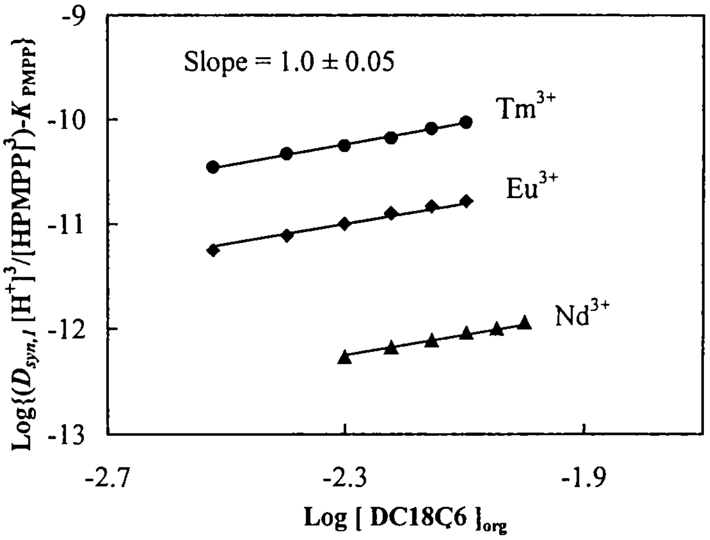


Fig. 4.12. Effect of DC18C6 concentration on the extraction of Ln^{3+} ions at constant HPMPP concentration (0.01 mol dm^{-3}).

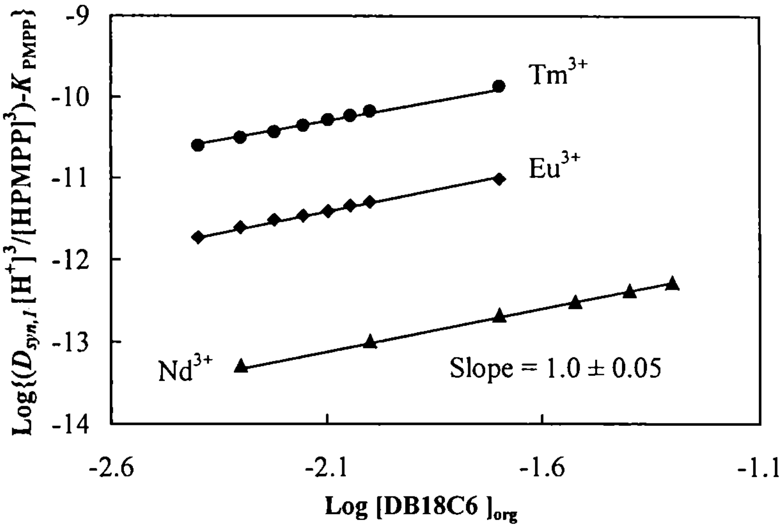


Fig. 4.13. Effect of DB18C6 concentration on the extraction of Ln^{3+} ions at constant HPMPP concentration (0.01 mol dm^{-3}).

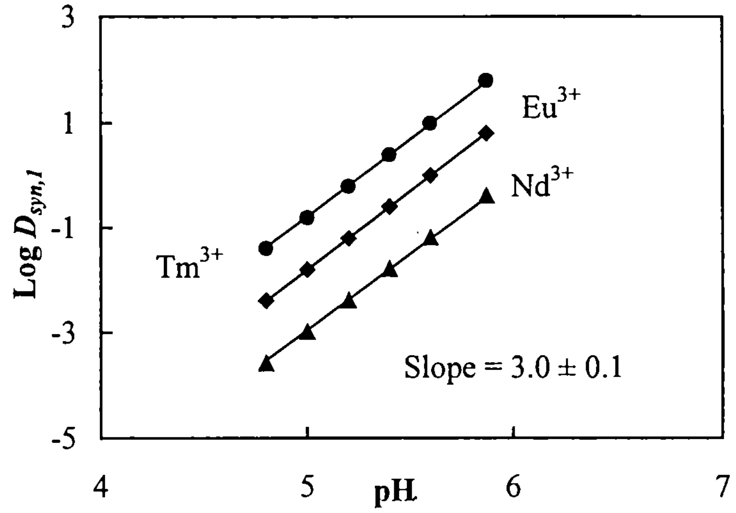


Fig. 4.14. Effect of pH on the extraction of Ln^{3+} ions at constant [HPMPP] = 0.01 mol dm^{-3} and [18C6] = 0.005 mol dm^{-3}.

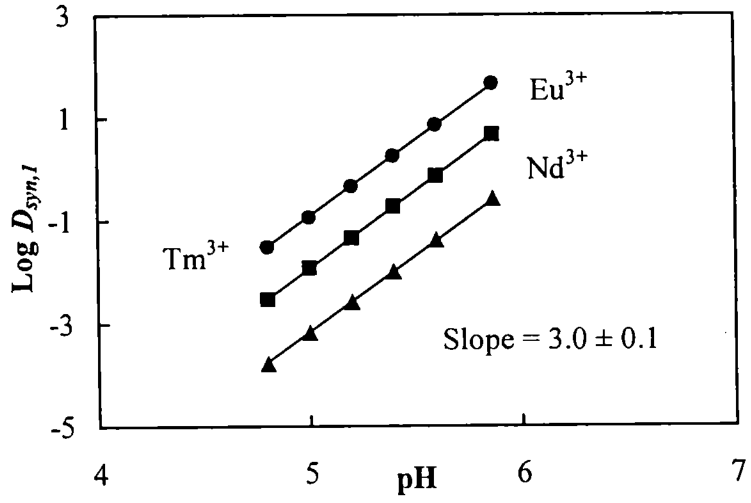


Fig. 4.15. Effect of pH on the extraction of Ln^{3+} ions at constant [HPMPP] = 0.01 mol dm^{-3} and [DC18C6] = 0.005 mol dm^{-3}.

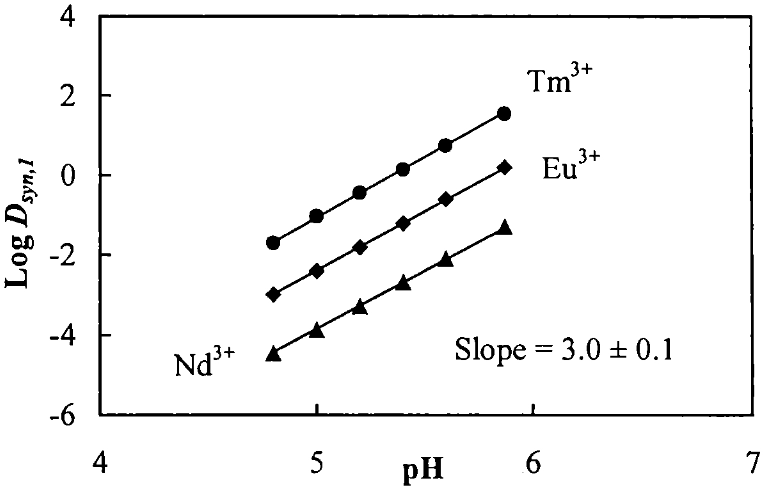


Fig. 4.16. Effect of pH on the extraction of Ln^{3+} ions at constant [HPMPP] = 0.01 mol dm^{-3} and [DB18C6] = 0.005 mol dm^{-3}.

Table 4.4. Synergistic enhancement factors of Nd^{3+}, Eu^{3+} and Tm^{3+} ions with HPMPP (0.01 mol dm^{-3}) in the presence of various CEs (0.005 mol dm^{-3}).

Extraction System	Synergistic Enhancement Factors		
	Nd^{3+}	Eu^{3+}	Tm^{3+}
HPMPP+18C6	24.0	17.2	4.5
HPMPP+DC18C6	17.3	16.2	4.3
HPMPP+DB18C6	2.5	5.6	3.0

The stability constants, β_1, for the organic synergistic reactions of Ln^{3+}-HPMPP chelate with various CEs were calculated according to Eq. (8) and are given in Table 4.5. It can be seen from Table 4.5 that the log β_1 values with 18C6 and DC18C6 decrease with increasing atomic number of these Ln^{3+} ions unlike that of $K_{Syn,1}$. On the other hand, the log β_1 values of DB18C6 show an increasing trend up to Eu^{3+} ion and then follow a decreasing trend.

Table 4.5. Stability constants (β_l) for organic phase synergistic reaction of Ln^{3+}-HPMPP chelates with CEs in chloroform.

Extraction System	Log β_1		
	Nd^{3+}	Eu^{3+}	Tm^{3+}
HPMPP+18C6	3.36 ± 0.02	3.27 ± 0.03	2.54 ± 0.03
HPMPP+DC18C6	3.54 ± 0.02	3.12 ± 0.02	2.31 ± 0.01
HPMPP+DB18C6	2.10 ± 0.03	2.50 ± 0.02	2.06 ± 0.02

In general, the complexation strength of Ln^{3+} ions with various crown ethers follows the order: 18C6 > DC18C6 > DB18C6. The sharp decrease in the complexation from 18C6 to DB18C6 mostly reflects increasing steric effects and decreasing basicity. This seems reasonable, since the extensive thermodynamic studies on cation-CE complexation have shown that the cation binding ability of the CE containing benzo groups is lower than that for the parent CE and have demonstrated that the diminished complex stability is due to the decreased electron density of donor oxygens produced by the electron withdrawing aromatic ring [Liu et al. 2000]. The cyclohexano group has a less dramatic effect on the stability of the complex and on cation selectivity [Izatt et al. 1985]. A similar trend was observed in the extraction of Eu^{3+} ion with HPMTFP in the presence of these CEs. The higher extractability of Ln^{3+} ions with DC18C6 or 18C6 can also be explained in terms of size fitting effect of these CEs as described in the previous chapter. The adduct formation constant (log β_1 = 3.27) of Eu-HPMPP-18C6 system is less than that of Eu-HPMTFP-18C6 (log β_1 = 4.56) [Thakur et al. 1996]. It is well known that stable adduct formation reactions are usually brought out by strong acidic extractants like HPMTFP (pK_a value = 2.56) as compared to the present system, HPMPP (pK_a = 4.26). Thus it can be concluded that the unusual behaviour observed in the present investigations of CEs with Ln^{3+} ions in the presence of HPMPP may be due to a variety of geometric, enthalpic, and steric effects and may not be simply due to the cation size/cavity size relationship.

4.2.4. IR spectral data of Eu-PMPP-DC18C6 complex

In the IR spectrum of Eu-PMPP-DC18C6 complex (Fig. 4.17), the carbonyl stretching frequency of HPMPP has been shifted from 1620 to 1613 cm^{-1}, suggesting the involvement of carbonyl oxygen in complex formation. The C-O-C bond shows a shift from 1096 in DC18C6 to 1089 cm^{-1} in the complex indicating the involvement of oxygen of DC18C6 in complex formation.

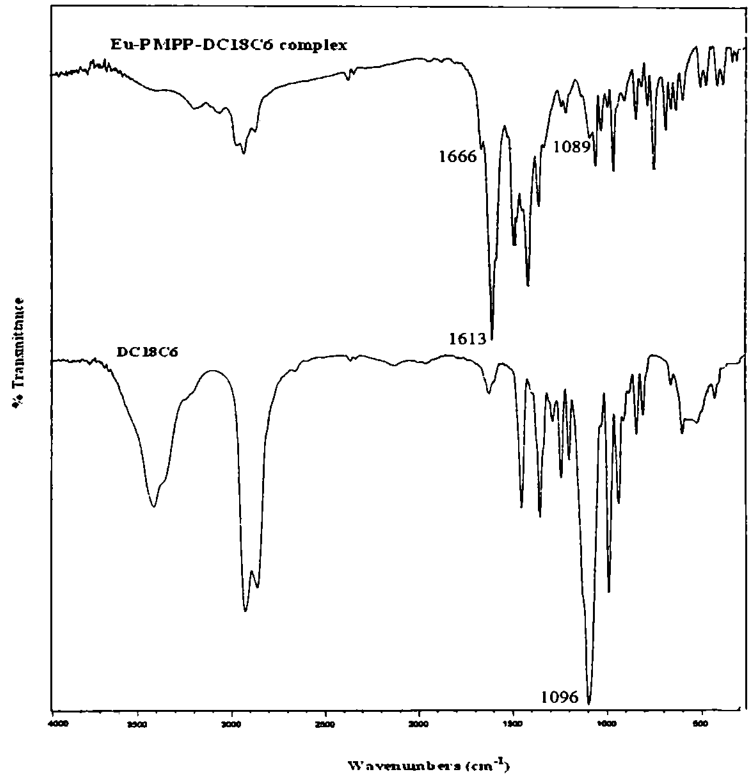


Fig. 4.17. IR spectrum of ternary Eu^{3+}-HPMPP-DC18C6 complex (KBr).

Table 4.6 gives the separation factors (S.F.) between these Ln^{3+} ions, defined as the ratio of the respective equilibrium constants in the HPMPP and HPMPP + CE systems. The addition of 18C6 or DC18C6 to the metal chelate system decreases the selectivities among these Ln^{3+} ions. Contrary to this, the addition of DB18C6 to the metal chelate system significantly improves the selectivity between Nd-Eu pair.

Table 4.6. Separation factors between Nd^{3+}, Eu^{3+} and Tm^{3+} ions with HPMPP and HPMPP + CE systems.

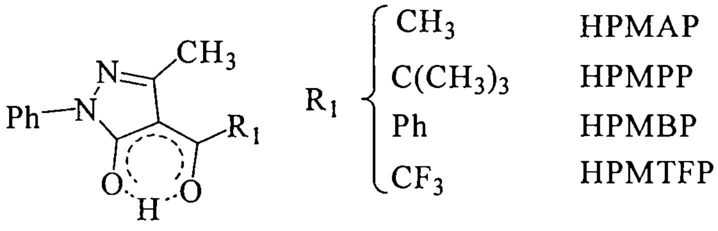
Extraction Systems	Separation Factors (S.F.)	
	Eu / Nd	Tm / Eu
HPMPP	19.00	37.00
HPMPP + 18C6	15.00	7.00
HPMPP + DC18C6	18.00	5.70
HPMPP + DB18C6	47.90	13.00
EHEHPA	3.94	24.00
D2EHPA	12.50	161.00

Chapter 5

Steric effects of Polymethylene Chain of 4-Acylbis(pyrazolones) on the Solvent Extraction of Trivalent Lanthanoids: Synergistic effect with Mono and Bifunctional Neutral Organophosphorus Extractants

A large number of acidic and neutral organophosphorus extractants have been widely employed industrially for the solvent extraction separation of lanthanoids [Bautista 1995; Powell 1979]. However, these reagents display various shortcomings such as poor selectivity, third phase formation etc. [Reddy et al. 1995]. Thus, there is a growing interest in the development of new and more selective solvent extraction reagents for the extraction and separation of trivalent lanthanoids in view of the ever-increasing demand for high purity lanthanoid elements, individually and collectively.

1-Phenyl-3-methyl-4-acyl-5-pyrazolones (**A**) are well known heterocyclic β-diketone type chelating ligands coordinating to the metal ion with oxygen atoms as "hard" Lewis bases.

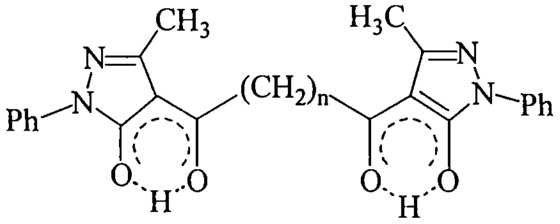


4-Acylpyrazolones

A

Further, these ligands have a strong affinity towards "hard" Lewis acids like lanthanoids [Umetani et al. 2000; Bond et al. 2000].

A 4-acylbis(pyrazolone) (**B**) designed by combining two 1-phenyl-3-methyl-4-acyl-5-pyrazolone subunits linked by a polymethylene chain of varying lengths -$(CH_2)_n$- (n = 0-8, 10, 20) exhibit several unique properties such as larger partition coefficients than the parent 4-acyl-5-pyrazolone and has two β-diketone donor sites on both sides of the polymethylene chain, is expected to give specific complexation towards metal ions depending on the polymethylene chain length. The dependence of the polymethylene chain length of 4-acylbis(pyrazolone) on the extraction behavior of Cu^{2+}, Ni^{2+}, Zn^{2+}, Am^{3+}, Cm^{3+}, Cf^{3+}, UO_2^{2+}, Th^{4+}, Np^{4+} and Pu^{4+} has been well documented [Miyazaki et al. 1989; Miyazaki et al. 1991; Reddy et al. 2000; Takeishi et al. 2001].

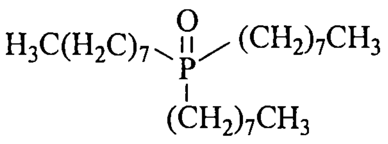


4-Acylbis(pyrazolones)

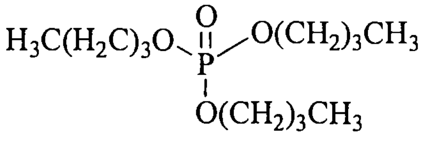
B

A synergistic effect is often set to bring about enhanced extraction but poorer separation among the metal ions. However, interestingly, in the extraction of Zn^{2+} and Ni^{2+} with 4-acylbis(pyrazolones), an enhanced extraction and an improved separation have been reported in the presence of TOPO as a synergist [Miyazaki et al. 1991]. The above factors prompted us to synthesize various derivatives of 4-acylbis(pyrazolones) of varying polymethylene chain length and investigate their extraction behavior with Ln^{3+} ions. The orientation and steric effects of the polymethylene substituent were examined by semi-empirical PM3 molecular modeling calculations. Further, the effect of addition of various mono- (TOPO and

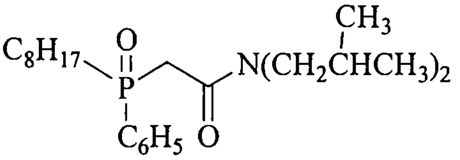
TBP) and bifunctional (CMPO) organophosphorus extractants on the extraction of Ln^{3+} ions with 4-acylbis(pyrazolone) has also been evaluated.



TOPO



TBP



CMPO

5.1. Experimental

5.1.1. Instrumentation

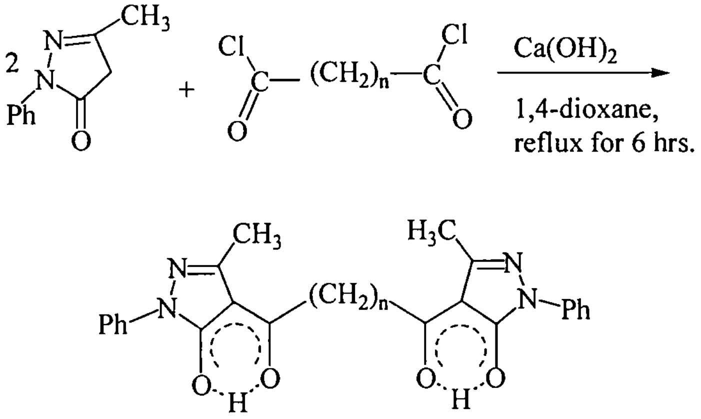
A Hitachi (Tokyo, Japan) 220 double-beam microprocessor-controlled spectrophotometer was used for measuring absorbance. ^{31}P NMR spectra of the synergistic complexes (in $CDCl_3$ and 85% H_3PO_4 as an external standard) were recorded using a Bruker 121.47 MHz NMR spectrometer. The methods for the preparation of stock solutions of Ln^{3+} ions and other instruments employed in this chapter are the same as described in chapter 3.

5.1.2. Materials

TBP, TOPO and the starting materials (1-phenyl-3-methyl-5-pyrazolone and various acid dichlorides) for the syntheses of ligands were obtained from Sigma-Aldrich. CMPO was synthesised and purified by standard procedures [Mathur et al. 1992; Gatrone et al. 1987]. All the other chemicals used were of analytical reagent grade.

Syntheses of ligands:

Various 4-acylbis(pyrazolones) were prepared by the acylation of 1-phenyl-3-methyl-5-pyrazolone with the corresponding acid dichloride [Jensen 1959] (**Scheme 5.1**).



n = 4, H_2AdBP; n = 6, H_2SuBP;
n = 8, H_2SbBP & n = 10, H_2DdBP

Scheme 5.1

The crude compounds were recrystallized from chloroform-hexane mixture and dried under reduced pressure. The purity of the compounds was established by elemental analyses, IR and ^{1}H NMR spectral data (Figs. 5.1-5.4).

4-Adipoylbis(1-phenyl-3-methyl-5-pyrazolone) (H_2AdBP): M.P. 199°C; Elemental analysis: Calc. for $C_{26}H_{26}O_4N_4$: C, 68.12; H, 5.68; N, 12.23. Found C, 68.27; H, 6.19; N, 12.04 %; ^{1}H NMR data ($CDCl_3$/TMS): δ 7.80-7.83, 7.42-7.47, 7.28-7.31 (m, 10H, Ph); 2.80-2.83 (t, 4H, $(CH_2)_2$); 2.49 (s, 6H, CH_3); 1.88 (m, 4H, $(CH_2)_2$) (Fig. 5.1); IR (KBr) data (υ cm^{-1}): 3409 (br, OH); 1633 (s, C=O); 1593 (s, phenyl C=C); 1560 (s, pyrazolone ring).

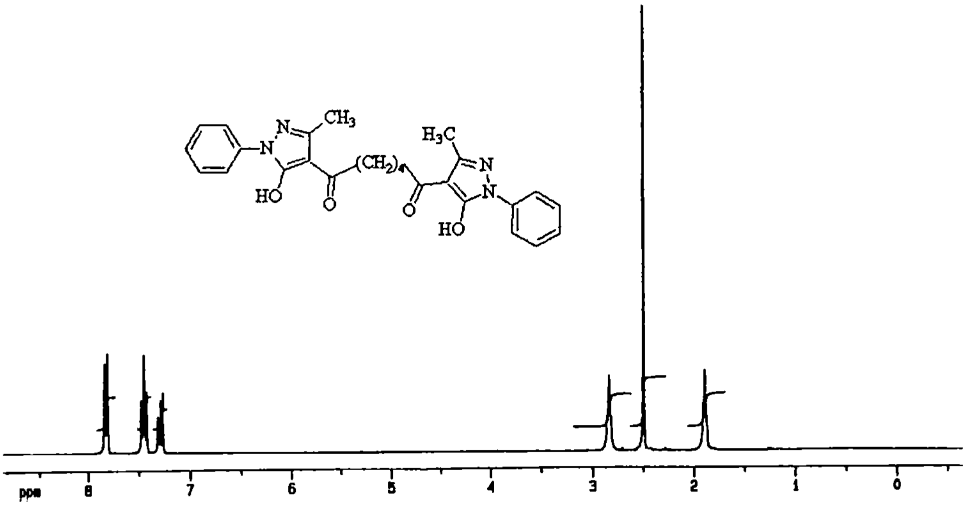


Fig. 5.1. ^{1}H NMR spectrum of H_2AdBP.

4-Suberoylbis(1-phenyl-3-methyl-5-pyrazolone) (H_2SuBP): M.P. 216°C; Elemental analysis: Calc. for $C_{28}H_{30}O_4N_4$: C, 69.13; H, 6.17; N, 11.53. Found C, 69.22; H, 6.43; N, 11.43 %; ^{1}H NMR data ($CDCl_3$/TMS): δ 7.81-7.84, 7.42-7.47, 7.28-7.31 (m, 10H, Ph); 2.74-2.79 (t, 4H, $(CH_2)_2$); 2.48 (s, 6H, CH_3); 1.79 (m, 4H, $(CH_2)_2$); 1.49 (m, 4H, $(CH_2)_2$) (Fig. 5.2); IR (KBr) data (υ cm^{-1}): 3409 (br, OH); 1627 (s, C=O); 1596 (s, phenyl C=C); 1546 (s, pyrazolone ring).

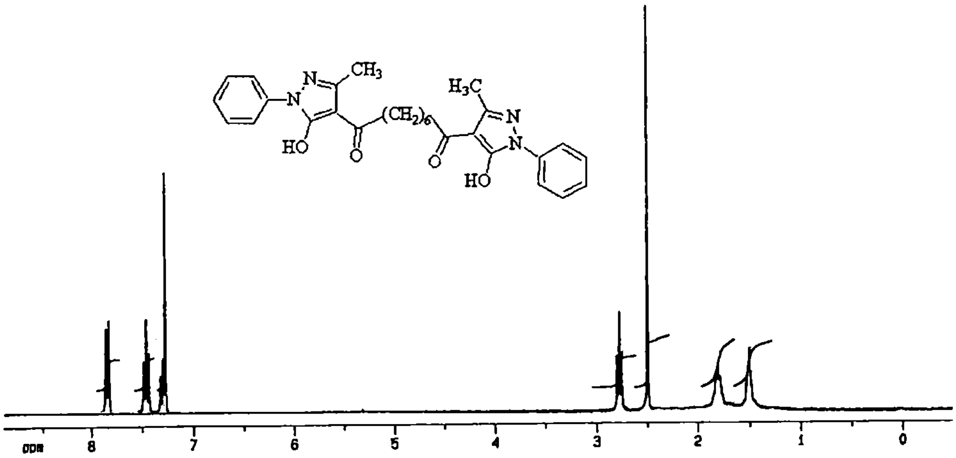


Fig. 5.2. ^{1}H NMR spectrum of H_2SuBP.

4-Sebacoylbis(1-phenyl-3-methyl-5-pyrazolone) (H_2SbBP): M.P. 136°C; Elemental analysis: calculated for $C_{30}H_{34}O_4N_4$: C, 70.03; H, 6.61; N, 10.89. Found C, 69.48; H, 6.51; N, 10.67 %; ^{1}H NMR data ($CDCl_3$/TMS): δ 7.81-7.84, 7.42-7.47, 7.28-7.30 (m, 10H, Ph); 2.71-2.76 (t, 4H, $(CH_2)_2$); 2.48 (s, 6H, CH_3); 1.73-1.77 (m, 4H, $(CH_2)_2$); 1.39 (m, 8H, $(CH_2)_4$) (Fig. 5.3); IR (KBr) data (υ cm^{-1}): 3430 (br, OH); 1633 (s, C=O); 1593 (s, phenyl C=C); 1553 (s, pyrazolone ring).

4-Dodecandioylbis(1-phenyl-3-methyl-5-pyrazolone) (H_2DdBP): M.P. 152°C; Elemental analysis: calculated for $C_{32}H_{38}O_4N_4$: C, 70.84; H, 7.01; N, 10.33; Found C, 71.32; H, 7.45; N, 10.35 %; ^{1}H NMR data ($CDCl_3$/TMS): δ 7.81-7.84, 7.42-7.47, 7.28-7.30 (m, 10H, Ph); 2.71-2.76 (t, 4H, $(CH_2)_2$); 2.48 (s, 6H, CH_3); 1.69-1.77 (m, 4H, $(CH_2)_2$); 1.33 (m, 12H, $(CH_2)_6$) (Fig. 5.4); IR (KBr) data (υ cm^{-1}): 3436 (br, OH); 1620 (s, C=O); 1593 (s, phenyl C=C); 1560 (s, pyrazolone ring).

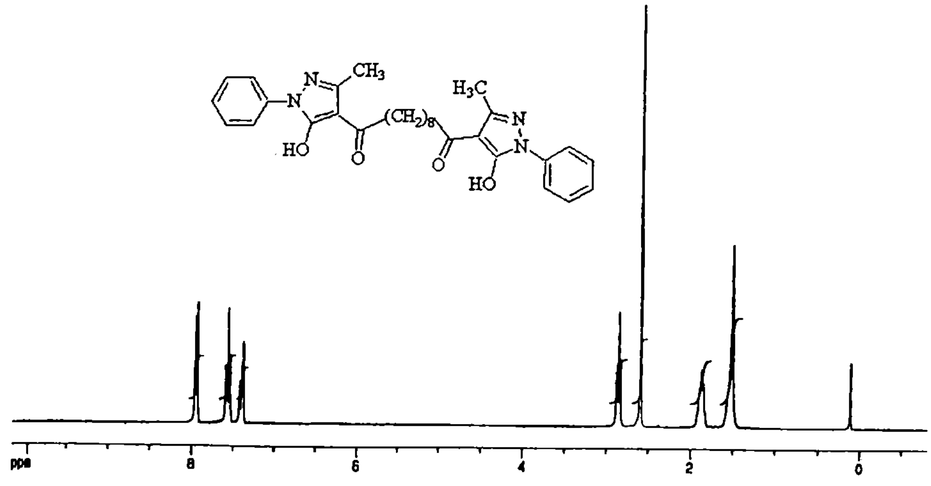


Fig. 5.3. ^{1}H NMR spectrum of H_2SbBP.

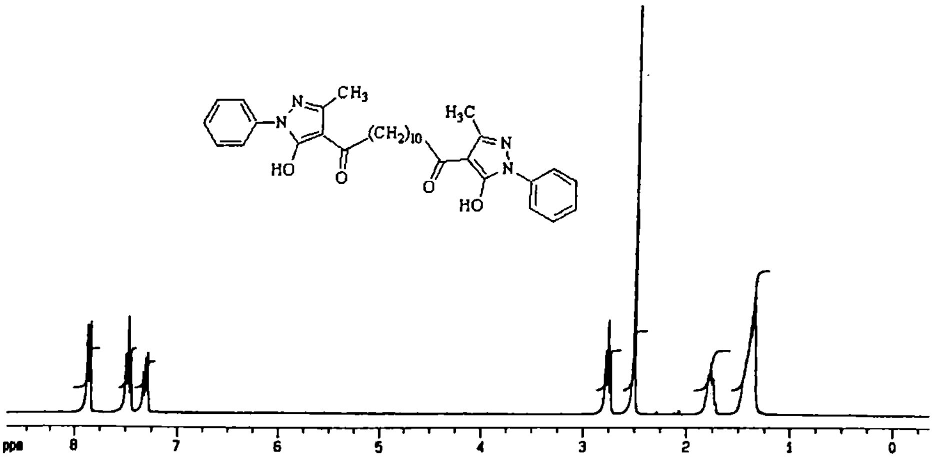


Fig. 5.4. ^{1}H NMR spectrum of H_2DdBP.

5.1.3. Solvent extraction and analytical procedure

Equal volumes of aqueous (1.0 mol dm^{-3} $NaNO_3$ and 1.0 × 10^{-4} mol dm^{-3} Ln^{3+} ions) and organic phases were shaken at 303 ± 1 K for 60 min. Preliminary experiments showed that the extraction equilibrium was attained within 15 min. The Ln^{3+} ion in the aqueous phase was determined spectrophotometrically by Arsenazo-1 method [Snell 1978]. After allowing the phases to settle, 5.0 cm^3 aliquots of the aqueous phase were pipetted into a 25.0 cm^3 beaker and 1.0 cm^3 ammonium acetate (0.1 mol dm^{-3}) solution and 5.0 cm^3 Arsenazo 1 (0.01 %) solution were added. After adjusting the pH to 7.5, the solution was made up to 25.0 cm^3. The absorbances of the solutions were measured at 575 nm and the metal concentrations were computed from the respective calibration graphs. The Ln^{3+} ion concentration in the organic phase was obtained by material balance. These concentrations were used to obtain the distribution ratio, D, defined as $D = [Ln^{3+}]_{org} / [Ln^{3+}]_{aq}$. All the experiments were performed in duplicate and the general agreement with D values obtained was within ± 5%. The extracted complexes were deduced from the distribution data by both graphical and theoretical methods taking into account aqueous phase complexation of Ln^{3+} ion with inorganic ligands and plausible complexes extracted into the organic phase.

5.2. Results and Discussion

5.2.1. Extraction of Ln^{3+} ions with various 4-acylbis(pyrazolones)

The extraction behaviour of Nd^{3+}, Eu^{3+} and Tm^{3+} ions as a function of H_2SbBP concentration (0.01-0.03 mol dm^{-3}) was investigated from 1.0 mol dm^{-3} $NaNO_3$ solutions of pH = 3.0 containing 1.0×10^{-4} mol dm^{-3} Ln^{3+} ion as the aqueous phase and the results are depicted in Fig. 5.5. The extraction efficiency of Ln^{3+} ion increases linearly with increasing concentration of H_2SbBP in the organic phase. Also the extraction efficiency increases monotonically with increase in the atomic number of

Ln^{3+} ion. From the slopes of the log-log plot it is clear that two moles of H_2SbBP are involved in the extracted complexes. The effect of pH (2.75-3.06) on the extraction behaviour of Ln^{3+} ion at constant H_2SbBP (0.02 mol dm^{-3}) shows an inverse dependence on acidity (Fig. 5.6).

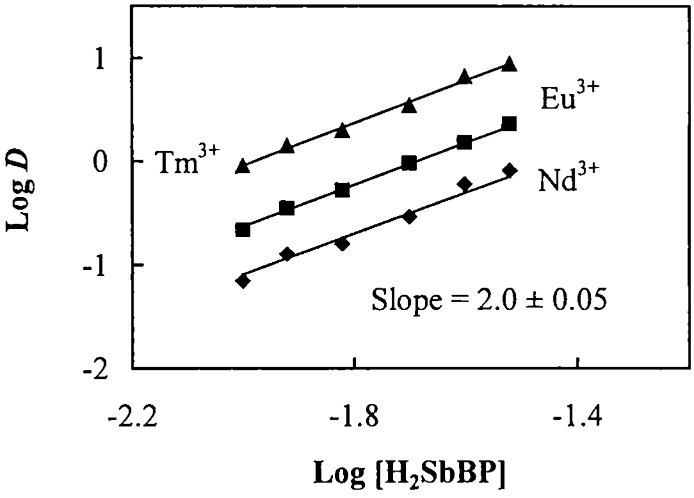


Fig. 5.5. Effect of H_2SbBP concentration on the extraction of Ln^{3+} ions.

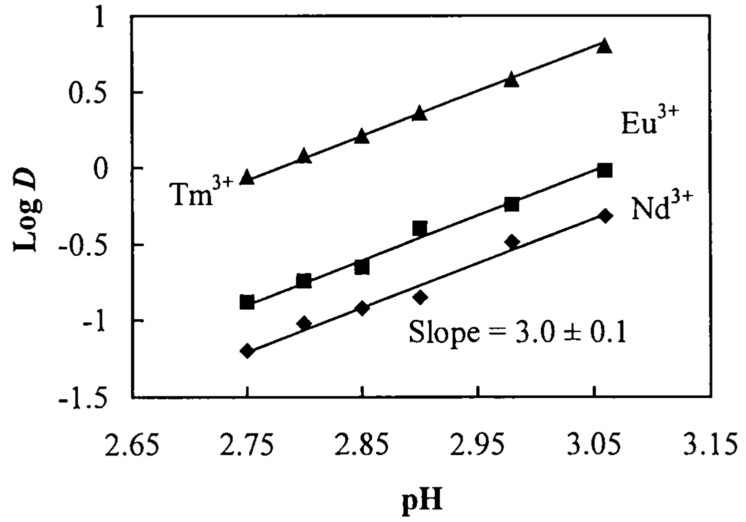


Fig. 5.6. Effect of pH on the extraction of Ln^{3+} ions.
$[H_2SbBP]$=0.02 mol dm^{-3}.

A slope of 3.0 ± 0.1 observed in log D vs. pH plot, indicates the release of three hydrogen ions by the interaction of Ln^{3+} ion with two moles of H_2SbBP.

Based on the preceding studies, the extraction equilibrium involved in the extraction of Ln^{3+} ions from dilute nitric acid solutions with 4-acylbis(pyrazolone) (H_2X) alone may be expressed as:

$$Ln^{3+}_{aq} + 2\,H_2X_{org} \xrightleftharpoons{K_{ex}} Ln(X)(HX)_{org} + 3\,H^+_{aq} \quad (1)$$

where K_{ex} denotes the equilibrium constant.

$$K_{ex} = \frac{[Ln(X)(HX)]_{org}\,[H^+]^3_{aq}}{[Ln^{3+}]_{aq}\,[H_2X]^2_{org}} \quad (2)$$

Ln^{3+} ions in the aqueous phase form a variety of complexes with nitrate ions. Then the total concentration of Ln^{3+} ion ($[Ln^{3+}]_T$) in the aqueous phase can be expressed as:

$$[Ln^{3+}]_T = [Ln^{3+}] + [Ln(NO_3)^{2+}] + [Ln(NO_3)_2^+]$$

$$= [Ln^{3+}]\,(1 + \beta_1\,[NO_3^-] + \beta_2\,[NO_3^-]^2) \quad (3)$$

where β_1 and β_2 are the stability constants [Smith and Martell 1976] of the following reactions:

$$Ln^{3+} + NO_3^- \xrightleftharpoons{\beta_1} Ln(NO_3)^{2+} \quad (4)$$

$$Ln^{3+} + 2\,NO_3^- \xrightleftharpoons{\beta_2} Ln(NO_3)_2^+ \quad (5)$$

The distribution ratio, D, of Ln^{3+} ion can be written from Eqs. (2) & (3) as:

$$D = \frac{K_{ex}\,[H_2X]^2_{org}}{[H^+]^3\,(1 + \beta_1[NO_3^-] + \beta_2\,[NO_3^-]^2)} \quad (6)$$

The K_{ex} values of the extracted complexes were determined by non-linear regression analysis with the aid of suitable chemically based model developed taking into account the aqueous phase complexation of Ln^{3+} ion with inorganic ligands and all plausible complexes extracted into the organic phase using Eq. (6), as described in Chapter 3. The K_{ex} values thus calculated refer only to concentration quotients, calculated on the assumption that the activity coefficients of the species involved do not change significantly under the present experimental conditions. The log K_{ex} values of H_2SbBP (Log $K_{ex,Nd} = -5.64 \pm 0.04$, Log $K_{ex,Eu} = -5.21 \pm 0.03$ and Log $K_{ex,Tm} = -4.79 \pm 0.04$) increase with decreasing ionic radii of Ln^{3+} ion. In a polar diluent such as chloroform, this can be attributed to the increasing coulombic interactions with charge density of the Ln^{3+} ion [Manchanda et al. 1988]. The increase in the extractability across the Ln^{3+} series can be due to the increase in electrostatic interactions between the cation and the ligand with decrease in ionic radii. The trend observed in the present system is similar to that of various 4-acyl-5-pyrazolones [Umetani et al. 2000; Bond et al. 2000].

Fig. 5.7 shows the results on the effect of polymethylene chain length of bis(pyrazolone) on the extraction of Eu^{3+} ion. Solubility limitations and third phase formation have prevented the extraction studies with H_2SuBP (n = 6). Extraction efficiency of Eu^{3+} ion increases with an increase in the number of $-CH_2-$ groups from n = 4 to n = 8 and thereafter it decreases. This has been attributed to the increasing steric effect, caused by increasing polymethylene chain length from n = 8 to n = 10. The effect of hydrogen ion concentrations on the extraction of Eu^{3+} ion with various 4-acylbis(pyrazolones) has also been investigated and observed an inverse dependence on the acidity (Fig. 5.8). The Log K_{ex} values of Eu^{3+} ion with various 4-acylbis(pyrazolones) follow the order: H_2SbBP (-5.21 ± 0.03) > H_2AdBP (-5.75 ± 0.04) > H_2DdBP (-6.02 ± 0.04). A similar trend has also been observed in the extraction of trivalent actinides [Takeishi et al. 2001; Reddy et al. 2000].

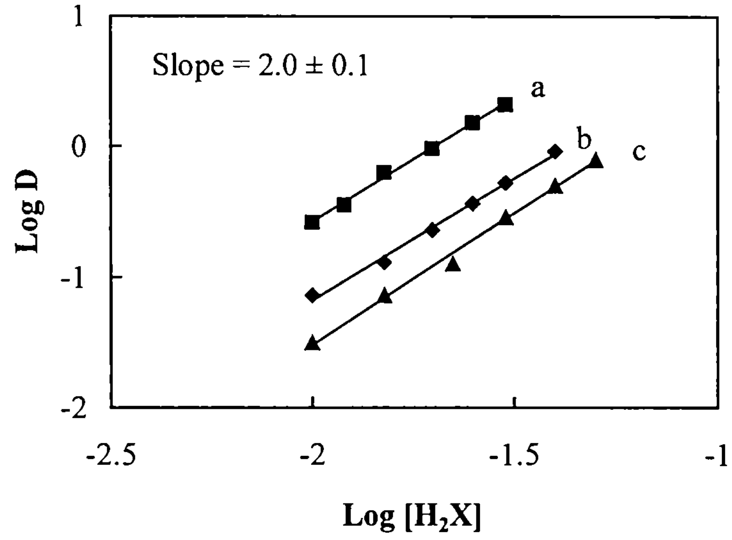


Fig. 5.7. Effect of [H_2X] on the extraction of Eu^{3+} ion **a**: H_2SbBP, **b**: H_2AdBP and **c**: H_2DdBP.

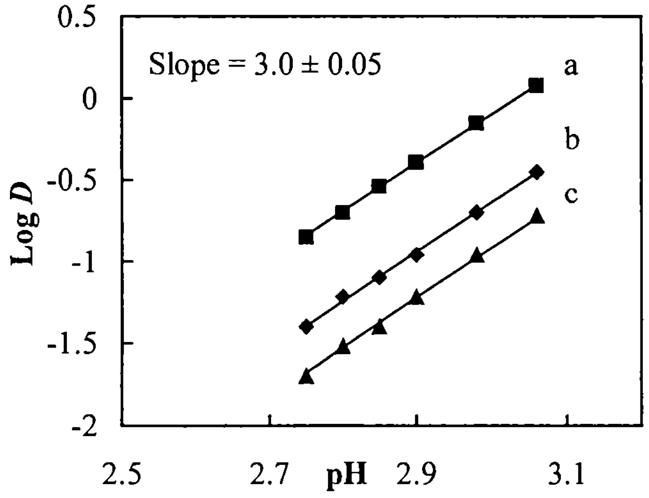
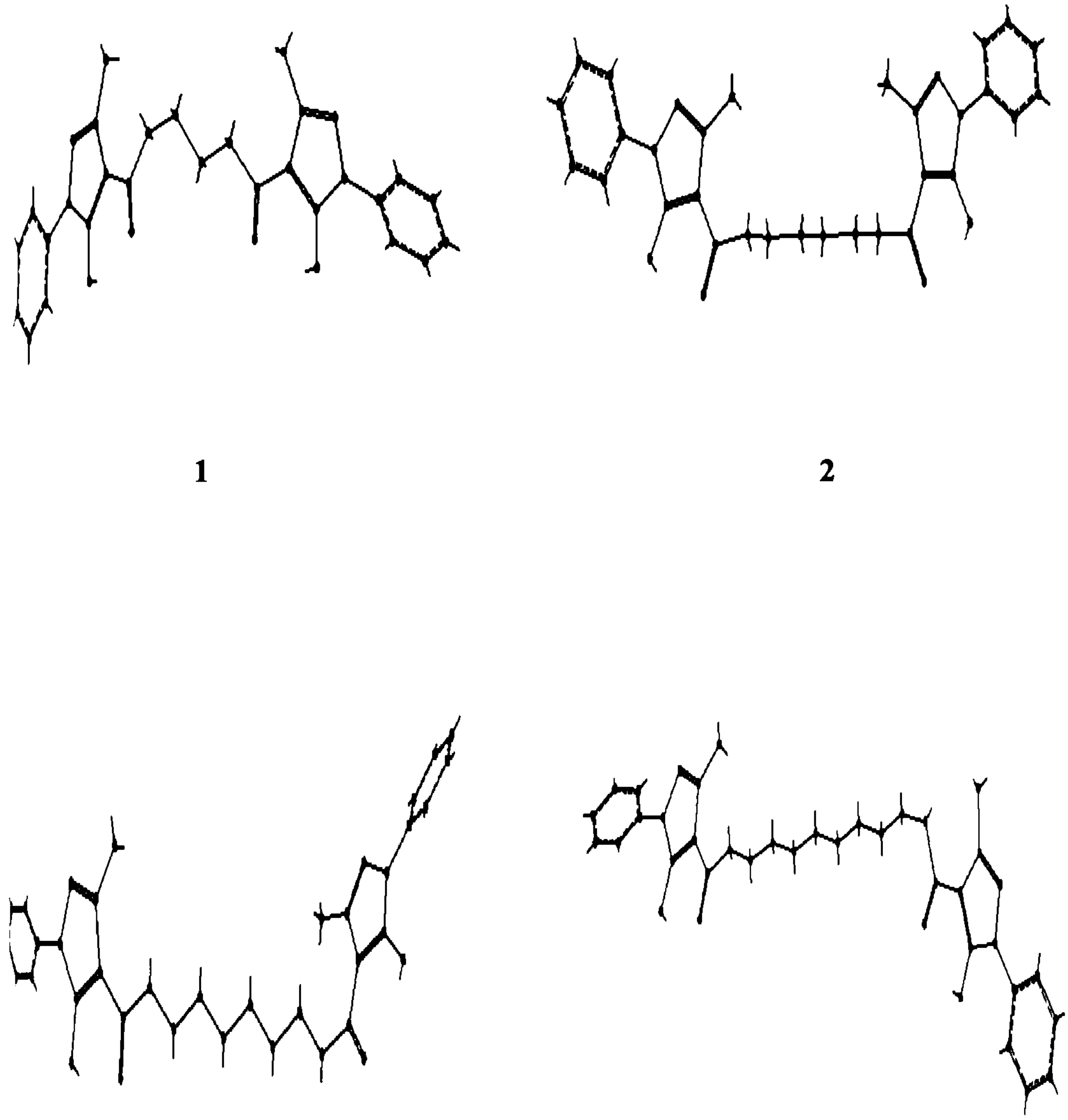


Fig. 5.8. Effect of pH on the extraction of Eu^{3+} ion **a**: H_2SbBP, **b**: H_2AdBP and **c**: H_2DdBP.

In order to have a better understanding of the effect of polymethylene chain length on the extraction efficiency of Ln^{3+} ion, semi-empirical PM3 molecular orbital calculations were carried out for 4-acylbis(pyrazolones) by considering the H-bonding [Stewart 1989]. The keto-enol structures of various bis(pyrazolone) derivatives are shown in Fig. 5.9. The O---O distance (distance between the carbonyl oxygens connected to the polymethylene chain), thus calculated are correlated with the Log K_{ex} values of Eu^{3+} ion (Fig. 5.10). The Log K_{ex} values increase to a maximum with increasing O---O distance up to 12.18 Å (n = 8) and then decreases for a distance > 12.18 Å.

Thus, a minimum distance of 12.18 Å between the carbonyl oxygens connected to the polymethylene chain, is required to achieve an optimal extraction of Ln^{3+} ions. Further, for a distance greater than 12.18 Å, the decrease in the extraction efficiency of Ln^{3+} ions may be due to steric factors. From the molecular modeling calculations, it can be concluded that the differences in the number of methylene groups and rigidity of these groups in the ligands, hence different steric effects and different orientations of the displaceable hydroxyl groups in the ligands are apparently the vital factors that govern the complexation of Ln^{3+} ion.



1 2

3 4

Fig. 5.9. Keto-enol structures of 4-acylbis(pyrazolones) suggested by molecular modeling: **1.** H_2AdBP **2.** H_2SuBP **3.** H_2SbBP **4.** H_2DdBP.

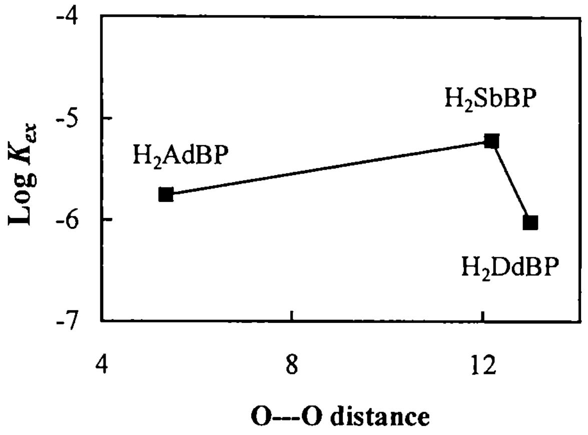


Fig. 5.10. Correlation between the O---O distance (Å) of 4-acylbis(pyrazolones) and Log K_{ex} values of Eu^{3+} ion.

IR spectrum of the Eu^{3+}-H_2SbBP binary complex shows a broad absorption in the region 3000-3500 cm^{-1} indicating the presence of water molecules in the complex (Fig. 5.11). The presence of water molecules in the extracted β-diketone complexes of Ln^{3+} ion is well documented [Mathur and Choppin 1993]. Further, strong bands due to $\upsilon_{C=O}$, $\upsilon_{C=N}$, and $\upsilon_{C=C}$ of the aromatic rings were observed in the 1500-1650 cm^{-1} region, where the carbonyl band (1633 cm^{-1}) was shifted to lower frequency (1625 cm^{-1}), suggesting the involvement of oxygen of the carbonyl group in the complex formation with Eu^{3+} ion. The above results clearly show that Ln^{3+} ion is interacting with three of the β-diketone donor sites of the two H_2SbBP molecules involved in the extraction process, releasing three H^+ ions to the aqueous phase as shown in Fig. 5.12.

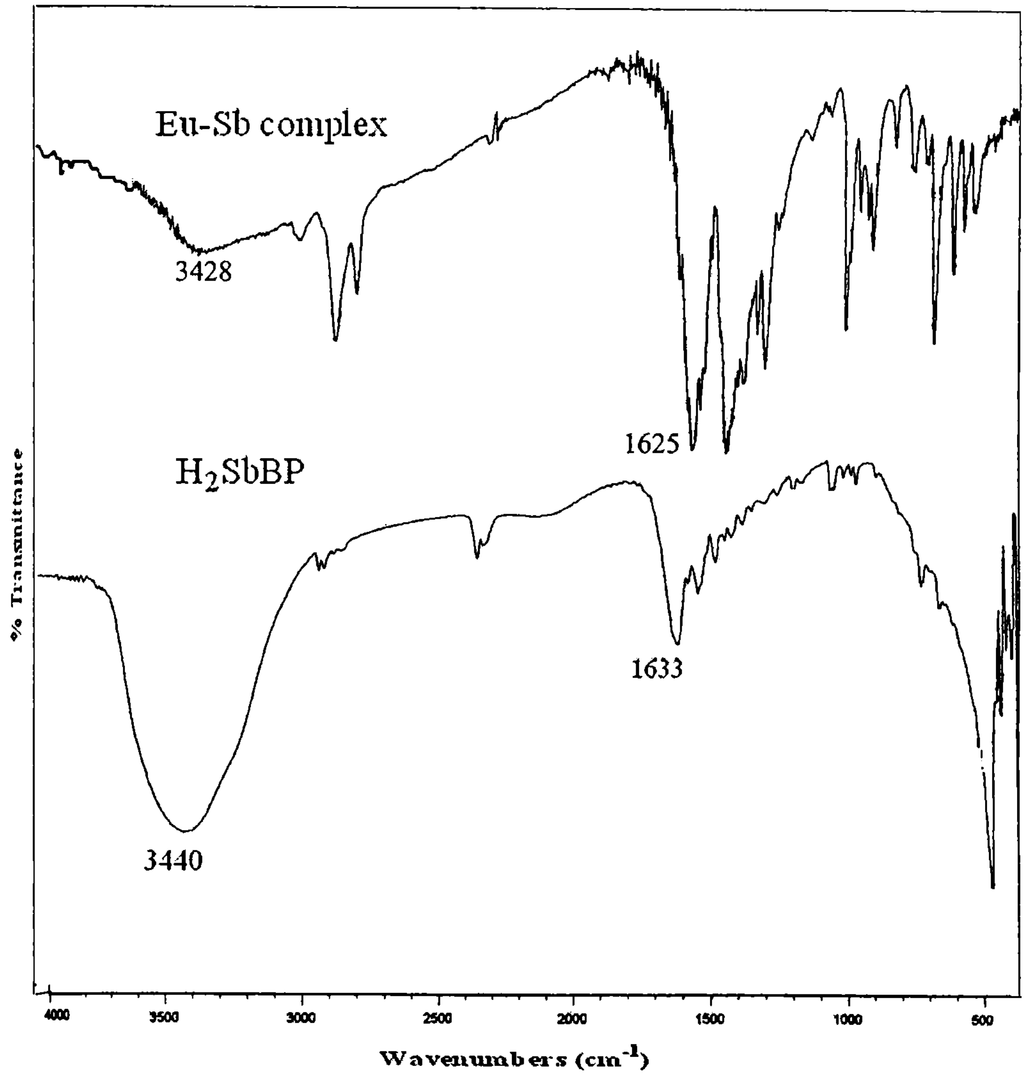


Fig. 5.11. IR spectrum of binary Eu^{3+}-H_2SbBP complex.

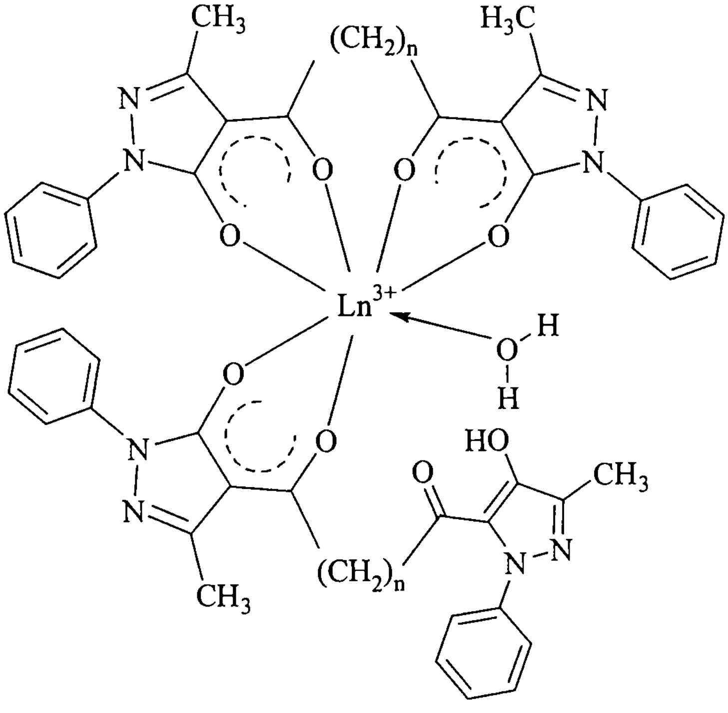


Fig. 5.12. Proposed structure of the extracted binary complexes.

5.2.2. *Extraction of Ln^{3+} ions with mixtures of H_2SbBP and neutral organophosphorus extractants*

In view of the better extraction efficiency observed, H_2SbBP was chosen for further experimentation, especially to study the synergistic extraction in the presence of various mono and bifunctional organophosphorus extractants (S). To evaluate the synergistic effect, the extraction behaviour of Ln^{3+} ions from 1.0 mol dm^{-3} sodium nitrate solution of pH = 3.0 with mixtures of H_2SbBP and S was investigated. The extraction efficiency of Ln^{3+} ion was found to be negligible with S alone under the investigated conditions. However, with mixtures of H_2SbBP and S, considerable synergistic enhancement in the extraction efficiency of Ln^{3+} ions was observed (Table 5.1). Synergistic enhancement factor was also found to increase with increasing concentration of S. It is clear from the plots (Figs. 5.13-5.15) of log $D_{syn,m}$ vs. log [H_2SbBP] at constant S that two molecules of H_2SbBP are involved in the synergistic extracted complexes. Further, the extraction efficiency of Ln^{3+} ion increases linearly with increasing H_2SbBP concentration. The effect of concentrations of various S on the extraction efficiency of Ln^{3+} ion was also examined at constant H_2SbBP concentration (Figs. 5.16-5.18). The extraction efficiency of Ln^{3+} ion was found to increase linearly on increasing the concentration of S. From the log-log plots, it is clear that one molecule of S is involved in the synergistically extracted complexes. The effect of pH on the extraction behaviour of Ln^{3+} ions at constant H_2SbBP and S concentrations shows an inverse dependence on acidity and indicates the release of three H^+ ions to the aqueous phase by reacting with three β-diketone donor sites of two molecules of H_2SbBP (Figs. 5.19-5.21).

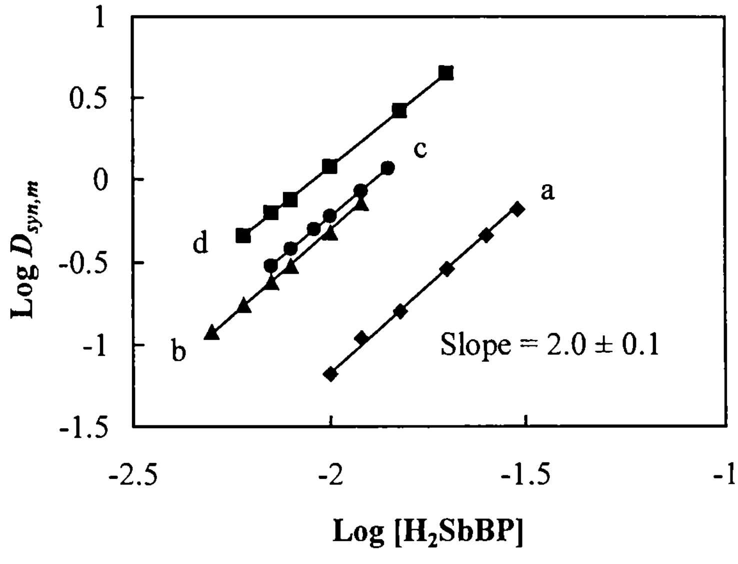


Fig. 5.13. Effect of concentration of H_2SbBP on the extraction of Nd^{3+} ion at a: [S] = 0, b: [TBP] = 0.1 mol dm^{-3}, c: [CMPO] = 0.005 mol dm^{-3}, d: [TOPO] = 0.01 mol dm^{-3}.

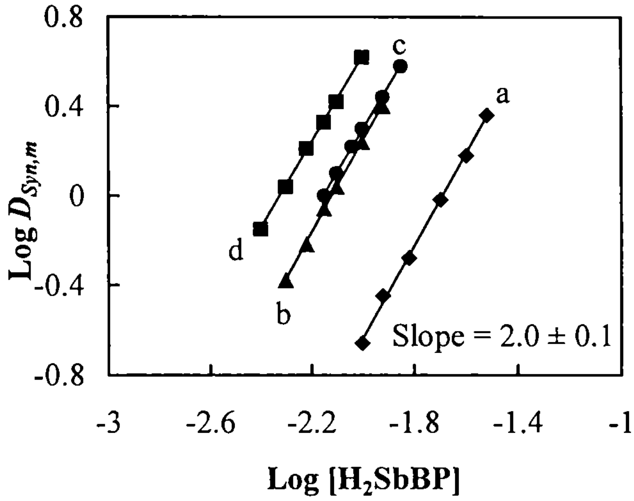


Fig. 5.14. Effect of concentration of H_2SbBP on the extraction of Eu^{3+} ion at a: [S] = 0, b: [TBP] = 0.1 mol dm^{-3}, c: [CMPO] = 0.005 mol dm^{-3}, d: [TOPO] = 0.01 mol dm^{-3}.

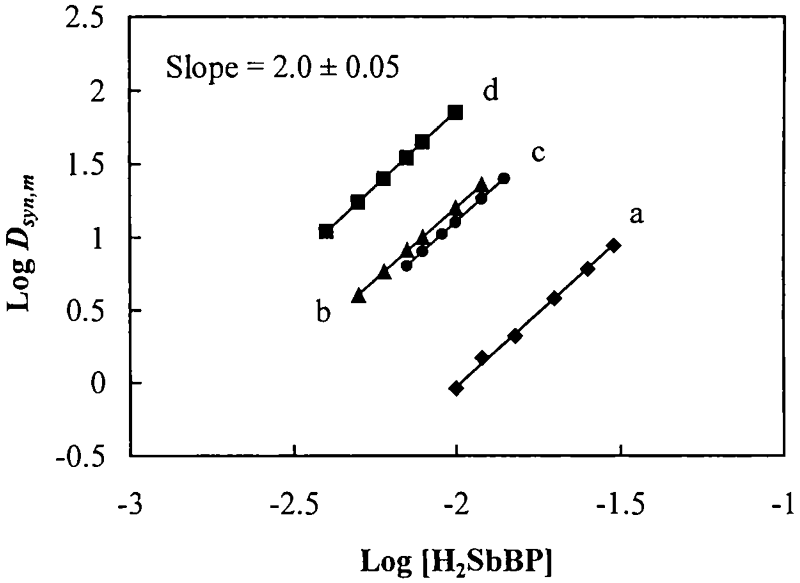


Fig. 5.15. Effect of concentration of H_2SbBP on the extraction of Tm^{3+} ion at a: [S] = 0, b: [TBP] = 0.1 mol dm^{-3}, c: [CMPO] = 0.005 mol dm^{-3}, d: [TOPO] = 0.01 mol dm^{-3}.

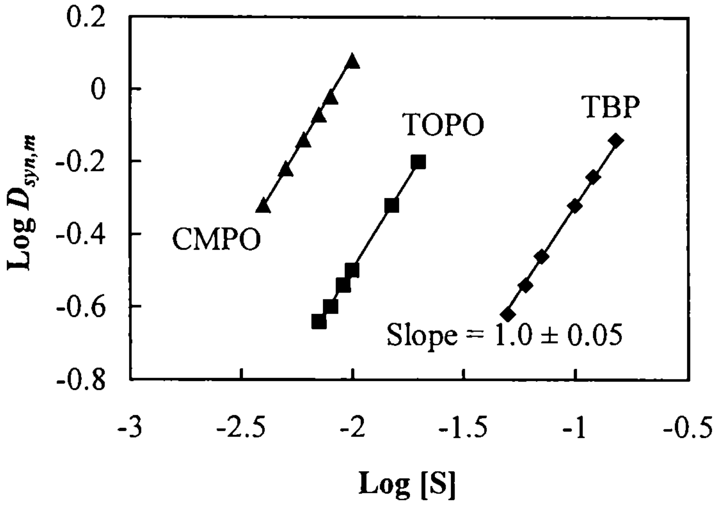


Fig. 5.16. Effect of concentration of S on the extraction of Nd^{3+} ion at constant $[H_2SbBP]$ = 0.005 mol dm^{-3} for TOPO and 0.01mol dm^{-3} for TBP and CMPO.

Table 5.1. Synergistic enhancement factors of Ln^{3+} ions with H_2SbBP in the presence of neutral organophosphorus extractants.

S	$[H_2SbBP]$	[S]	Synergistic enhancement factors		
			Nd^{3+}	Eu^{3+}	Tm^{3+}
TOPO	5×10^{-3}	7×10^{-3}	15	16	59
	5×10^{-3}	8×10^{-3}	17	17	63
	5×10^{-3}	1×10^{-2}	21	22	79
CMPO	1×10^{-2}	7×10^{-3}	14	13	20
	1×10^{-2}	8×10^{-3}	16	14	22
	1×10^{-2}	1×10^{-2}	20	18	27
TBP	1×10^{-2}	5×10^{-2}	4	4	9
	1×10^{-2}	10×10^{-2}	8	8	17
	1×10^{-2}	15×10^{-2}	12	12	26

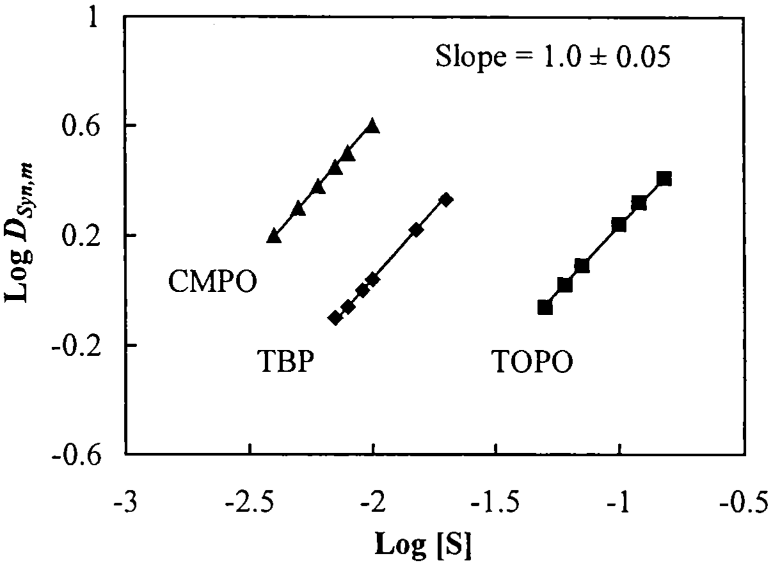


Fig. 5.17. Effect of concentration of S on the extraction of Eu^{3+} ion at constant $[H_2SbBP]$ = 0.005 mol dm^{-3} for TOPO and 0.01mol dm^{-3} for TBP and CMPO.

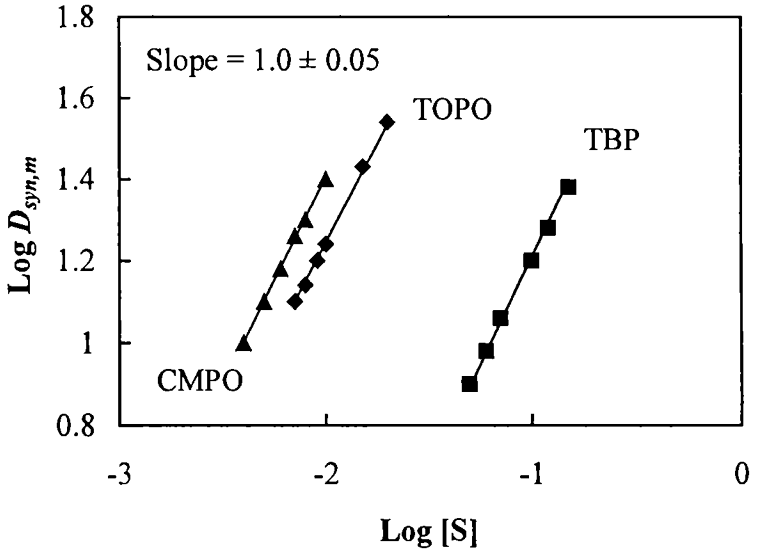


Fig. 5.18. Effect of concentration of S on the extraction of Tm^{3+} ion at constant $[H_2SbBP]$ = 0.005 mol dm^{-3} for TOPO and 0.01mol dm^{-3} for TBP and CMPO.

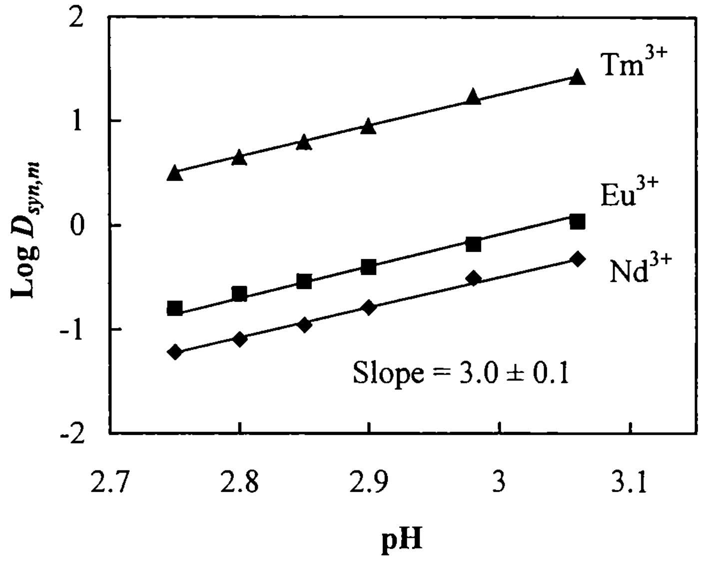


Fig. 5.19. Effect of pH on the extraction of Nd^{3+}, Eu^{3+} and Tm^{3+} ions; [H_2SbBP] = 0.005 mol dm^{-3} and [TOPO] = 0.01 mol dm^{-3}.

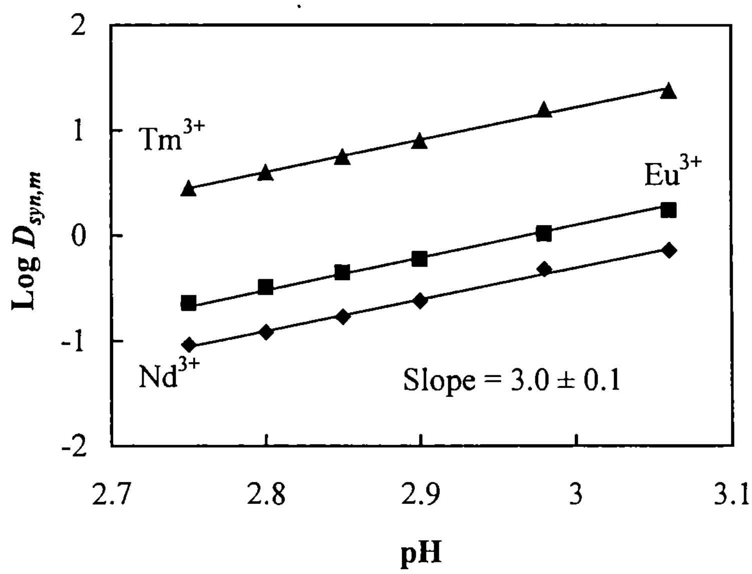


Fig. 5.20. Effect of pH on the extraction of Nd^{3+}, Eu^{3+} and Tm^{3+} ions; [H_2SbBP] = 0.01 mol dm^{-3} and [TBP] = 0.1 mol dm^{-3}.

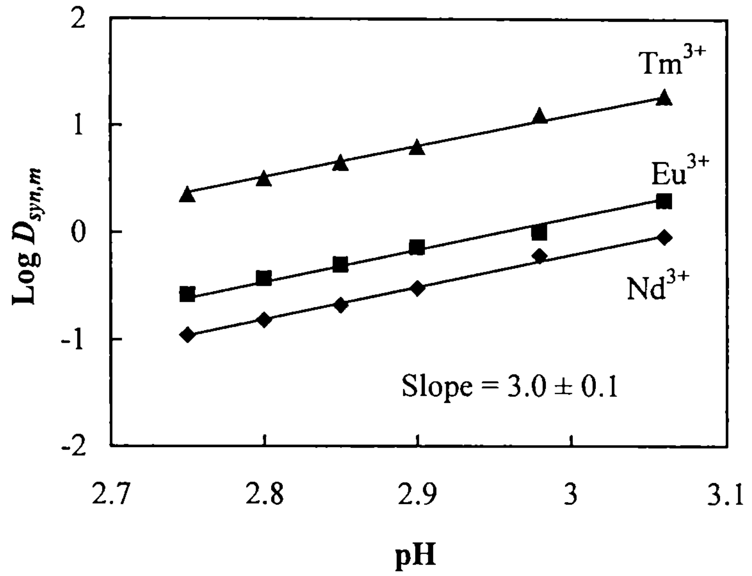


Fig. 5.21. Effect of pH on the extraction of Nd^{3+}, Eu^{3+} and Tm^{3+} ions; $[H_2SbBP] = 0.01$ mol dm^{-3} and $[CMPO] = 0.005$ mol dm^{-3}.

Based on the preceding results, the synergistic extraction equilibrium of Ln^{3+} ion with H_2SbBP in the presence of TBP, CMPO or TOPO (S) may be expressed as:

$$Ln^{3+}_{aq} + 2\,H_2X_{org} + m\,S_{org} \overset{K_{syn,m}}{\rightleftharpoons} Ln(X)(HX).mS_{org} + 3\,H^+_{aq} \qquad (7)$$

where m = 0 or 1. $K_{syn,m}$ represents the synergistic equilibrium constant.

$$K_{syn,m} = \frac{[Ln(X)(HX).mS]_{org}\,[H^+]^3_{aq}}{[Ln^{3+}]_{aq}[H_2X]^2_{org}\,[S]^m_{org}} \qquad (8)$$

Thus the distribution coefficient, $D_{syn,m}$, from Eqs. (3) and (8) can be written as

$$D_{Syn,m} = \frac{[H_2X]^2_{org}\,\{K_{ex} + K_{syn,m}\,[S\,]^m_{org}\}}{[H^+\,]^3\,(1 + \beta_1[NO_3^-\,] + \beta_2\,[NO_3^-\,]^2)} \qquad (9)$$

The interactions between a β-diketone and a neutral oxo-donor in chloroform are in general, weaker when the diluent itself has strong interaction with the neutral oxo-donor [Sekine et al. 1983]. Hence, it is assumed to have negligible interaction between H_2SbBP and S in chloroform.

The adduct formation reaction in the organic phase and the stability constant, K_s, is given by

$$\mathrm{Ln(X)(HX)_{org}} + m\,\mathrm{S}_{\mathrm{org}} \overset{K_s}{\rightleftharpoons} \mathrm{Ln(X)(HX)}.\,m\,\mathrm{S}_{\mathrm{org}} \qquad (10)$$

$$K_s = K_{syn,\,m} \,/\, K_{\mathrm{ex}} \qquad (11)$$

The equilibrium constants of synergistic complexes ($K_{\mathrm{syn},1}$) of these metal ions were deduced by non-linear regression analysis and are given in Table 5.2. The $K_{\mathrm{syn},1}$ value increases with decreasing ionic radii of these metal ions, for all the systems studied here.

The stability constant, K_s, for the organic phase synergistic reaction of Ln^{3+} ion–H_2SbBP chelate with S has also been calculated according to Eq. (11) and are given in Table 5.3. The complexation strength of Ln^{3+} ions with various S follows the order: TOPO > CMPO > TBP, which is in accordance with their oxygen basicity values.

Fig. 5.22 shows the correlations of Log $K_{\mathrm{syn},1}$ values of Ln^{3+} ions and the oxygen basicity values of S in terms of their K_{H} values, where K_{H} is the equilibrium constant for the HNO_3 uptake by S expressed as: $\mathrm{H^+_{aq}} + \mathrm{NO^-_{3\,aq}} + \mathrm{S_{org}} \overset{K_{\mathrm{H}}}{\rightleftharpoons} \mathrm{HNO_3.\,S_{org}}$, of various S [Sahu et al. 2000]. The sharp decrease of Log $K_{\mathrm{syn},1}$ value of Ln^{3+} ions from TOPO to TBP *mostly reflects in the decrease of their K_H values. On the other hand,* in the case of CMPO the Log $K_{\mathrm{syn},1}$ values are found to be almost equal to that of TOPO even though their K_H values are widely different. This may be due to the bidentate nature of CMPO in the complexation with Ln^{3+} ions [Nakamura and Miyake 1994].

Table 5.2. Two phase equilibrium constants ($K_{syn,1}$) for organic phase synergistic reaction of Ln^{3+}-H_2SbBP with S in chloroform.

Extraction system	Log synergistic constant (Log $K_{syn,1}$)		
	Nd^{3+}	Eu^{3+}	Tm^{3+}
H_2SbBP + TOPO	-2.90 ± 0.03	-2.36 ± 0.02	-1.15 ± 0.03
H_2SbBP + CMPO	-2.92 ± 0.02	-2.40 ± 0.03	-1.60 ± 0.02
H_2SbBP + TBP	-4.32 ± 0.02	-3.76 ± 0.03	-2.80 ± 0.02

Table 5.3. Organic phase synergistic stability constants of Ln^{3+}-H_2SbBP-S in chloroform.

Extraction system	Log stability constant (Log K_s)		
	Nd^{3+}	Eu^{3+}	Tm^{3+}
H_2SbBP + TOPO	2.74 ± 0.03	2.85 ± 0.02	3.63 ± 0.03
H_2SbBP + CMPO	2.72 ± 0.03	2.81 ± 0.02	3.19 ± 0.03
H_2SbBP + TBP	1.32 ± 0.03	1.44 ± 0.02	1.99 ± 0.02

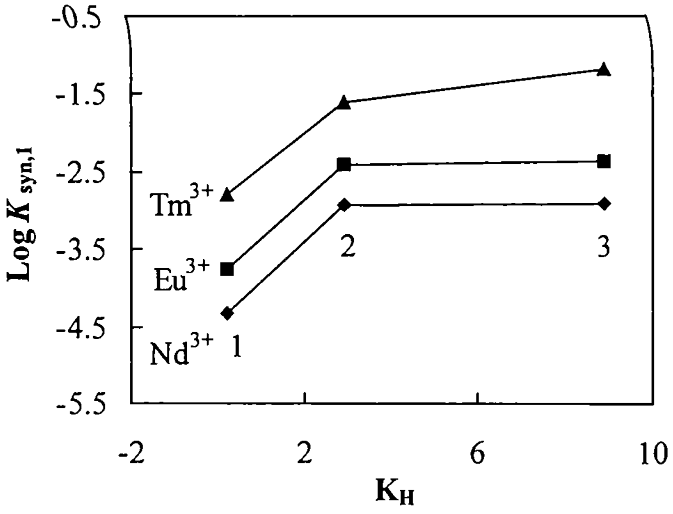


Fig. 5.22. Correlation between the basicity values of neutral oxo-donors and Log $K_{Syn,l}$ values of Ln^{3+} ions. 1. TBP 2. CMPO 3. TOPO.

5.2.3. Correlation of ^{31}P NMR chemical shifts of neutral organophosphorus extractants with the synergistic equilibrium constants

^{31}P NMR spectral data may help in studying the influence of neutral organophosphorus extractants in the synergistic extraction systems, as there exists a strong correlation between the electron donor density on oxygen of P=O group in neutral organophosphorus extractant molecule and the extraction efficiency [Ionova et al. 2001]. Fig. 5.23 shows that the Log $K_{syn,1}$ value of Eu^{3+} ion increases linearly with increase in δ (^{31}P) NMR chemical shift of the neutral O-bearing organophosphorus extractant (TBP < CMPO < TOPO). However, CMPO was found to have deviated from linearity. It may be due to the bidentate nature of CMPO in the complex formation with Eu^{3+} ion as is also evident from the IR spectral data (Fig. 5.24) of Eu^{3+}-H_2SbBP-CMPO complex, where both P=O (1266 cm^{-1}) and

C=O (1633 cm^{-1}) stretching frequencies of CMPO have been shifted to lower wave numbers (1211 & 1622 cm^{-1}, respectively), indicating the involvement of oxygen atoms of both carbonyl and phosphoryl groups in complexation.

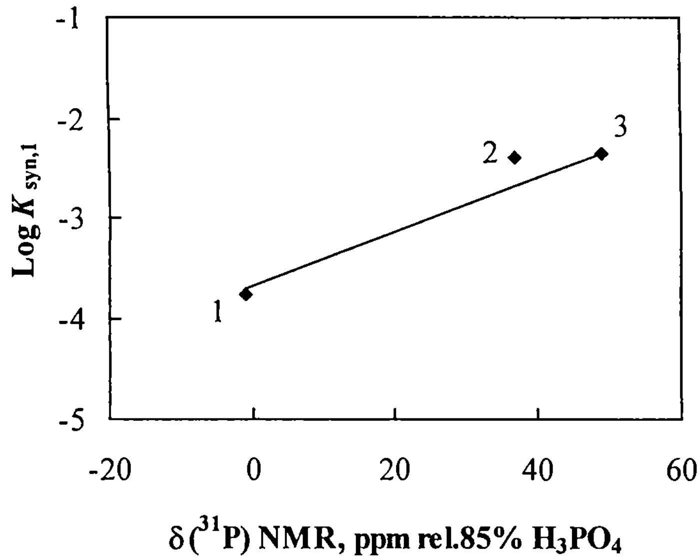


Fig. 5.23. Variation of Log $K_{syn,1}$ values of Eu^{3+} ion with δ ^{31}P NMR chemical shift values of neutral organophosphorus extractants. 1. TBP 2. CMPO 3. TOPO.

Thus, the donor ability of the phosphoryl oxygen, which is correlated with the δ (^{31}P) NMR chemical shift (i.e., a high electron density on the oxygen atom induces a low electron density on the phosphorus atom and thus a high value of the δ (^{31}P) NMR chemical shift) is the key parameter for the increase in the extraction efficiency of Ln^{3+} ion with H_2SbBP in the presence of neutral organophosphorus extractants.

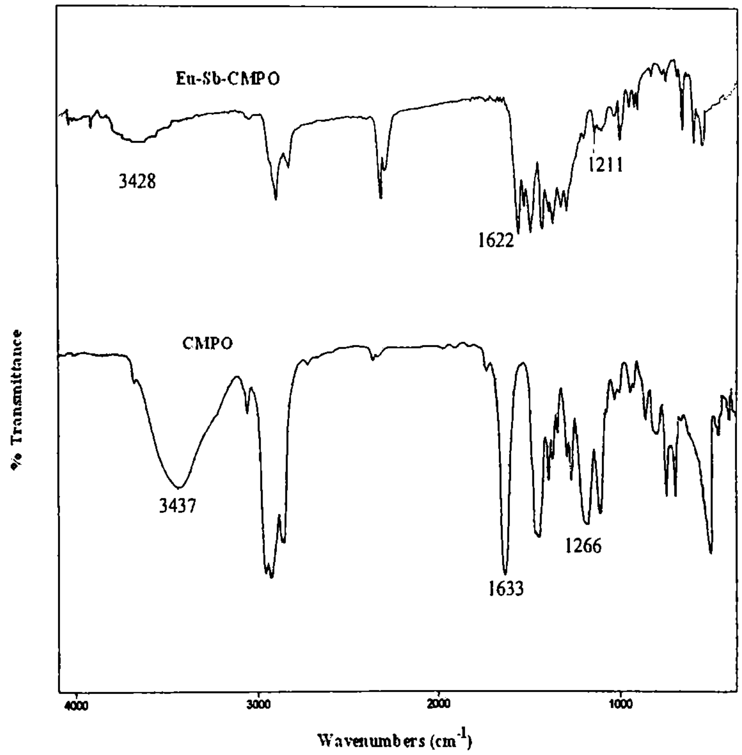


Fig. 5.24. IR spectrum of ternary Eu^{3+}-H_2SbBP-CMPO complex (KBr).

In the extracted complexes of Eu^{3+}-H_2SbBP-TOPO and Eu^{3+}-H_2SbBP-TBP, the P=O stretching frequencies (1143 and 1277 cm^{-1} of the free ligands) were shifted to lower wave numbers (1140, 1264 cm^{-1}, respectively in TOPO and TBP) indicating the involvement of phosphoryl oxygen in the complex formation. Further, in the synergistic extracted complexes, the carbonyl stretching frequency of H_2SbBP (1633 cm^{-1}) was also shifted to lower frequencies (1622, 1629 & 1622 cm^{-1} in Eu^{3+}-H_2SbBP-CMPO, Eu^{3+}-H_2SbBP-TOPO and Eu^{3+}-H_2SbBP-TBP, respectively) indicating the involvement of carbonyl oxygen of H_2SbBP in the complex formation with Eu^{3+} ion (Figs. 5.24-5.26). The IR spectra of the Eu^{3+} ternary complexes show a broad absorption in the region 3000-3500 cm^{-1} indicating the presence of water molecules in the complexes.

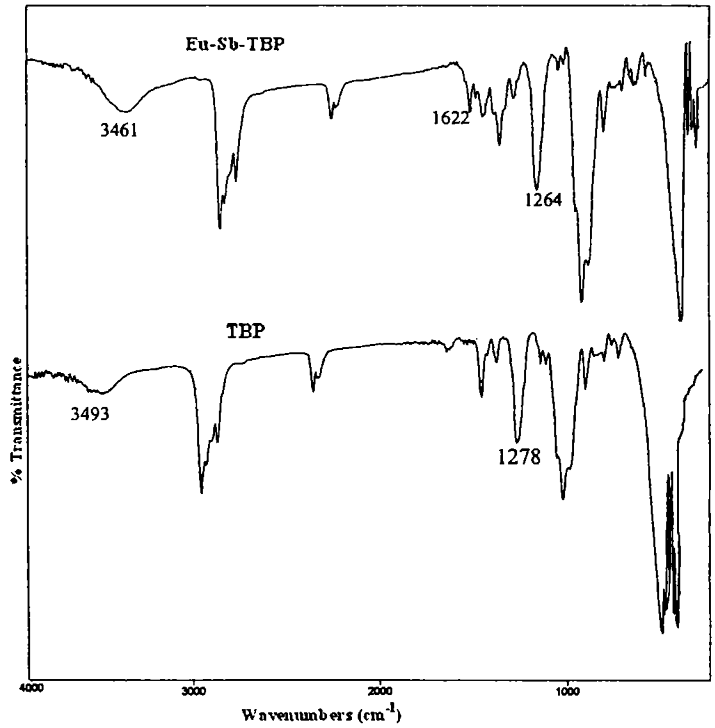


Fig. 5.25. IR spectrum of ternary Eu^{3+}-H_2SbBP-TBP complex (KBr).

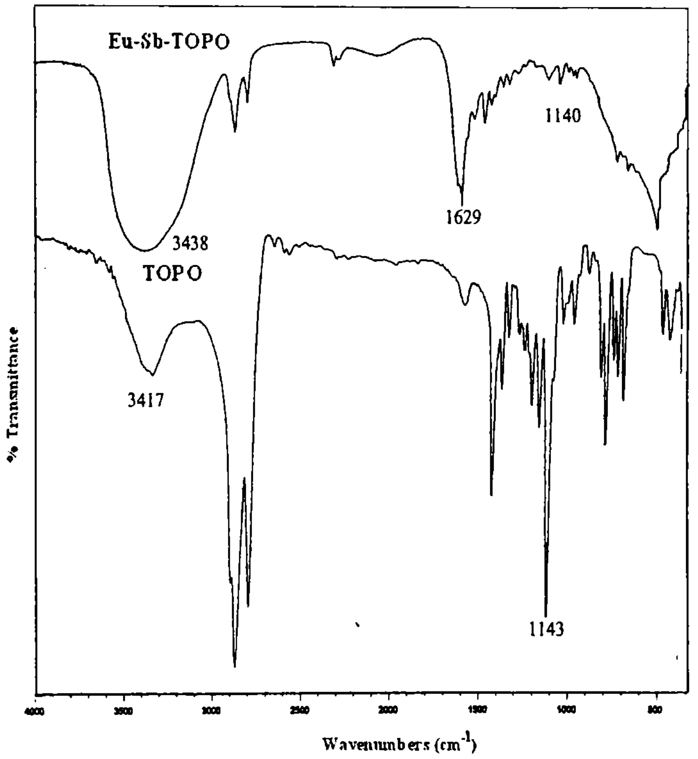


Fig. 5.26. IR spectrum of ternary Eu^{3+}-H_2SbBP-TOPO complex (KBr).

Table 5.4 gives the separation factors (S.F.) between these Ln^{3+} ions, defined as the ratio of the respective equilibrium constants in H_2SbBP + S and H_2SbBP systems. The addition of a neutral oxo-donor to the Ln^{3+}-chelate system significantly improves the selectivity among Eu^{3+}-Tm^{3+} and Tm^{3+}-Nd^{3+} pairs. On the other hand, a moderate increase in the S. F. value has been observed in the case of Eu^{3+}-Nd^{3+} pair. However, the separation factors observed in the present synergistic systems are found to be lower than EHEHPA (Eu/Nd = 3.94) system [Bautista 1995], which is widely used as an extractant in Rare Earth Industry. Thus, the present synergistic systems may find potential applications for the extraction and separation of lanthanoids as a group from mineral resources.

Table 5.4. Separation factors between Ln^{3+} ions with H_2SbBP and H_2SbBP + S systems.

Extraction system	Separation Factors (S.F.)		
	Eu / Nd	Tm / Eu	Tm / Nd
H_2SbBP	2.72	2.63	7.17
H_2SbBP + TOPO	3.49	16.15	56.40
H_2SbBP + CMPO	3.32	6.36	21.10
H_2SbBP + TBP	3.58	9.26	33.19

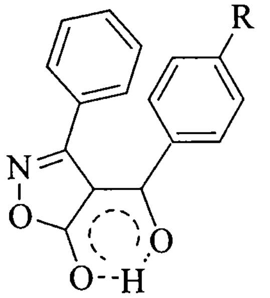
Chapter 6

Luminescent Properties of Eu^{3+} mixed complexes of 3-Phenyl-4-aroyl-5-isoxazolone and Lewis Bases

Europium complexes have been regarded as attractive for use as luminescent materials because of their red emissions (615 nm). Characteristic emissions of Eu^{3+} complexes mainly come from electric dipole transitions. Transition from the 4f inner shell of free Eu^{3+} ion is forbidden because it does not correlate with the change of parity. However, transitions that are forbidden by odd parity become partially allowed by mixing 4f and 5d states through ligand field effects of designed Eu^{3+} complexes. Eu^{3+} complexes that exhibit both high emission quantum yields and fast radiation rates are desirable luminescent materials for several applications. To increase emission quantum yields, it is first necessary to suppress radiationless transitions caused by vibrational excitations. According to the energy gap theory, such radiationless transitions are promoted by ligands and solvents with high frequency vibrational modes. Suppression of such vibrational excitations in Eu^{3+} complexes requires deuteration of C-H and O-H bonds or replacement of C-H bonds with C-F bonds in ligating molecules [Hasegawa et al. 2003]. Second, geometric structures of Eu^{3+} complexes should be eight-coordinate (square-antiprism structure) in order to achieve stronger electric dipole radiation. Square anti prism structured Eu^{3+} complexes are expected to have increased radiation rates and quantum yields because of increases in $^5D_0 \rightarrow {}^7F_2$ emissions (electronic dipole transition), related to odd parity. Phosphine oxide ligands can produce antisymmetrical structures that promote faster radiation rates [Gao et al. 1999]. Further, increased emission quantum yields can be expected for europium β-diketonate complexes with phosphine oxide ligands, because phosphine oxide molecule prevents coordination of water or solvent molecules and lowers vibrations.

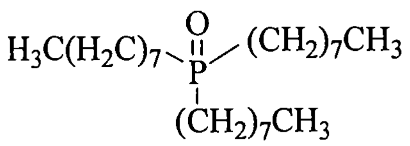
It is clear from the literature review that a large number of 1,3-β-diketones have been used along with various adduct forming reagents for the preparation of lanthanoid luminescent complexes [de Sa et al. 2000; Kido and Okamoto 2002]. Recently, 4-acyl-5-pyrazolonates have also been used for the preparation of terbium and europium luminescent complexes [Pettinari et al. 2004a]. The luminescence data suggested a strong influence of the nature of the acyl moiety in these complexes on luminescence.

However, to our knowledge, no heterocyclic 4-aroyl-5-isoxazolones have been so far utilized in the preparation of LCMDs. The above factors prompted us to synthesize europium-4-aroyl-5-isoxazolonate complexes with TOPO or TPhPO as adduct forming reagents with a view to study their photophysical properties for use in electroluminescent devices as emitting layers.

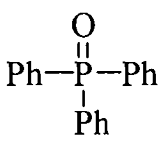


R = F : HFBPI
R = H : HPBI

3-phenyl-4-aroyl-5-isoxazolones



$H_3C(H_2C)_7P(=O)(CH_2)_7CH_3(CH_2)_7CH_3$



$Ph_3P=O$

TOPO **TPhPO**

6.1. Experimental

6.1.1. Instrumentation

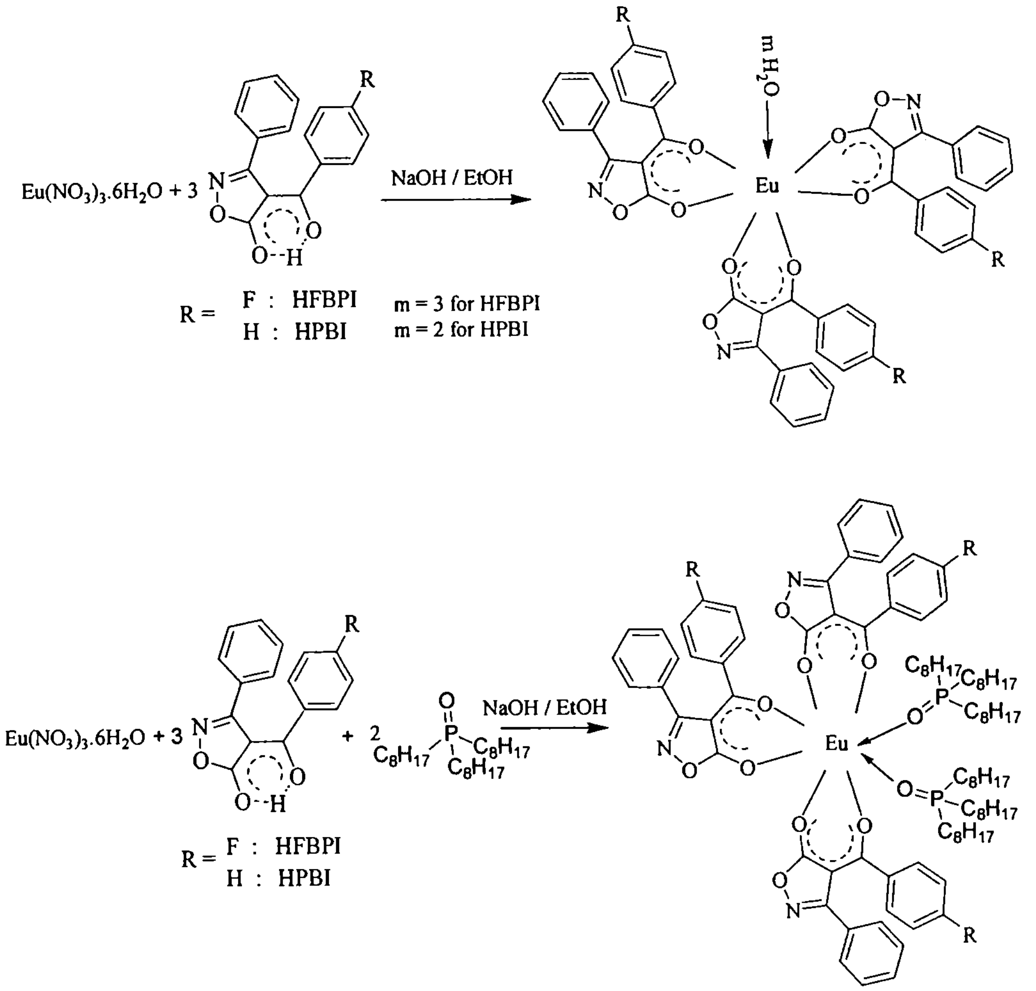
The excitation and luminescence spectra of the powdered samples were obtained by using a SPEX-Fluorolog DM3000F spectrofluorometer with double grating 0.22m Spex 1680 monochromators, and a 450 W Xenon lamp as the excitation source using the front face mode. The lifetime measurements were carried out at room temperature using SPEX 1934D phosphorimeter, accessory coupled with the spectrofluorometer. The decay curves were recorded monitoring the hypersensitive $^5D_0 \longrightarrow {}^7F_2$ transition of the Eu^{3+} ion. The photophysical properties such as emission spectra, excitation spectra and lifetime measurements were carried out using Y_2O_3:5%Eu phosphor as the standard. Thermogravimetric analysis studies were carried out using TGA-50H (Shimadzu, Japan). The instruments used for IR and C, H and N analyses were the same as that described in chapter 3.

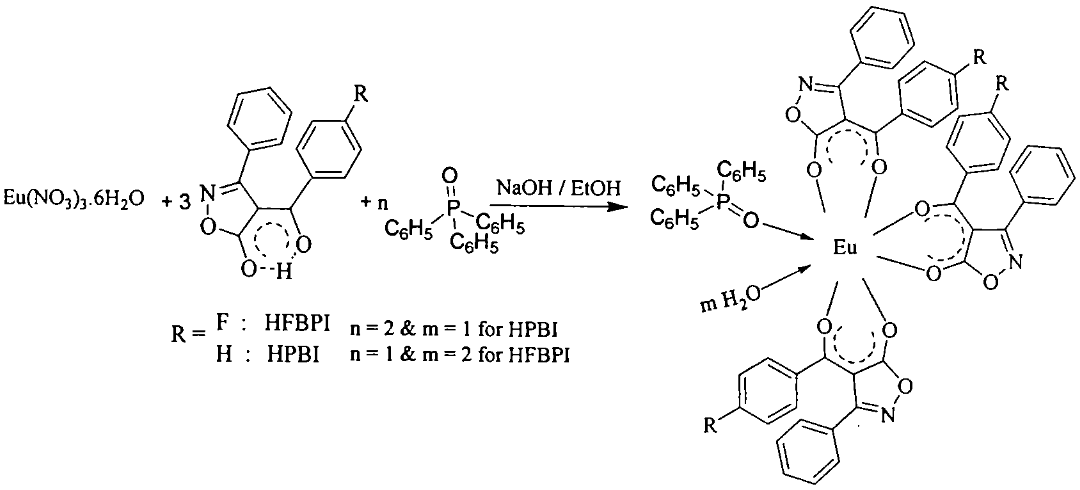
6.1.2. Chemicals

The commercial Y_2O_3: 5% Eu phosphor used in our experiments was kindly supplied by Prof. E. Zych, (Warsaw University, Poland) as a gift sample. TOPO and TPhPO were obtained from Sigma Aldrich. HPBI and HFBPI were synthesized by the method described in chapter 3. All the other chemicals used were of analytical reagent grade.

6.1.2.a. Syntheses of complexes

The various binary and ternary complexes of Eu^{3+} ion have been synthesized as described in **scheme 6.1** using stoichiometric amounts of europium nitrate, 4-aroyl-5-isoxazolones and Lewis base in ethanol medium in the presence of NaOH.





Scheme 6.1

6.2. Results and Discussion

6.2.1. Characterization of Eu^{3+} complexes

The synthesized complexes were characterized by C, H, and N analyses (Table 6.1), IR spectral studies (Table 6.2), and thermogravimetric analysis (Figs. 6.1-6.2).

The IR spectra of the complexes of Eu^{3+} show a broad absorption in the region 3000-3500 cm^{-1}, indicating the presence of water molecules in the complexes (Eu(PBI)$_3$.2H$_2$O; Eu(PBI)$_3$.2TPhPO.H$_2$O; Eu(FBPI)$_3$.3H$_2$O and Eu(FBPI)$_3$.TPhPO.2H$_2$O). The carbonyl stretching frequencies have been shifted from 1699 cm^{-1} (HPBI) and 1702 cm^{-1} (HFBPI) to lower frequencies in all the complexes, indicating the involvement of carbonyl oxygen atoms in complexation (Table 6.2). The P=O stretching frequencies have also been shifted to lower frequencies in the complexes indicating the involvement of phosphoryl oxygen of TOPO or TPhPO in complex formation with Eu^{3+} ion.

Table 6.1. Elemental analyses.

Complex	% C Calcd. (found)	% H Calcd. (found)	% N Calcd. (found)	% Eu Calcd. (found)
$Eu(PBI)_3.2H_2O$	58.78 (58.42)	3.47 (3.88)	4.28 (4.49)	15.51 (15.47)
$Eu(PBI)_3$.2TOPO	67.08 (67.57)	7.69 (7.76)	2.44 (2.73)	8.85 (8.93)
$Eu(PBI)_3$.2TPhPO. H_2O	66.38 (66.11)	4.08 (3.86)	2.76 (3.05)	10.01 (10.10)
$Eu(FBPI)_3.3H_2O$	54.75 (54.29)	3.13 (3.29)	3.99 (4.06)	14.44 (14.62)
$Eu(FBPI)_3$.2TOPO	65.04 (65.17)	7.28 (7.68)	2.37 (2.56)	8.57 (8.63)
$Eu(FBPI)_3$.TPhPO.$2H_2O$	60.85 (61.09)	3.50 (3.08)	3.20 (3.63)	11.58 (11.61)

Table 6.2. IR spectral data of Eu^{3+}-isoxazolonate-neutral organophosphorus reagent complexes.

Complex / Ligand	C=O stretching frequencies (cm^{-1})	P=O stretching frequencies (cm^{-1})
HPBI	1699	-
HFBPI	1702	-
TOPO	-	1143
TPhPO	-	1182
$Eu(PBI)_3.2H_2O$	1620	-
$Eu(PBI)_3$.2TOPO	1651	1134
$Eu(PBI)_3$.2TPhPO. H_2O	1646	1165
$Eu(FBPI)_3.3H_2O$	1646	-
$Eu(FBPI)_3$.2TOPO	1646	1136
$Eu(FBPI)_3$.TPhPO.$2H_2O$	1646	1155

Fig. 6.1 shows the thermogravimetric analysis (TGA) results for Eu(FBPI)$_3$.3H$_2$O. The precursor Eu(FBPI)$_3$.3H$_2$O undergoes a mass loss of 5% up to 100-175°C, which corresponds to the removal of three water molecules coordinated to the metal ion (5.13%, calculated). Further, decomposition takes place between 200 and 575°C. There is no step characteristic of "free" ligand, indicating that the ligands are coordinated to the metal centers. On the other hand, for the complex, Eu(FBPI)$_3$.2TOPO, a plateau was observed between 50-230°C indicating the absence of water molecules (Fig. 6.2).

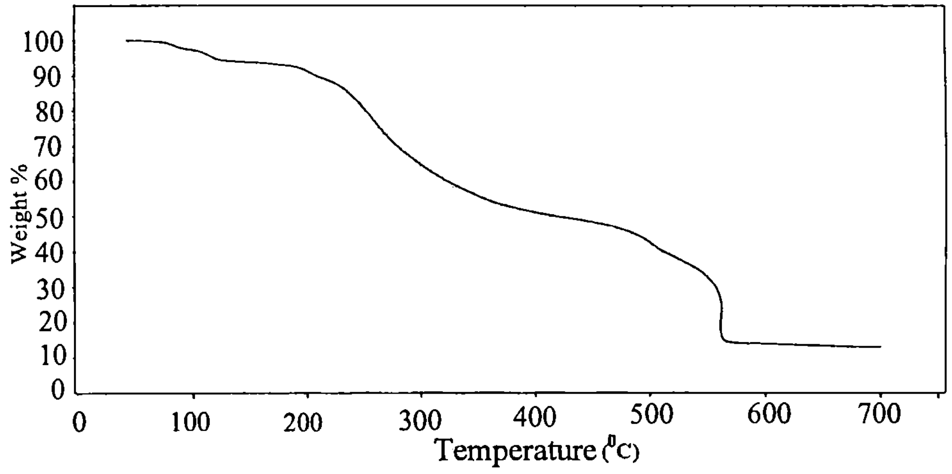


Fig. 6.1. TG Analysis for Eu(FBPI)$_3$.3H$_2$O.

From the above results, it is evident that the coordination number is eight in complexes Eu(PBI)$_3$.2H$_2$O, Eu(PBI)$_3$.2TOPO and Eu(FBPI)$_3$.2TOPO and nine in Eu(PBI)$_3$.2TPhPO.H$_2$O, Eu(FBPI)$_3$.3H$_2$O and Eu(FBPI)$_3$.TPhPO.2H$_2$O complexes. The eight oxygen atoms form square-antiprism coordination polyhedra around the central Eu^{3+} ion in the former complexes and the nine oxygen atoms form tri-capped trigonal prismatic geometry around the Eu^{3+} ion in the latter complexes.

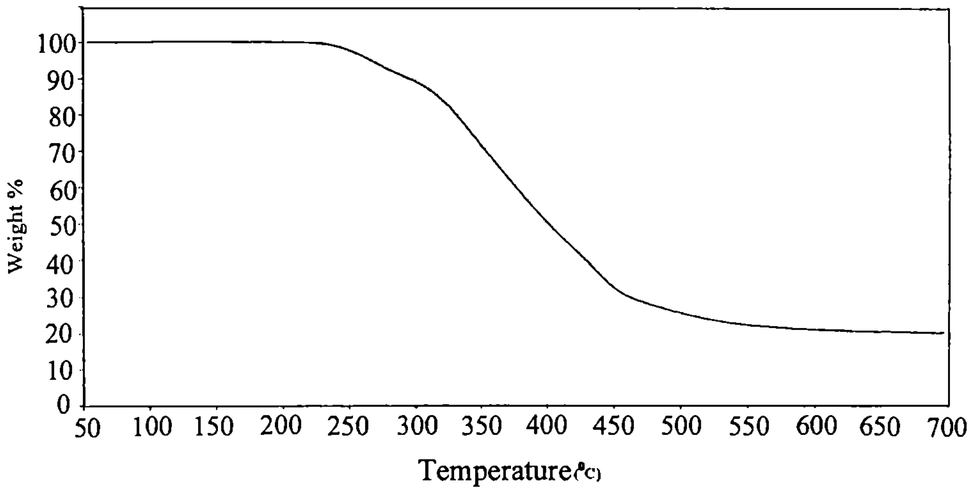


Fig. 6.2. TG Analysis for $Eu(FBPI)_3.2TOPO$.

6.2.2. Photophysical studies

The typical excitation spectra of $Eu(PBI)_3.2TOPO$ and $Eu(FBPI)_3.2TOPO$ at 303K are shown in Figs. 6.3 & 6.4, respectively. The excitation spectra evidence an efficient ligand-to-metal energy transfer, since the most intense feature is a broad band corresponding to transitions populating ligand-centered excited states. All weak bands of f-f transitions of Eu^{3+} ion are hidden by the strong band except $^7F_0 \rightarrow {}^5D_2$ and $^7F_1 \rightarrow {}^5D_1$ bands, appeared as weak bands at 463.6 nm and 534 nm, respectively. The relative intensity of the broad UV band to the intrinsic Eu^{3+} lines in fact shows the so-called 'antenna' role played by the heterocyclic β-diketone molecule.

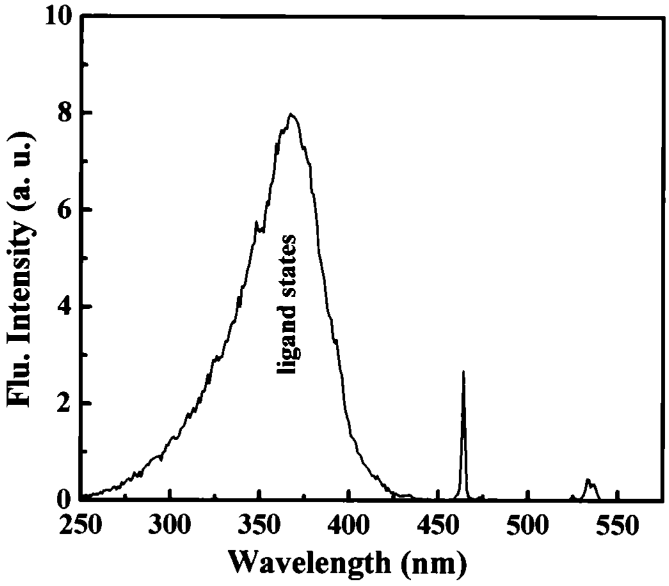


Fig. 6.3. The excitation spectrum of the $^5D_0$ emission (λ_{em} 614 nm) of Eu^{3+} ion in $Eu(PBI)_3.2TOPO$ complex.

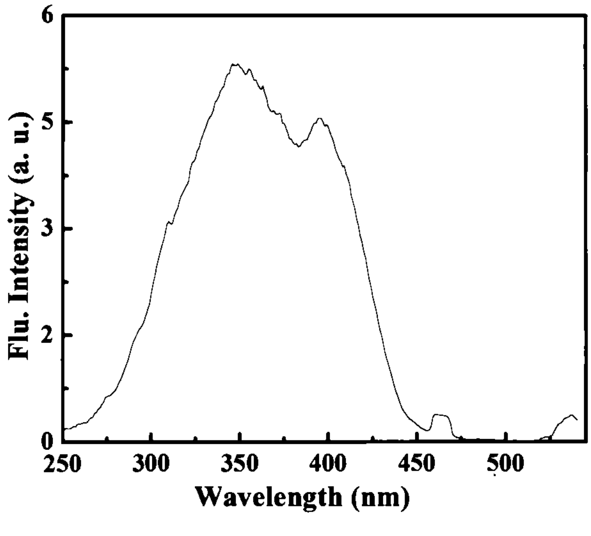


Fig. 6.4. The excitation spectrum of the $^5D_0$ emission (λ_{em} 614 nm) of Eu^{3+} ion in $Eu(FBPI)_3.2TOPO$ complex.

The luminescence spectra of Eu^{3+} complexes with HPBI/HFBPI in the presence of TOPO/TPhPO at 303K are shown in Figs. 6.5-6.6. For comparison, the emission spectrum of Y_2O_3: (5%) Eu phosphor is also given in Fig. 6.7. The emission spectra of the complexes display characteristic sharp peaks associated with the $^5D_0 \rightarrow {}^7F_J$ transitions of the Eu^{3+} ion. The five expected Stark components of the $^5D_0 \rightarrow {}^7F_{0\text{-}4}$ transitions are well resolved and the hypersensitive $^5D_0 \rightarrow {}^7F_2$ transition is very intense, pointing to a highly polarizable chemical environment around the Eu^{3+} ion. Further, an important result is that the emission band (525 nm), corresponding to the emission from the lowest triplet state of the ligand, is not observed in these Eu^{3+} complexes indicating that energy transfer from the lowest triplet state of 4-aroyl-5-isoxazolone to the Eu^{3+} ion is efficient.

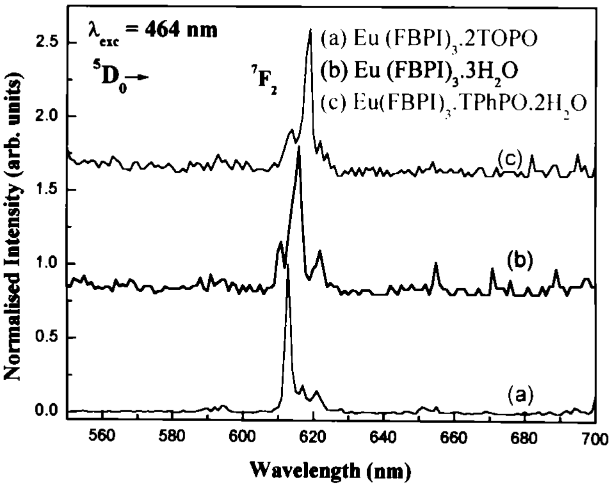


Fig. 6.5. Emission spectra of Eu-FPBI complexes.

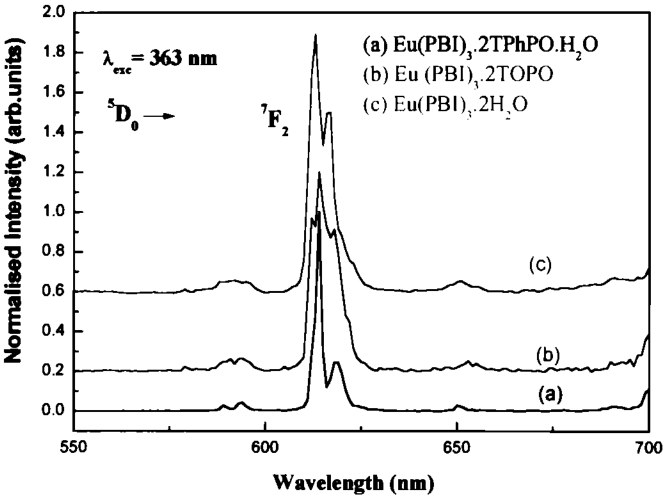


Fig. 6.6. Emission spectra of Eu-PBI complexes.

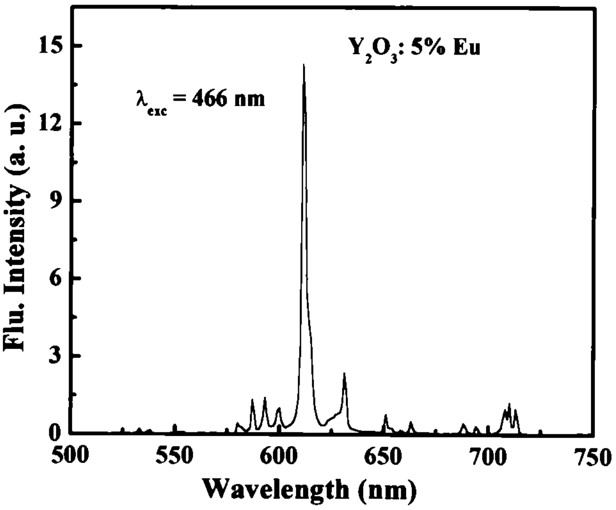


Fig. 6.7. Emission spectrum of Y_2O_3: 5%Eu phosphor.

The logarithmic decay profiles for the phosphorescence lifetime of Eu^{3+} complexes with HFBPI/HPBI and TOPO/TPhPO are shown in Figs. 6.8-6.9. The solid line indicates the best fitted line with respect to experimental values along with the measured data points for respective systems. The decay curves are monitored from ${}^5D_0 \rightarrow {}^7F_2$ transitions. The radiative decay curves have been fitted with the following equation:

$$I_t = I_0 e^{-t/\tau}$$

where I_0 is the initial intensity at $t = 0$, I_t is the decay intensity after time t and τ is the lifetime. With the help of Origin programme, the decay curves are well fitted with a single exponential decay and automatically the lifetime, τ can be evaluated by taking the first e-folding time of decay curve.

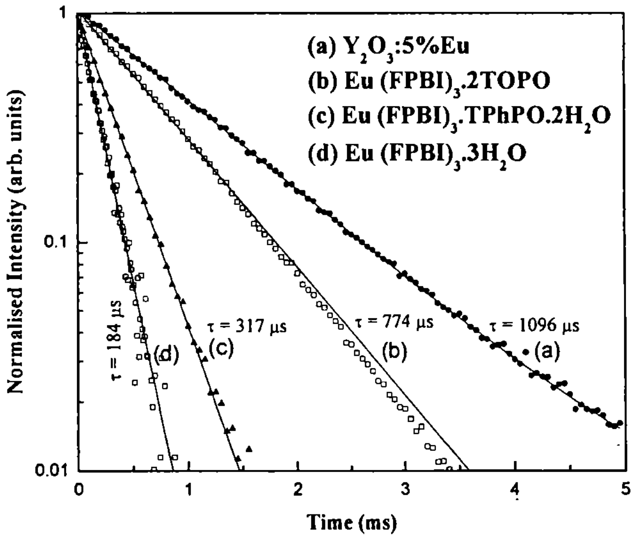


Fig. 6.8. Decay profiles of the $^5D_0$ level in Eu-FBPI complexes. The solid line represents the decay curve with best fit.

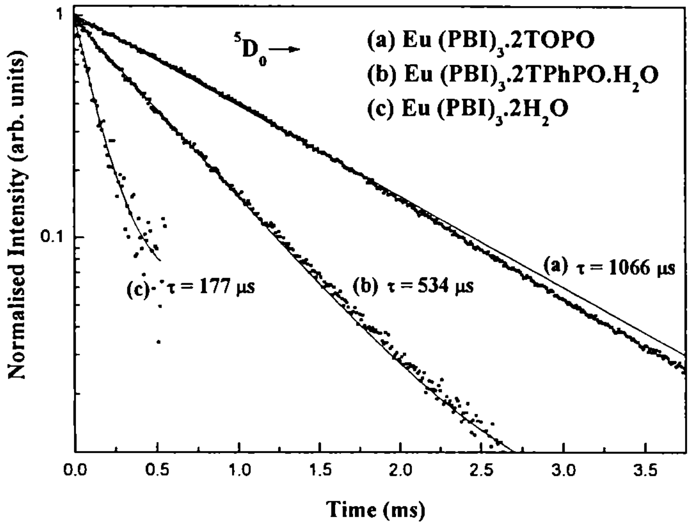


Fig. 6.9. Decay profiles of the $^5D_0$ level in Eu-PBI complexes. The solid line represents the decay curve with best fit.

Table 6.3. Lifetime (τ) of the emitting levels in the Eu-HPBI/HFBPI-TOPO/TPhPO complexes at 303K.

Complex	Lifetime (τ) μs
Eu(FBPI)$_3$.3H$_2$O	184 ± 2.0
Eu(FBPI)$_3$.TPhPO.2H$_2$O	317 ± 2.0
Eu(FBPI)$_3$.2TOPO	774 ± 3.0
Eu(PBI)$_3$.2H$_2$O	177 ± 1.0
Eu(PBI)$_3$.2TPhPO. H$_2$O	534 ± 2.0
Eu(PBI)$_3$.2TOPO	1066 ± 3.0
Y$_2$O$_3$:(5%) Eu	1096 ± 7.0

As can be seen from the magnitudes of the measured (Table 6.3) lifetimes, relatively shorter τ_{expt} (184 μs and 177 μs) were obtained for Eu(FBPI)$_3$.3H$_2$O and Eu(PBI)$_3$.2H$_2$O, respectively, due to dominant non-radiative decay channels associated with vibronic coupling due to the presence of water molecules. Shorter lifetimes due to the presence of water molecules have been well documented for Eu(btfa)$_3$.2H$_2$O (380 μs) and Eu(bzac)$_3$.2H$_2$O (300 μs) complexes [Junior et al. 1997]. On the other hand, Eu(FBPI)$_3$.2TOPO and Eu(PBI)$_3$.2TOPO complexes exhibit longer τ_{expt} of 774 μs and 1066 μs compared to τ_{expt} of 317 μs and 534 μs for Eu(FBPI)$_3$.TPhPO.2H$_2$O and Eu(PBI)$_3$.2TPhPO.H$_2$O, respectively, due to dominant multiphonon relaxation in the latter complexes. This is in good agreement with the observed IR P=O stretching frequencies of 1134 cm^{-1} for Eu(PBI)$_3$.2TOPO and 1165 cm^{-1} for Eu(PBI)$_3$.2TPhPO.H$_2$O complexes since multiphonon relaxation is proportional to these frequencies. Further, the present lifetime values are found to be significantly higher than that of Eu(bzac)$_3$.Phen (410 μs) or Eu(bzac)$_3$.PhenNO (855 μs) [Junior et al. 1997]. Also, the lifetime obtained for Eu(PBI)$_3$.2TOPO (1066 μs) is found to be comparable to that of the standard phosphor (1096 μs). Thus Eu(PBI)$_3$.2TOPO may find potential applications as emitting layers in electroluminescent devices.

Chapter 7

Summary and Conclusions

The conclusions drawn from the work reported in this thesis are described below:

1. Para-substituted 4-aroyl derivatives of highly acidic heterocyclic β-diketones, 3-phenyl-5-isoxazolones, namely, 3-phenyl-4-(4-fluorobenzoyl)-5-isoxazolone (HFBPI) and 3-phenyl-4-(4-toluoyl)-5-isoxazolone (HTPI), by introducing both electron withdrawing (-F) and electron donating (-CH_3) groups, have been synthesized and characterized by elemental analyses, IR and ^1H NMR spectral data. The synthesized ligands have been utilized for the extraction of trivalent lanthanoids from dilute nitric acid solutions in the presence and absence of various crown ethers. For comparison, studies have also been performed with HPBI. The extraction data have been analyzed by both graphical and theoretical methods. The equilibrium constants for the extracted complexes have been deduced by a non-linear regression analysis with the aid of suitable chemically based models developed taking into account, aqueous phase complexation and all plausible complexes extracted into the organic phase. The equilibrium constants have been correlated with the pK_a values of these ligands. The O---O distances between the two oxygens in the para-substituted 4-aroyl-5-isoxazolones have been determined by semi-empirical PM3 molecular orbital calculation taking into account the hydrogen bond. The selectivity

among these Ln^{3+} ions has been determined and compared with commercially available extractants, D2EHPA and EHEHPA. Solid complexes of Eu^{3+} ion with HFBPI alone and with mixtures of HFBPI and various crown ethers have been isolated and characterized by IR and ^1H NMR spectral data to further clarify the nature of the extracted complexes. The conclusions drawn from the above investigations are listed below:

(i) The extraction efficiency of trivalent lanthanoids with various para-substituted 4-aroyl-5-isoxazolones follows the order: HFBPI > HPBI > HTPI. The substitution of an electron withdrawing fluorine atom in the fourth position of the benzoyl moiety in HPBI molecule significantly improves the extraction efficiency of these metal ions as compared to HPBI. On the other hand, the substitution of an electron-releasing group ($-CH_3$) diminishes the extraction efficiency as compared to HPBI. Further, the extraction efficiency observed with various 4-aroyl-5-isoxazolones, is found to be significantly higher than that with β-diketones like 4-acylpyrazolones and HTTA.

(ii) The results demonstrated that these trivalent metal ions have been extracted into chloroform as $Ln(FBPI)_3$ with HFBPI alone and as $Ln(FBPI)_3 \cdot CE$ in the presence of a CE (18C6, DC18C6 or DB18C6).

(iii) Comparing the equilibrium constants of various 3-phenyl-4-aroyl-5-isoxazolones for the extraction of lanthanoids from nitrate solutions with their pK_a values, it can be concluded that log equilibrium constant value increases as pK_a value decreases.

(iv) The O---O distances (bite size) obtained by semi-empirical PM3 molecular modeling calculations for various 3-phenyl-4-aroyl-5-isoxazolones clearly highlight that the para-substitution in 3-phenyl-4-aroyl-5-isoxazolone does not affect the O---O distances (O---O distance for HPBI = 2.72Å; HFBPI = 2.72Å; HTPI = 2.72Å) between the two donating oxygen atoms. The larger O---O distances observed in 4-aroyl-5-isoxazolones would decrease the stability of the intramolecular H-bonding resulting in a great enhancement of acidity.

(v) The elemental analyses of solid complexes show that Eu^{3+} ion has reacted with HFBPI or HTPI or HPBI in the metal:ligand mole ratio of 1:3.

(vi) The FT-IR spectra and elemental analyses data of the binary complexes indicate the presence of water molecules in the coordination sphere of the metal ion. The stretching frequencies of the C=O group of HFBPI have shifted to lower frequencies, indicating the involvement of carbonyl oxygen in the complex formation with Ln^{3+} ions. The absence of enolic -OH peak in the ^1H NMR spectra of complexes further supports complex formation of Eu^{3+} ion with these ligands.

(vii) The selectivity among Ln^{3+} ions with various 4-aroyl-5-isoxazolones follows the order: HPBI > HTPI > HFBPI. This trend clearly highlights that the separation of lanthanoids becomes poorer as the extractability increases. These results also strongly suggest the relationship between the selectivity and pK_a value of the ligand. The S.F. values observed with various 4-aroyl-5-isoxazolones, especially, between Eu and Nd pair, are comparable with that obtained in the presence of EHEHPA and D2EHPA, which are widely used as extractants in the Rare Earth Industry. Hence such systems would be of practical value in the extraction separation of these metal ions.

(viii) The addition of a CE to the metal-chelate systems significantly improves the extraction efficiency of these metal ions but, at the same time, it diminishes the selectivity among these metal ions. This may be due to the absence of ion pair extraction of lighter lanthanoids in the presence of CEs.

(ix) The complexation strength of Ln^{3+} ions with various CEs follows the order: DC18C6 > 18C6 > B18C6 > DB18C6. The sharp decrease in the complexation from 18C6 to B18C6 and to DB18C6 mostly reflects increasing steric effects and decreasing basicity. The higher extractability of these Ln^{3+} ions with DC18C6 or 18C6 can also be explained on the basis of size fitting effect of these CEs.

(x) The stretching frequencies of the C=O group of HFBPI have been shifted to lower frequencies in the IR spectra of all ternary complexes which suggests that the carbonyl group is involved in the complex formation. The IR bands of C-O-C and Ph-C-O stretching vibrations in CE ligands show a significant shift to lower frequencies or diminution in intensity on complexation with the metal ion indicating the involvement of oxygen of the CE in the adduct formation.

(xi) ^{1}H-NMR studies of ternary complexes highlight that Ln^{3+} ion may not be interacting uniformly with all the potential donor oxygens of CEs in the presence of chelating agent, HFBPI.

(xii) The stability constants of these trivalent lanthanoids with various CEs do not follow a simple pattern with decrease in ionic radii of these metal ions unlike that of synergistic constants. The unusual behaviour observed in the present investigations of CEs with Ln^{3+} ions in the presence of HFBPI may be due to a variety of geometric (cavity size and steric repulsion between the extractant classes), enthalpic (donor basicity) and entropic effects (cation dehydration). A better understanding of the interactions of crown ethers with metal-chelate systems require more detailed investigations of the solution structures of these complexes by X-ray absorption fine structure (XAFS) measurements.

2. 1–Phenyl–3-methyl–4–pivaloyl–5–pyrazolone (HPMPP) has been synthesized by introducing a bulky pivaloyl group at the 4th position of the pyrazolone ring with a view to reduce the bite size and to achieve better selectivity among the Ln^{3+} ions. The extraction behaviour of Nd^{3+}, Eu^{3+}, and Tm^{3+} ions from perchlorate solutions into chloroform with HPMPP in the presence and absence of various crown ethers, 18C6, DC18C6, and DB18C6 has been studied. Binary and ternary solid complexes of Eu^{3+} ion with HPMPP and in the presence of DC18C6 have been synthesized and characterized

by spectroscopic techniques. The conclusions from the above findings are as follows:

(i) The results demonstrated the extraction of the species as $Ln(PMPP)_3$, with HPMPP alone, and $Ln(PMPP)_3.CE$, in the presence of crown ethers.

(ii) The S.F. values obtained especially between Eu and Nd pair with HPMPP is found to be significantly higher than that obtained with D2EHPA or EHEHPA. Also the S.F. value with HPMPP is found to be higher than that obtained with 4-aroyl-5-isoxazolones. This may be due to shorter O---O distance in HPMPP (2.48Å) than in para-substituted 4-aroyl-5-isoxazolones (2.72Å). Further, this would strongly suggest the relationship between the selectivity and the O---O distance of the β-diketones. Thus HPMPP may find potential application in the separation of lanthanoids.

(iii) The increase in the extractability of lanthanoid complexes from Nd^{3+} to Tm^{3+} ion can be due to the increase in electrostatic interactions between the cation and the ligand with decrease in ionic radii.

(iv) The addition of a CE to the metal-chelate system not only enhances the extractability of these metal ions but also improves the selectivities among Nd-Eu pair, especially with DB18C6.

(v) The complexation strength of Ln^{3+} ions with various crown ethers follows the order: 18C6 > DC18C6 > DB18C6. The sharp decrease in the complexation from 18C6 to DB18C6 mostly reflects increasing steric effects and decreasing basicity.

(vi) The FT-IR spectra of binary and ternary complexes show the involvement of carbonyl and polyether oxygen atoms in complex formation with Ln^{3+} ion.

3. Various 4-acylbis(pyrazolones), namely, 4-adipoylbis(1-phenyl-3-methyl-5-pyrazolone) (H_2AdBP), 4-suberoylbis(1-phenyl-3-methyl-5-pyrazolone) (H_2SuBP), 4-sebacoylbis(1-phenyl-3-methyl-5-pyrazolone) (H_2SbBP), 4-dodecandioylbis(1-phenyl-3-methyl-5-pyrazolone) (H_2DdBP) have been synthesized and characterized by elemental analyses, IR and ^{1}H NMR spectral data. These ligands have been utilized in the investigations on the extraction behavior of Ln^{3+} ions from nitrate solutions in the presence and absence of neutral organophosphorus extractants (TOPO, TPhPO and CMPO). The orientation and steric effects of the polymethylene substituent have been examined by semi-empirical PM3 molecular modeling calculations. The equilibrium constants of the extracted complexes have been deduced by non-linear regression analysis and have been correlated with the polymethylene chain length. The synergistic equilibrium constants have been correlated with the donor ability of the phosphoryl oxygen of the neutral organophosphorus extractants in terms of their ^{31}P NMR chemical shifts and their nitric acid uptake constant (K_H) values. The extracted complexes have been characterized by IR and ^{31}P NMR spectral data to understand the interactions of neutral organophosphorus extractants with metal chelates. The conclusions from the above investigations are as follows:

(i) The extracted complexes have been elucidated as: Ln(X)(HX) in the presence of H_2X (H_2AdBP, H_2SbBP or H_2DdBP) alone and as Ln(X)(HX).S in the presence of a neutral organophosphorus extractant (S), respectively.

(ii) The extraction of Ln^{3+} ions with 4-acylbis(pyrazolones) was found to increase monotonically with increasing atomic number of these metal ions.

(iii) 4-acylbis(pyrazolones) showed an initial increase in the extraction efficiency of Ln^{3+} ion with increasing polymethylene chain length, $-(CH_2)_n-$, from n = 4 to 8 and thereafter a decreasing trend, for n = 10. Thus, a minimum distance of 12.18 Å between the carbonyl oxygens connected to the polymethylene chain, is required to achieve an optimal extraction of Ln^{3+} ions. Further, for a distance greater than 12.18 Å, the decrease in extraction efficiency can be due to steric factors.

(iv) From the molecular modeling calculations, it can be concluded that the differences in the number of methylene groups and rigidity of these groups in the ligands, hence different steric effects and different orientations of the displaceable hydroxyl groups in the ligands are apparently the vital factors that govern the complexation of Ln^{3+} ion.

(v) The addition of a neutral organophosphorus extractant to the Ln^{3+}-chelate system improves both the extraction efficiency and the selectivity appreciably among these Ln^{3+} ions.

(vi) The complexation strength of Ln^{3+} ions with neutral organophosphorus extractants follows the order: TOPO > CMPO > TBP. The sharp decrease of Log $K_{syn,1}$ value of Ln^{3+}

ions from TOPO to TBP mostly reflects in the decrease of their phosphoryl oxygen basicity values.

(vii) The Log $K_{\mathrm{syn},1}$ values of Eu^{3+} ion increase linearly with increase in $\delta(^{31}P)$ NMR chemical shift of the neutral O-bearing organophosphorus extractant. However, CMPO was found to deviate from linearity. It may be due to the bidentate nature of CMPO in the complex formation with Eu^{3+} ion as is also evident from the IR spectral data, where both P=O and C=O stretching frequencies of CMPO have shifted to lower wave numbers, indicating the involvement of oxygen atoms of both carbonyl and phosphoryl groups in complexation.

4. Eu-4-aroyl-5-isoxazolonate complexes of the type $Eu(X)_3.L$ (X = anion of 3-phenyl-4-aroyl-5-isoxazolone; L = TOPO or TPhPO) have been synthesized and characterized by elemental analyses, thermogravimetric analysis, IR and photoluminescence spectroscopy. The conclusions from the above studies are as follows:

(i) The analytical data show that Eu^{3+} ion reacted with HPBI and HFBPI in the metal: ligand mole ratios of 1:3. The same metal: ligand ratio is valid in the ternary complexes of Eu-HFPBI/HPBI-TOPO/TPhPO.

(ii) The IR spectra of the complexes of Eu^{3+} ion ($Eu(FBPI)_3.3H_2O$ or $Eu(PBI)_3.2H_2O$) show a broad absorption in the region 3000-3500 cm^{-1}, indicating the presence of water of hydration in the complexes. This is also in consistent with the TG analyses, where a small weight loss of 5.0 % at 100-175°C was noticed. Carbonyl stretching frequencies have been shifted to lower frequencies in all the complexes, indicating the involvement of carbonyl oxygen atoms in complexation.

(iii) The P=O stretching frequencies have also been shifted to lower frequencies in the complexes indicating the involvement of phosphoryl oxygen of TOPO or TPhPO in complex formation with Eu^{3+} ion.

(iv) The excitation spectra evidence a ligand-to-metal energy transfer, since the most intense feature is a broad band corresponding to transitions populating ligand-centered excited states.

(v) The room temperature photoluminescence spectra of the complexes display characteristic sharp peaks associated with the $^5D_0 \rightarrow {}^7F_J$ transitions of the Eu^{3+} ion. Further, the emission spectra of the Eu^{3+} ion shows a very high intensity for the hypersensitive $^5D_0 \rightarrow {}^7F_2$ transition pointing to a highly polarizable chemical environment around the Eu^{3+} ion.

(vi) The results clearly show that the substitution of water molecules by TOPO/TPhPO in the Eu-isoxazolonate complexes leads to longer $^5D_0$ lifetimes (184 μs for $Eu(FBPI)_3.3H_2O$ vs. 774 μs for $Eu(FBPI)_3.2TOPO$ and 177 μs for $Eu(PBI)_3.2H_2O$ vs. 1066 μs for $Eu(PBI)_3.2TOPO$). This can be ascribed to a more efficient ligand-to-metal energy transfer and to less efficient non-radiative $^5D_0$ relaxation processes.

(vii) The shorter lifetime of the $^5D_0$ level in the hydrated complex is associated with the non-radiative decay channel associated with vibronic coupling due to the presence of water molecules.

(viii) The lifetime of $Eu(PBI)_3.2TOPO$ (1066 μs) is found to be significantly higher than that of $Eu(PBI)_3.2TPhPO.H_2O$ (534 μs). This may be due to the presence of water molecules in the latter complex.

(ix) The complex $Eu(PBI)_3.2TOPO$ shows a long $^5D_0$ lifetime (1066 μs), which is comparable to that of standard commercial Y_2O_3:(5%)Eu phosphor (1096 μs). Thus the complex $Eu(PBI)_3.2TOPO$ may find potential applications in electroluminescent devices as emitting layers.

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