STRUCTURAL STUDIES ON SOME METAL COMPLEXES OF EMBELIN

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DECLARATION

I hereby declare that the thesis entitled, **Structural Studies on Some Metal Complexes of Embelin**, is an authentic record of research carried out by me under the supervision and guidance of Dr. P.N.Krishnan Nambisan and Dr. Jacob Chacko in partial fulfilment of the requirements of the Ph.D. Degree in the Faculty of Science of the Cochin University of Science and Technology and that no part of it has previously formed the basis for the award of any degree, diploma or associate-ship in any University.

K.K. Abdul Rashid

CERTIFICATE

This is to certify that the thesis bound herewith is an authentic record of the research work carried out by Mr.K.K. Abdul Rashid. M.Sc., in the Division of Chemical Oceanography, School of Marine Sciences under our supervision, in partial fulfilment of the requirements for the degree of Doctor of Philosophy of the Cochin University of Science and Technology, and further that no part thereof has been presented before for any other degree.

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(Supervising teacher)

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PREFACE

Benzoquinones and their substituted derivatives are well known as versatile redox agents and are among the most pervasive natural products on the earth's surface. They possess numerous biologically significant properties and are present in several living organisms. Embelin (2,5-dihydroxy-3-undecyl-1,4-benzoquinone or 2,5-dihydroxy-3-undecyl-2,5-cyclohexadiene-1,4-dione) an orange pigment isolated from the berries of the Indian shrub Embelia Ribes is of great medicinal importance because of its anthelmintic, analgesic and antifertility properties. Biological studies on embelin have received considerable amount of attention in recent years. However, only very scant information is available on the metal chelates of embelin which could function as possible basis for the development of therapeutic drugs. We have undertaken a systematic study of the preparation and properties of some metal complexes of embelin in view of its relevance in biological systems.

This thesis deals with the studies on the synthesis and characterisation of the complexes of embelin with manganese (II), cobalt(II), nickel (II), copper (II), zinc (II), cadmium (II), chromium (III), iron (III) lanthanum(III), praseodymium (III) neodymium (III) samarium (III), gadolinium (III) dysprosium (III), yttrium (III) thorium (IV) and uranium (VI).

Elemental analysis as well as spectral, thermal and magnetic data were used to ascertain the composition of the complexes and to establish the structures of the metal complexes. Wherever possible, the electronic spectra and magnetic data were used to predict the stereochemistry of the complexes. The thesis is divided into four chapters: Chapter 1 surveys briefly the general field of coordination chemistry of the 3d-metals, the lanthanides and the actinides. Coordination polymers, biological aspects of embelin and coordination of metal ions with biologically important ligands have also been discussed. Chapter 2 deals with the reagents used, the preparation of the ligand and the physicochemical techniques employed for structure elucidation. Isolation and characterisation of 3d (divalent and trivalent) metal complexes of embelin are described in Chapter 3. Lanthanide and actinide complexes of embelin are discussed in Chapter 4.

The work described in this thesis has been published/or are under publication as indicated below.

1. Thermal, spectral and magnetic studies on some transition metal complexes of embelin, Polyhedron, 2, 293 (1983)

2. Complexes of embelin with chromium (III) and Iron (III) -under publication.

3. Lanthanide and actinide complexes of embelin - under publication.

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INTRODUCTION

1.1. General Remarks

In recent years, there have been interesting developments in inorganic chemistry inspired by the understanding of structure and bonding in the broad class of coordination complexes. The chemistry of coordination compounds occupies a major part of the current research in inorganic chemistry and reports of newer and exotic complexes are appearing in the recent publications. Indeed there are now special journals devoted exclusively to a description of the chemistry of coordination compounds.

Development of sophisticated instrumentation techniques provides powerful methods of investigating the thermal, spectral and magnetic properties of coordination compounds, thereby helping to understand their stereochemistries. Studies on the reaction mechanisms have provided stimulating problems to be resolved in the exciting field of catalysis by transition metal complexes (1,2). Recent advances in bioinorganic chemistry are centered on the role of coordination compounds in biological systems(2,3).

1.2. Some Aspects of the Coordination Chemistry of 3d-Transition Metals.

1.2.1. Electronic configuration, orbital splitting and structural considerations.

Transition elements may be,, strictly, defined as those which have partially filled d or f shells in their commonly occurring oxidation states (2). The main transition series include those elements which have partially filled (n-1)d shells. General electronic configuration of the 3d-transition series is $[Ar]3d^n4s^2$. Because of the extra stability associated with empty, half-filled and filled subshells, there are some apparent anomalies in the electronic arrangements in the transition series. Thus the outer electornic configurations of chromium and copper are $3d^5 4s^1$ and $3d^{10} 4s^1$ respectively.

In free metal ions,the d orbitals are five-fold degenerate. However the d orbitals are split in various ligand fields (octahedral, tetrahedral, square planar etc.), owing to their particular shapes and spatial orientation (1-3). As a consequence of this splitting, the electronic and magnetic properties of the complexes will be different. The structural changes of the complexes will be reflected in the values of their magnetic moments. This enables one to predict their stereochemistries (4,5).

Electronic transitions occurring between the split d levels of the central atom give rise to d-d or ligand field spectra. Absorption bands due to these transitions are generally observed in the near infrared and visible regions of the spectra of transition metal complexes. The study of absorption spectra of these complexes has provided major contributions towards an understanding of their stereochemistries (6,7). The electronic spectra could be interpreted with the help of Tanabe-Sugano diagrams. Tanabe-Sugano diagrams are employed for both strong and weak ligand fields, while Orgel diagrams are used generally in the case of weak ligand fields. But for the more commonly found ligand fields of intermediate strength, either of these could be used (3,6).

Infrared absorptions of the complexes generally occur in the region 4000-200 cm^{-1} and they provide valuable information about the bonding present in complexes by studying the frequency shifts of ligand vibrations upon coordination (8). The appearance or disappearance of certain bands has been used to deduce structural information.

The concept of hard and soft acids and bases has been useful in predicting the relative stability of the complexes of a given ligand with various metal ions (9). One of the earliest stability correlations was the 'Irving-Williams' series (10) in which complexes of divalent transition metals are arranged in the following order of increasing stability: Mn(II) < Fe(II) < Co(II) < Ni(II) < Cu(II) > Zn(II). The increasing stability is a measure of the increasing inherent 'acidity' of the metals due to decreasing size. Superimposed upon this is a hardness-softness factor in which the softer species (with greater number of d electrons) favour ligands in the order S > N > O (3).

Complexes of transition metals have been well documented (2,11,12). Coordination complexes find application in diverse fields from industrial catalysis to biological systems. Oxidation of ethylene to acetaldehyde, hydroformylation of olefins, methanol carbonylation and polymerisation of olefins are some of the industrial processes catalysed by transition metal complexes (2,13,14).

1.2.2. Complexes of transition metals with oxygen containing ligands.

Transition metals form a wide range of coordination compounds with various types of ligands. However, complexes with nitrogen, oxygen and sulfur containing ligands are abundant. Several reviews have appeared on the complexes with such ligands (11,12,15). Since an oxygen donor ligand, embelin, was selected for our studies, the present discussion will be limited to a few oxygen containing ligands only.

A great many bi- and multi-dentate ligands contain the phenolate and/or carbonyl functional group as the donors. Much work has been reported on the complexes with several Schiff bases (16). Copper(II) complexes with N-isopropyl and N-sec-butylsalicylideneamine were studied by Sacconi and Ciampolini (17). They found these complexes to be isomorphous with the analogous complexes of cobalt(II), nickel(II), and zinc(II). Manganese(II) complexes with Schiff bases derived from salicylaldehyde and tri- or tetra-amines(18) and trinuclear copper(II) complexes involving catechol aldehyde and hetero-aromatic amines have been recently investigated (19). All the above mentioned Schiff bases coordinated to the metal through nitrogen and oxygen atoms. Metal complexes of the Schiff's base derived from salicoylhydrazine and biacetylmonoxime were found to coordinate <u>via</u> carbonyl oxygen, azomethine nitrogen and phenolic hydroxyl group with the replacement of proton by metal ions (20). There are exceptions where the phenolate oxygen remains uncoordinated. In the dimeric N, N -dimethyl salicylaldimine-nickel(II) complex containing one molecule of catechol mono-anion per metal ion, the unionised phenolic group is not coordinated. The coordinated catechol oxygen in this case acts as a bridge between the two metal atoms (21). Bridging of O-H group has been proposed for a novel trinuclear copper(II) hydroxo complex (22).

The most extensively studied ligands among the carbonyl compounds are β -diketones (23,24). They are effective in the formation of 5-membered chelate rings and the deprotonated ligand neutralizes the charge on the metal ions in the complexes. Chelate ring electron delocalisation through conjugation within the enolate ion can lead to extra stability of these complexes. Coordination of the carbonyl group is indicated by the lowering of carbonyl stretching frequency in the infrared spectra of the complexes. Similar shifts in C=O frequencies have been observed for some metal β -diketonates (25) and several other complexes containing this group (26-30).

In the case of iron(III) chelates of salicylaldehyde-semi thiosemi-, and S-methylthiosemi-carbazones, the coordination through phenolic oxygen was observed for all the complexes and the carbonyl group was found to coordinate in the semicarbazone based ligand (31). The coordination behaviour of neutral, mononegative and dinegative forms of N-(thiophene-2-carboxamido) salicylaldimine(H_2TCS) towards 3d-metal ions has been investigated (32). Spectral studies indicate that H_2TCS behaves as a neutral bidentate ligand (bonding sites being carbonyl oxygen, azomethine nitrogen), as a mononegative tridentate ligand (bonding sites being deprotonated phenolic oxygen, carbonyl oxygen and azomethine nitrogen) and as a binegative tridentate ligand (bonding through phenolic oxygen, enolic oxygen and azomethine nitrogen). However, the phenolic group participation with the ligand behaving neutrally has been observed for the copper(II) and nickel(II) complexes of 5,8-diethyl-7-hydroxy-6-dodecanone oxime.In this case the deprotonated ligand forms polymeric complexes whereas the neutral ligand forms monomeric complexes (33).

Spectral behaviour of the polymeric metal chelates of several hydroxyquinoid ligands has been investigated (34-35). 2,5-dihydroxy-1,4-benzoquinone acts as a tetradentate ligand coordinating through its carbonyl and phenolic oxygens (34).

Complexes of quinizarin or 1,4-dihydroxyanthraquinone with manganese(II), cobalt(II), copper(II), zinc(II) and ruthenium(II) have been prepared and characterised by the use of infrared and electronic spectra and magnetic studies (36). Magnetic moment vs. temperature data were used to calculate the interaction parameter (2J). The thermal and spectral properties of the chelates of lawsone (2-hydroxy-1,4-naphthoquinone) and juglone (8-hydroxy-1,4-naphthoquinone) with divalent cobalt, nickel, copper and zinc ions were investigated and compared with the complexes of 2,5-dihydroxy-1,4-benzoquinone (37). Oxygen coordination was observed in all the complexes. The chelates of several hydroxy quinoid ligands have been investigated recently (38,39). The monoanionic form of 1,2-dihydroxy-9,10-anthracenedione acts as a bidentate ligand using one carbonyl and one phenolic oxygen for coordination with metal ions. The chelate rings thus formed were expected to be stabilised by considerable delocalisation of π electron density (38).

1.3. Some Aspects of the Chemistry of Lanthanides.

1.3.1. General remarks

In the past few decades there has been considerable progress in the science and technology of the rare earth compounds (40). Some of the recent advances in this area are directed towards development of improved methods of catalysis as well as of newer techniques in organometallic and biochemical studies. Application of rare earth oxides in catalysis has been reviewed by Rosynek (41) and Minachev (42). Rare earth compounds have been used for improving the activity of some methanation catalysts (43). The catalytic properties of rare earth oxides in the dehydrogenation of cyclohexane, the dehydrocyclisation of heptane, the cracking of butane, the hydrogenation and isomerisation of olefins, the dehydrogenation, dehydration and ketonisation of alcohols and the oxidation of propylene have also been reported (42). Dependance of catalytic activity on the magnetic moment values of the trivalent rare earth ions has been observed for the oxidation of carbon monoxide(44). Polymerisation of acetylene by rare earth coordination catalysts has been investigated (45). Rare earth ions are used to replace the acid sites in zeolites and for making them extremely effective for petroleum processing, particularly for the formation of gasoline fractions (46).

The commercial use of rare earth phosphors in colour television tubes has received much attention in electronics. The red phosphor produced by europium activated yttrium vanadate is well known for its clarity, intensity and other desirable characteristics (47). Lanthanide complexes with sterically hindered β-diketones exhibit anti-knock activity (48) and may catalytically eliminate some undesirable combustion products of fuels (49). The properties of lanthanide chelates of 2,2,7-trimethyl-3,5-octane dione, for use in the fields such as extraction of metal ores, vapour deposition of metals and fuel combustion modification has been reported (50).

The potential use of rare earth cations as reporter sites in biological systems requiring calcium has been suggested on the basis of their comparable physico-chemical properties. Since rare earth ions are classified as typical hard acids (9) and have sizes comparable to Ca^{++}, it is not surprising that biological activity due to lanthanide ions is observed in a number of calcium enzymes. The studies on calcium(II) sites in proteins require the application of special techniques due to spectroscopic inertness of this ion. Substitution of lanthanide ions for calcium(II) in proteins is employed for spectroscopic studies (51). Lanthanide cations were also reported as excellent NMR probes of their immediate environment in enzymes (52).

Lanthanide ions are characterised by the gradual filling up of the 4f subshells. The electronic configuration for the lanthanides is $[Xe]4f^{n} 5d^{o} 6s^{o}$. However there are certain exceptions to this arrangement. Europium(II) and ytterbium(II) are stabilised by $4f^{7}$ and $4f^{14}$ configurations. Such a system having a maximum number of parallel spins will be stabilised by the exchange energy resulting from their more favourable spatial distribution compared to that of paired electrons.

The free lanthanide metals are more reactive, and in this respect these could be compared more with alkali or alkaline earth metals than 3d-transition metals. These have lower ionisation energies and heats of atomisation than 3d metals.

An important feature of the chemistry of rare earth elements is the lanthanide contraction. It is the manifestation of a steady and significant decrease in the size of atoms and ions with increasing atomic number,that is from La to Lu. This contraction is caused by the imperfect shielding of one 4f electron by another, owing to the shapes of the orbitals (2). Consequently the effective nuclear charge experienced by the 4f electrons increases with increasing atomic number (La to Lu), thus causing a reduction in size . The observed trends in the chromatographic separation of lanthanides as well as in the stability of their complexes can be regarded as the summation of the effects of lanthanide contraction(3). The striking similarity in the properties of yttrium to those of the lanthanides is another consequence of the lanthanide contraction. The atomic and ionic radii of yttrium are very close to those of terbium and dysprosium. The resulting resemblance in size coupled with equality in ionic charge accounts reasonably for the invariably natural occurrence of yttrium with the heavier lanthanides (53).

The magnetic (54) and spectroscopic properties (55) of lanthanides are entirely different from the d block elements because the 4f electrons are well shielded from the external ligand fields by the $5s^2 5p^6$ octet. Hence these properties are mostly independent of the stereochemistries of the lanthanide complexes.

The coordination chemistry of lanthanides is receiving increasing attention and there has been considerable progress in this area in the past two decades. Several review articles on various aspects of the coordination chemistry of lanthanides have been published during this period (56-64).

1.3.2. Comparison of transition metal ions and lanthanide ions(64).

	Lanthanide ions	3d-metal ions
Metal orbitals	4f	3d
Inoic radii	1.06-0.85 Å	0.75-0.60 Å
Common coordination numbers	6, 7, 8, 9	4, 6
Typical coordination polyhedra	Trigonal prism Square antiprism Dodecahedron	Square planar, Tetrahedron, Octahedron
Bonding	Weak metal-ligand orbital interaction	strong metal-ligand orbital interaction
Bond direction	Weak preference in bond direction	Strong preference in bond direction
Bond strengths	Ligands bind in order of electronegativity F^-, OH^-, H_2O, NO_3^-, Cl^-	Bond strengths determined by orbital interaction normally in the following order CN^-, NH_3, H_2O, OH^-, F^-
Non-isolable complexes	Ionic, rapid ligand exchange	Often covalant; covalent complexes may exchange slowly.

1.3.3. Features of lanthanide ions which determine their coordination behaviour.

(a) Electronic configuration

The most common oxidation state of lanthanides is +3. The tripositive lanthanide ion possesses the electronic configuration $[\mathrm{Xe}]4f^{n} 5s^{2} p^{6} d^{o}$. The 4f orbitals seem to be buried so deeply within the atom that they are unaffected by the environment to any great degree. Hence these orbitals are expected to have only very weak interactions with the ligand orbitals. Usually the higher energy orbitals are only available for bond formation. This restricts the possibilities of complex formation. Ligand field stabilisation energies of lanthanides are too low as compared to those of 3d-metal ions.

(b) Ionic size

The trivalent lanthanide ions are somewhat larger than the other tripositive ions. This minimises the electrostatic nature of the metal-ligand interaction. Increasing covalency is expected with decrease in size (La to Lu) of the metal ions.

(c) Ligand exchange reactions

Ligand exchange reactions of lanthanide ions are very rapid.

This limits the number of isolable complexes. The composition of a complex in the solid state may not be the same as that in solution, and once the solid complex is dissolved, it may remain unrecoverable.

(d) Coordination number and stereochemistry

Since the ligand field stabilisation energies of lanthanide complexes are negligible, greater flexibility in geometry and coordination number is observed (59). The change in LFSE will be very small, when the complex transforms from one geometry to another. Lack of directional bonding due to electrostatic nature of the metal-ligand interactions is also responsible for the observed flexibility in geometries. Coordination number is mostly determined by the spatial accommodation of the ligands around the metal ion, and in the solution it may be different from that in crystals. In many cases the geometry of the complexes has been reported ignoring the possibility of the coordination with solvent molecules like water, benzene, alcohol, etc.(61).

(e) Donor atoms

Lanthanides are regarded as hard acids, and are expected to interact strongly with hard bases (9,65). The general preference for bonding to donor atoms is in the order O > N > S. Majority of the complexes are formed with oxygen donor ligands, especially anionic ones such as carboxylates and β-diketonates.

(f) Complexation of lanthanides in aqueous media

The coordination of water molecules with lanthanides has been observed in many of its complexes (59,62); under alkaline conditions the OH^- ion is an even stronger ligand than the water molecule. Thus in aqueous media these two ligands compete with each other for complexation thereby limiting the number and types of isolable complexes from aqueous media. In general, the complexation of lanthanide ions in aqueous media is governed by the molar ratio of the ligand to cation, the nature and concentration of starting material, hydrolysis of the product formed, and finally the pH and temperature of the solution (61).

1.3.4. Lanthanide complexes with oxygen containing ligands

Majority of the lanthanide complexes are prepared from oxygen donor ligands. Earlier studies have devoted more attention to the isolation of lanthanide complexes with carboxylates and β-diketonates (56). Koppikar et al. have reviewed the complexes of lanthanides with neutral oxygen donor ligands (62). Moeller et al. (58) and Forsberg (60) have reviewed the complexes of lanthanides with non oxygen-donor ligands.

Information on a large number of lanthanide complexes with C=O group ligands is available (56,61). The ligand to metal ratio is often found to be larger for the complexes in the presence of non-coordinating anions. Thus the ratio of L:M for the complexes of N,N-dimethylformamide with lanthanide nitrates,lanthanide chlorides and lanthanide acetates are 4:1, 2:1 and 1:1 respectively (62). The ligand to the metal ratio for the complexes of N,N-dimethylacetamide with lanthanide perchlorates is also found to decrease from eight for La(III)-Nd(III) to six for Tm(III)-Lu(III),apparently due to the decrease in cationic size (66). However the complexes of this ligand with lanthanide bromides do not exhibit a similar behaviour (67).

The steric hindrance to coordination caused by the bulkiness of the ligand molecules also affects the stoichiometry of the complexes. For example, complexes of lanthanide perchlorate with N,N-dimethylformamide have a L:M ratio of 8:1, but the corresponding diphenylformamide complexes have a ratio of only 6:1 (68).

Complexes of antipyrine derivatives have been studied extensively by several authors (69-73). Nair and co-workers have reported the complexes of lanthanide perchlorates (69) and nitrates (70,71) with 4-aminoantipyrine. The coordination of the ligand to the metal ion takes place through the carbonyl rather than the nitrogen of amino group. The phenolic group is coordinated in the 4-aminoantipyrine Schiff base complexes of lanthanides (72). Phenolic oxygen was also found to be a potential donor site in the rare earth iodide complexes of 4-N-(2-hydroxy-1-naphthylidine) aminoantipyrine.(73).

Complexes of lanthanide perchlorates with 2-N-(pyridyl) benzamide were studied (74). Coordination through oxygen of the amide group and nitrogen of the heterocylic ring were observed and hexacoordinated geometry was proposed for the complex.

Much work has been done on the lanthanide complexes with 1,3-diketone ligands (61,62). The neutral tris-chelates of these ligands are commonly precipitated as solvates. eg. $[Ln(diket)_3\ nH_2O]$ where n = 1-3. Unsolvated tris-chelates are obtained with bulky organic ligands such as dipivaloylmethane (57). In many of these complexes the lanthanide ion exhibits 8-coordination. It is interesting to note that some of these chelates with bulky diketonate ligands exhibit volatility (50). This is due to the minimised interaction of metal ion with ligands which is caused by the shielding of the bulky alkyl groups. Early methods used for preparation of lanthanide tris β -diketonates have been critically examined by Moeller et al (56). Some of the β -diketonate complexes prepared from aqueous ethanolic mixtures showed undesirable compositions. Based on such observations, the advantages of synthesising lanthanide complexes in non-aqueous media using metal alkoxides as starting materials have been proposed (61).

The participation of phenolic oxygen in coordination at certain ligand to metal ratios has been observed for some lanthanide isopropoxide complexes with mendelic acid and salicylic acid (75). In the crystal structure determination for aquo-tris-salicylatosamarium, Burns and Baldwin (76) have found that there are no discrete molecules and instead each metal atom is linked to six different salicylato ions through a variety of donation modes in which both the carboxylic and phenolic oxygen atoms participate. Lanthanide complexes of the composition $Ln(Sal)_3$ (where Sal corresponds to salicylaldehyde) for the lighter lanthanides are obtained by complexation with salicyladehyde. Heavier lanthanides give the hydroxy derivatives corresponding to the composition $Ln(Sal)_2OH$. Phenolic oxygen is found to coordinate in these complexes (77).

The physico-chemical properties of the lanthanide benzohydroxamates have been studied by Schelokov et al. (78). The complexes correspond to the composition $M(C_6H_5CONHO)_3$ where M is La(III) to Lu(III). Infrared spectra of these complexes show that there is bidentate cyclic coordination of the benzohydroxamate ion. Absence of phenolic O-H vibration in the complexes and the shift in carbonyl group frequency indicate the participation of these groups in the coordination. Octahedral geometry is proposed for the complexes. New lanthanide complexes with salicyloylhydrazide-salicylaldehyde Schiff base and anthranilic acid - salicylaldehyde Schiff base were synthesised and characterised(79). Infrared spectra of these complexes reveal the bidentate binding of both the Schiff base ligands to lanthanide ions.

1.4. Some Aspects of the Coordination Chemistry of Actinides, particularly Thorium and Uranium

The actinides are characterised by a general electronic configuration $5f^n 6d^o 7s^o$. The 5f electrons are effectively shielded by $6s^2 6p^6$ octet. The main difference between the 4f and 5f orbitals seems to depend upon the relative energies and spatial distribution of the orbitals. The 4f electrons are deeply buried in the atom, whereas the 5f electrons are available for bonding. Consequently, the binding energies of 4f electrons in lanthanides are much greater than the binding energies of 5f electrons in actinides. The 5f electrons can be removed more easily, thus causing the actinides to possess positive oxidation states as high as a value equal to the sum of the 7s,6d and 5f electrons.

Similar to that of lanthanide contraction, actinide contraction is also the result of imperfect shielding of the 5f electrons leading to increased nuclear charge and concomitant reduction in size. Actinide contraction initially parallels that of lanthanides, but the elements from curium onwards are smaller than might have been expected, probably resulting from poorer shielding of 5f electrons in these elements.

Thorium and uranium are the most abundant elements among the actinides in nature. They are now regarded mainly as the potential source of nuclear energy. A large number of complexes have been reported for uranium and thorium.

The loosely bound nature and the less effective shielding of the 5f electrons make the actinides more susceptible to complex formation. The complex forming tendency is controlled by factors such as ionic size and charge so that the order is generally $M^{4+} > MO_2^{2+} > M^{3+} > MO_2^{+}$

Thorium is the second member of the actinide series, and is less basic than the trivalent lanthanides. Nevertheless, it resembles lanthanides in the physical properties of many of its compounds (53).

Among the best known complexes of thorium are those with β-diketones. The acetyl acetonato complex, $Th(acac)_4$ has been extensively studied(80,81). Complexes of 8-quinolinol (82,83) and some oxalates(80) have been synthesised and characterised.

A ten coordinate oxobridged thorium complex μ-oxo-bis [aquanitrato (2,9-diformyl-1,10-phenanthroline-disemicarbazone- Th(IV) nitrate] with an unusual polyhedron was synthesised and characterised (84). A coordination number of 10 has also been proposed for the complexes $[NH_4Th(L)_5]\cdot H_2O$ and $Li[Th(trop)_5]\cdot H_2O$ where NH_4L = cupferron and trop = tropolone anion (85,86).

An oxygen coordinated complex of pyridine N-oxide with $Th(NCS)_4$ having the composition $[Th(NCS)_4(PyO)_4]$ has been reported (87). An 8-coordinated structure has been suggested for this complex. Some polymeric complexes of $Th(NO_3)_4$ with N-methylpiperazine and 2-methylpiperazine are reported (88). A coordination number higher than 10 was proposed for these complexes. Complexes of thorium(IV) with 2,6-lutidine-N-oxide and tetramethylenesulfoxide were reported to have coordination through oxygen and the coordination number varied from 6-10, depending upon the nature of anions(89).

Uranium(VI) complexes, particularly the uranyl complexes, represent the most extensively studied among the complexes of uranium. Preparation of several β-diketanato complexes have been reported in the literature (90,91). Mixed nitrogen and oxygen coordination is well illustrated in some uranyl complexes with polyaminopolycarboxylates (92,93). Several uranyl complexes with sulfur donor ligands have been recently investigated (94). Several workers have reported uranyl complexes with Schiff base ligands (72,95,96). Eight coordinated complexes of dioxo uranium with 8-quinolinol-5-sulphonic acid (H_2L) with the composition $Na_4[UO_2L_3]{\cdot}H_2O$ and $K_4[UO_2L_3]{\cdot}0.5H_2O$ have been reported(97). Mixed oxygen and nitrogen bonding from 3 bidentate ligands are observed for these complexes. Spectral studies on uranyl complexes with 3-benzamidorhodanine and its derivatives show the bidentate coordination of the ligand through amide nitrogen and carbonyl oxygen (98). Dioxouranium complex with N-phenylbenzoylhydroxamate has been prepared and characterised (85). Two bidentate hydroxamato ligands and one methanol molecule are equatorially bonded to the linear uranyl group in the pentagonal bipyramidal geometry. Uranyl complexes with isonicotinamido salicylaldimine were found to coordinate through the carbonyl oxygen, phenolic oxygen, azomethine nitrogen and ring nitrogen (99). Uranyl complexes of glycine, aniline and aminobutanoic acid were prepared and characterised (100). The uranyl group is equatorially bonded to the bidentate carboxylate groups of the 3 molecules of the organic ligand forming a distorted hexagonal bipyramidal coordination geometry around the metal.

1.5. Coordination Polymers

1.5.1. Nature of coordination polymers

Most of the metal complexes of embelin (101) and 2,5-dihydroxy-1,4-benzoquinone (34) are polymeric in nature. Hence it would be relevant to have a discussion here on the nature of coordination polymers. The term coordination polymer has been used to describe any macromolecular entity which contains coordinate covalent bonds (102). The concept of coordination polymer is restricted to the limitation that a metal ion has to be involved in the coordinate covalent bond. They are generally classified as inorganic polymers. The ligands commonly incorporated are mostly organic in nature. Two types of coordination polymers are usually investigated, one in which the metallic part functions as the backbone of the macromolecular unit and the other in which the metallic elements are coordinated to a polymer repeating unit containing donor groups. Metal complexes of embelin belong to the former group.

1.5.2. Thermal stability of some coordination polymers

Simple organic compounds are greatly stabilised by coordination with metal ions (103,104). In several cases, it has been found that coordination increases the thermal stability of the ligand (105,106). However there are instances where the pyrolysis behaviour of certain complexes is not in conformity with the above statement. The complexes of acetyl acetone decomposes significantly at 270°C whereas the ligand has got only very little decomposition under similar conditions (107,108). Usually it is found that the coordination polymers are thermally more stable than their monomeric types. Here also some exceptions are noticed. The complexes of Schiff bases and phthalocyanines are thermally more stable than their highly polymerised analogs (109-111).

Coordination polymers of hydroxyquinones are generally more stable than their monomeric ligands. It has long been known that the hydroxyl and carboxyl groups readily form bridges between metal ions, thus forming polymeric species (112). Dihydroxyquinones are ligands which can attach itself simultaneously to two metal ions.

Frank and co-workers (113) were able to synthesise the metal complexes of 2,5 dihydroxy-1,4-benzoquinone. They considered these complexes as simple monomeric types. However, complexes of 2,5-dihydroxy-1,4-benzoquinone with copper(II), nickel(II) and cobalt(II)were shown to have polymeric nature (114).

Bottei and Gerace had prepared and characterised the copper(II), nickel(II) and cobalt(II) complexes of naphthazarin (5,8-dihydroxy-1,4-naphthoquinone) (115). Copper(II) complex was recognised as anhydrous and other complexes were dihydrates. The metal to ligand ratio was 1:1 for all chelates except for copper complex for which it was 3:4. The thermal stability of the naphthazarin chelates was found to decrease in the order Ni > Zn > Cu > Co. The greater thermal stability found for the nickel(II) complex is attributed to the spatial arrangement of the polymer in which metal ion appears to be more planar in nature. The greater stability of naphthazarin chelates over 2,5-dihydroxy-1,4-benzoquinone chelates is due to the greater unsaturation of the organic ligand leading to increased stabilisation of metal-oxygen bonds through π electron delocalisation.

Knobloch and Rauscher (116) have used various techniques to prepare coordination polymers; they prepared quinizarin (1,4-dihydroxyanthraquinone) complex of copper (II) using an aqueous solution of $Cu(NH_3)_4^{++}$ and quinizarin solution in benzene. Synthesis and characterisation of some polymeric transition metal chelates of quinizarin has been recently reported (117).

Studies on the thermal and spectral properties of some polymeric chelates of chloranilic acid (2,5-didroxy-3,6-dichloro-1,4-benzoquinone) rhodizonic acid and 2,3,5,6-tetrahydroxyparabenzoquinone were also reported (118). The chelate of chloranilic acid is thermally much more stable than those of rhodizonic acid and of tetrahydroxyquinone. The lowest lying carbonyl peak in the infrared spectra of these complexes was also found for the chloranilic acid chelate and this was attributed to the inductive effect due to the steric hindrance of the chloride ions.

Coble and Holtzclaw have studied the thermal stability of polymeric copper(II) chelates of 2,5-dihydroxy-1, 4benzoquinone, 5,8-dihydroxy-1,4-naphthoquinone, 1,4-dihydroxy-anthraquinone, 1,5-dihydroxyanthraquinone, 1,2,5,8-tetrahydroxyanthraquinone and 6,11-dihydroxynaphthoquinone (35). The compounds were prepared under similar conditions and the relative thermal stabilities were determined by differential thermal analysis. The thermal stability is not related to thermodynamic stability as indicated by the shift in carbonyl absorption frequency, but is almost found to be a linear function of the number of fused rings in the ligand portion of the chelate.

1.5.3. Applications of coordination polymers

It has long been known that coordination polymers have got some applications in industrial processes. Tanning of leather, which is an ancient art depends on the coordination of metal ions with the polypeptides of the hide(112). The complexes which are thus formed are more resistant to bacterial attack,weather and wear than the original hide.

Coordination polymerisation is involved in the formation of a water repellent basic chromic stearate, basic chromic acrylate and an analogous hydrophobic, and oleophobic perflourocarboxylate. The monomers of these substances are soluble in alcohol and they are applied to the surfaces to be protected. When the material is heated, a strong protection of the coordination polymer is formed on the surface of the material (112).

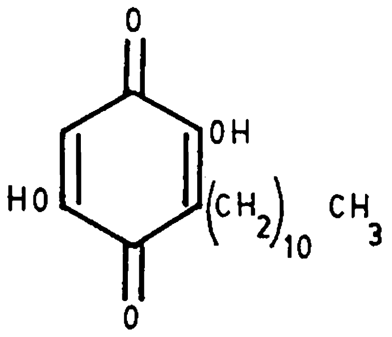
Other applications include the use of coordination polymers as viscosity stabilizers for oil and grease thickeners, as antistatic agents and also as corrosion resistant coatings for metals (112). Chelating resins with multi-dentate ligands in the polymeric matrix are used as metal ion collectors in the field of environmental chemistry. In view of this application, preparation and chelating properties of polymeric and matrix bound ligands have been reported (119,120). Corley has patented the application of coordination polymers as a combustion modifier for propellants and it has been reported that the burning rate of a propellant is increased by the addition of a certain amount of the copper complex of 2,5-dihydroxy-1,4-benzoquinone to the propellant(121).

Catalytic applications of the coordination polymers are also receiving considerable importance in industrial processes. It has long been known that the chemistry of the adsorbed molecules and the chemistry of coordination compounds are intimately related. Several examples can be cited to illustrate the use of transition metal complexes as catalysts for several conversions (13,14). Coordination polymers are finding use in heterogenising homogeneous catalysts. If a homogeneous catalyst is attached to a polymer which is insoluble in the reaction medium, it may still retain the selectivity of the homogeneous catalyst, but like other heterogeneous catalysts, it can be recovered readily by filtration. Catalysts bound to polymers do not loose selectivity and in some cases are more active than the parent homogeneous catalyst. Polymeric rhodium carbonyl complexes are effective and highly selective in the hydroformylation of olefins(112). Bruner and Bailar used polymeric diphenylbenzylphosphine polymer with coordinated platinum(II) chloride or palladium(II) chloride in the selective hydrogenation of olefins (122).

In the Wacker process, the oxidation of ethylene to acetaldehyde in aqueous media is catalysed by a solution containing palladium(II) chloride and copper(II) chloride. Nevertheless, organic quinone polymers containing sulfonic acid functional groups combined with palladium(II) were found to function as heterogeneous catalysts for the oxidation of ethylene to acetaldehyde without any co-catalyst such as coper(II) chloride(123).

1.6. A Brief Review of the Constitution, Biological Aspects and Analytical Applications of Embelin.

Embelin (2,5-dihydroxy-3-undecyl-2,5-cyclohexadiene-1,4-dione), an orange pigment isolated from the berries of the Indian shrub Embelia ribes is of great medicinal importance because of its anthelmintic properties(124). In Bengali and Sanskrit Embelia ribes is known as 'Vidanga', as 'Baberang' in Hindustani and as 'Vizhalari' in Malayalam. Charaka recommended the use of the berries of Embelia ribes in dyspepsia, flatulence, gripes etc; Hakkims regarded it as an anthelmintic, particularly for the expulsion of tape worms (125).



EMBELIN

Embelia ribes is a large scandent shrub growing mainly in the valleys of the Vindhya hills. It bears fruit towards the end of autumn. The fruit is intense pink in colour and globular in shape. On drying, it becomes shrivelled up and the colour changes to dark brown.

Heffter and Feuerstein (126) showed that natural embelin contained a side chain $C_{11}H_{23}$ as they were able to isolate n-lauric acid by oxidation. They also prepared a dibenzoyl derivative and showed that embelin condensed with primary amines in the same way as did benzoquinone. Fieser and Chamberlin (124) synthesised embelin using lauryl peroxide for the alkylation of 2,5-dihydroxy-1,4-benzoquinone and compared its properties with pure natural embelin. Constitution and preparations were also studied in detail by Kaul et al. (125). The embelin content in embelia ribes was estimated after extracting it with solvent ether. The crude embelin thus obtained as such or after some purification was subjected to chemical analysis by gravimetric or colorimetric techniques. Sarin and Ray estimated embelin in embelia ribes based on a colour reaction between aniline and embelin (127). Bheema Sankara Rao and Venkateswarlu (128) estimated embelin after precipitating it as Vilangin (2,5-dihydroxy-4-undecyl-3,6-benzoquinone) using 5% formaldehyde solution in methylalcohol. On an average, the embelin content in the berries was found to be ~ 2.5%.

1.6.1. Biological studies on embelin

Quinones and their substituted derivatives have long been known to possess numerous chemically and biologically significant properties with many important applications in several areas (129-131). The quinoid metabolites are found to inhibit the growth and metabolism of a range of bacterial genera and it has been reported that the antibiotic activity of 2,5-dihydroxy-1,4-benzoquinone derivatives depends on the nature of substituents at the 3 and 6 positions (132). Hence some of these biological activities could also be expected in the case of embelin.

The biological aspects and medicinal importance of embelin have received much attention during the last few years. Antifertility activity of embelia ribes have been studied by Krishnaswami _et al_. (133,134). The effect of embelin was tested in rats for estrogenic and anti-estrogenic activities. Embelin dosage upto 100 mg/kg did not increase or decrease any of the estrogen sensitive parameters like uterine weight, uterine glycogen and uterine alkali phosphatase levels. Dixit and Khanna (135) have patented the isolation of embelin as a male antifertility drug. Phosphatase activity in the testis and prostate of rats dosed with embelin were studied by Chawhan and Agarwal (136). The acid and alkali phosphatase levels in rats were elevated on administering embelin. Biochemical changes in the uterus and cervix of rats treated with embelin have been investigated (137).

The analgesic activity of embelin was studied in rats and mice (138). Embelin was shown to exhibit an activity entirely different from other opiates. There was no precipitation of abstinence syndrome as observed with morphine. A peripheral site of action of the drug is ruled out, as it lacks any demonstrable antiinflammatory action. The high oral efficacy and nonnarcotic property of embelin is expected to make it more acceptable than morphine. Effect of embelin on the germination rates of maize (or corn) and cowpea were also investigated (139). Embelin reduced the germination rates of corn and cowpea at 100 ppm and 250 ppm levels and stimulated germination at 50 ppm level. Data on respiratory rate and catalase activity indicate that such compounds inhibit respiration rates.

1.6.2. Analytical applications of embelin

The use of embelin as an analytical reagent for the precipitation and separation of various metals has been reported by Venkateswarlu and Bheema Sankara Rao (140-142). However, information regarding actual composition and stereochemistry of the complexes with some divalent metal ions has been reported only very recently (101).

The formation of water insoluble chelate complexes of embelin with many metals under suitable pH conditions have been observed (140). Most of the divalent metal ions form 1:1 complexes.

Complexes of uranium and thorium and their separation using embelin were also investigated (141a). Embelin precipitated uranium (VI) at pH 6.5 and thorium (IV) from a 0.3 to 0.4N HCl solution. Both the precipitates were ignited to oxides for weighing. Thorium(IV) can be separated from uranium (VI), rare earths and some other divalent metal ions using this method. Titanium and iron showed interference in the determinations.

Separation of aluminium and beryllium and their estimations were also reported (141b). Aluminium was precipitated with an alcoholic solution of embelin at pH 4 to 4.5. The precipitate was filtered, ignited and weighed as Al_2O_3 ~~Be~~O. Since the beryllium complex is soluble in alcohol, the removal of excess alcohol by boiling was suggested.

Estimation of copper and cadmium and their separation have also been studied (142). Copper(II) was separated from cadmium(II) by its precipitation with embelin at pH 2.5-3.0. Cadmium(II) precipitates at pH 6.0 - 6.5. Precipitation of divalent calcium, barium,, strontium and magnesium using embelin were also carried out under controlled pH conditions using ammonium acetate-acetic acid buffer (141c).

1.7. Coordination of Metal Ions with Biologically Important Ligands.

Our studies are mainly centered on the coordination behaviour of various metal ions towards embelin. Embelin is quite well known for its anthelmintic, antifertilitic and analgesic activities. Therefore, a brief discussion on biologically active ligands as well as their metal complexes would not be out of place in the present context.

1.7.1. Metal ions in living systems.

Transition metal ions in biological systems is receiving increasing attention, because of its wide application in the field of biochemistry and medicine(2,3,143). Metalloproteins are intimately involved in several metabolic processes. Binding sites on proteins have some chelation character, and stability is gained through coordination with a metal ion (143). The iron containing proteins hemoglobin, myoglobin, chlorocruorin and hemrythrin are associated with oxygen carriage. Oxygen utilisation in living systems is catalysed by cytochrome-c-oxidase which contains two iron atoms bound in a heme unit [an iron(II) porphyrin] and two copper atoms. Chlorophyll, participating in photosynthesis, is a magnesium(II) porphyrin ring system. Vitamin B_{12} or cyanocobalamin is involved in the reduction of organic species. It also helps the acceptance of a methyl group and its transfer in the biosynthesis of methionine which in turn is involved in trans methylation reactions in biosynthesis (3). The enzyme system nitrogenase in plants is known to contain both iron and molybdenum. It has been reported that the molecular nitrogen forms a dinitrogen complex with one of these metals and other serves as an electron source leading to the eventual reduction of nitrogen to ammonia (144). The discovery that molecular nitrogen was capable of forming stable complexes with transition metals led to extensive investigation of the possibility of nitrogen fixation <u>via</u> such complexes (3).

1.7.2. Metal ions and chelating agents in medicine.

Role of chelating agents in medicine has been discussed in detail by Hughes (145) and Perrin (146). An excess of highly toxic metal ion in the living system can be removed using a chelating agent. Certain drugs are good ligands which may bind with the native metal ions. Excessive calcium deposits resulting in the formation of stones can be treated with EDTA. Chelating agents can seek out toxic metal ions to bind and excrete them as complexes, they may deliver the essential trace elements to tissues that require them. The most important complex forming species in animal and plant tissues are amino acids, peptides, carboxylic acids, phosphates and the mercapto, dithio, amino, imidazole, phenolic and free carboxyl groups of proteins. The toxic effects of heavy metal ions are due to their strong complexing ability towards these active complexing groups on tissues. Hence a suitable chelating agent, more powerful than these groups is administered to remove the toxic cations. Chelated drugs are also finding application in the treatment of various diseases. The use of chelated drugs could represent a better route of administration associated with smaller risk of toxic effects (145,146). The copper dependence of rheumatoid arthritis is well established (147,148) and the observation that copper complexes involving anti-inflammatory drugs can be more effective and involve less gastrointestinal irritations than the free drug (149) has stimulated a great deal of investigations involving drug complexation(150). A physiological approach to treatment of inflammatory diseases using copper complexes has been given by Sorenson et al (151). Ligands such as anthranilic acid is inactive, but their copper complexes are found to be potent anti-inflammatory agents. Aspirin and D-pencillamine are also known to have therapeutic applications in rheumatoid arthritis (148,152). Nevertheless, their coper complexes are more effective than the free drugs lending credence to the hypothesis that the active metabolites of anti-arthritic drugs are their copper complexes (151). The antibiotic action of tetracyclines is related to the ability of these compounds to form complexes with metal ions (145,153,154). Antifungal activity of thiosemicarbazones has been found to increase on complexing with transition metals (155).

1.7.3. Structural studies on chelated drugs

It is quite wellknown that metal complexes of ligands which have biological activity are more active than the free ligands (156,157). The study of stereochemistries and the chemical reactivity of the coordination compounds of the drugs will help to determine the nature and extent of the relationships existing between the chemical structure and biological activity (158).

Studies on complex formation of antibiotics (as ligands) such as cycloserine, 4-aminoisoxazolidin-3-one (159-161) and its derivative N_4,N_4'-terephthal-bis-cycloserine (162) have been reported. Harrison *et al.* have studied the complexes of iron(III), cobalt(II), nickel(II), copper(II) and zinc(II) with an antiinflammatory drug azapropazone(163). The preparation, characterisation and anti-tumour activity of some metal(II) chelates of 4-(m-aminophenyl)-2-formylpyridine thiosemicarbazone has been reported (164).

Complexes of manganese(III), iron(II), nickel(II), copper(II) and zinc(II) with Schiff bases of N,N-diethyl~~diamino~~dithiocarbamates were prepared and characterised to study the effect of antifungal and antibacterial activities upon complexation,(165). Similar investigations on structural and biological aspects were also reported for the metal complexes with dicamba (166) and alkyl pyrazines (167). Pyrazine is a constituent of plants like Cocoa and Coffee.

Sarkar and Ghosh (168) have studied the complexes of uracil with manganese(II), iron(II), cobalt(II), nickel(II) and copper(II). Octahedral geometry is proposed for the complexes. Uracil is a constituent of RNA in biological system. Spectral and magnetic studies were carried out on some complexes of pyrazole derived carbohydrazide, a potential ligand of biological importance (169). Metal complexes of antiinflammatory drugs have also been investigated recently(170,171). In view of the above mentioned merits of the structural studies on chelated drugs, we are anticipating the role of metal complexes of embelin to function as possible basis for further studies on its medicinal properties. Very little is known on the behaviour of embelin towards transition metal ions. Hence, a systematic study on the metal complexes of embelin is warranted and it is expected that the investigation reported herein would help provide a better insight into the relevant role of metal complexes in biological systems.

CHAPTER 2

MATERIALS AND METHODS

Included in this chapter is a brief description of the reagents and the procedure employed for the preparation of the ligand as well as details of the physicochemical techniques used for structure elucidation. Details regarding the preparation of the transition metal,lanthanide and actinide complexes are given in the respective chapters (i.e. chapter 3 and chapter 4).

2.1. Reagents

2.1.1. Divalent metal salts.

The following divalent metal acetates were used.

$Mn(CH_3COO)_2.4H_2O$ (BDH, AR); $Ni(CH_3COO)_2.4H_2O$ (Merck, GR);
$Co(CH_3COO)_2.4H_2O$ (Merck, GR); $Cu(CH_3COO)_2.H_2O$ (Merck, GR);
$Zn(CH_3COO)_2.2H_2O$ (BDH, AR); $Cd(CH_3COO)_2.2H_2O$ (BDH, AR)

2.1.2. Trivalent metal salts

Chromium (III) hydroxide was precipitated out from an aqueous solution of chromium(III) nitrate($Cr(NO)_3.9H_2O$) by the dropwise addition of ammonia solution at pH 6 - 6.5. The precipitate was filtered, thoroughly washed to remove impurities and then dissolved in slight excess of acetic acid. Chromium(III) acetate, which crystallised out from this solution was filtered and dried in a vacuum desiccator over P_4O_{10}(172).

Iron(III) acetate was prepared by dissolving pure iron powder in excess of acetic acid. Air was blown through this solution at room temperature continuously for 24 hours. Evaporation of the filtrate yielded crystals of iron(III) acetate which were dried in a vacuum desiccator over P_4O_{10} (172).

2.1.3. Lanthanide salts

Acetates of lanthanum(III), praseodymium(III),neodymium(III), samarium(III), gadolinium(III), and dysprosium(III) used in the present investigation were prepared from the respective rare earth oxides (99.99% pure) obtained from M/s. Indian Rare Earths Ltd., Udyogamandal. This factory processes the mineral monazite available among the beach sands along the south west coast of India. The following individual rare earth oxides were purchased from the factory: La_2O_3, Pr_6O_{11}, Nd_2O_3, Sm_2O_3, Gd_2O_3 and Dy_2O_3. Since these oxides were only poorly soluble in acetic acid, the following method was used to prepare lanthanide acetates. Starting from these oxides, the respective lanthanide nitrates were prepared by dissolving a slight excess of the oxides in concentrated nitric acid. The undissolved oxides were filtered off. The respective rare earth carbonates were then precipitated out from these nitrate solutions using ammonium carbonate solution(5%w/v). The precipitates were filtered off, washed thoroughly to remove any adhering impurities. They were then dissolved in acetic acid, filtered, and the respective lanthanide acetates were crystallised out from these filtrates by evaporation. The crystals were filtered and dried in a vacuum desiccator over P_4O_{10}.

2.1.4. Yttrium salt

Y_2O_3 (99.99% pure) was purchased from M/s. Indian Rare Earths Ltd., Udyogamandal. Yttrium(III) acetate was prepared by a procedure exactly similar to that described for the lanthanide acetates.

2.1.5. Actinide salts

Only two actinides were used in the present study. Thorium nitrate (99.9% pure) was obtained as a gift from the Thorium Plant at Bombay of M/s. Indian Rare Earths Ltd.

Uranyl nitrate $UO_2(NO_3)_2.6H_2O$ was a BDH reagent (A.R. grade).

2.1.6. Solvents

Ethanol: Commercial ethanol was purified by standard procedures(173).

Diethyl ether: BDH samples of diethyl ether were used as such.

Petroleum ether (60-80 °C): BDH samples of petroleum ether (60-80 °C) were used as such.

2.2. Preparation of the Ligand

Pure natural embelin was prepared by the method of Fieser and Chamberlin (124). The sun-dried berries of embelia ribes were partially crushed and the outershell removed. These berries were extracted with solvent ether in a soxhlet apparatus. The crude embelin thus isolated was purified by defatting twice with petroleum ether (60-80 °C) and recrystallising twice from absolute alcohol. Pure embelin (mp 142 °C) was obtained in 2% yield.

2.3. Analysis of the Complexes

The complexes were decomposed with a mixture of concentrated hydrochloric-, nitric-, and perchloric acids in the ratio 3:1:1 and the metal content in the manganese, cobalt, copper, zinc and cadmium complexes were analysed volumetrically using EDTA and that in the nickel complex was determined gravimetrically (174). Chromium and iron contents were estimated by atomic absorption spectrophotometry (Instrumental Laboratories model 751). The lanthanide metals and thorium in the complexes were determined gravimetrically by the standard oxalate procedure, while uranium was estimated gravimetrically as the oxinate (174-176).

Carbon and hydrogen analyses of the metal complexes were carried at the micro analytical laboratory of National Chemical Laboratory, Pune and the modular laboratories of Bhabha Atomic Research Centre, Trombay.

2.4. Physicochemical Methods

2.4.1. Magnetic measurements

Magnetic susceptibility measurements were carried out on finely powdered solid samples using a simple Gouy - type magnetic balance at room temperature(28 ± 2^{o}C). Gouy tubes were standardised using mercury tetrathiocyanatocobaltate(II) as the calibrant (177). Diamagnetic corrections using Pascal's constants were applied by adding the diamagnetic contributions of various atoms and structural units (4,5).

2.4.2. Electronic spectra

Electronic spectra of the complexes in the region 200-900nm were recorded in the solid state by a mull technique following a procedure recommended by Venanzi (178) using a Hitachi 220 model recording spectrophotometer. Small filter paper strips were impregnated with a paste of the sample in Nujol mull and were placed at the entrance to the photocell housing. Nujol treated filter paper strip was used as the blank. Solid state spectra of cobalt(II) and chromium(III) complexes in the range 200 - 2000 nm were recorded on a Hitachi uv, visible, near infrared spectrophotometer.

2.4.3. Infrared spectra

The infrared spectra of the complexes (KBr disc or Nujol mull) were recorded either on a Perkin Elmer 397 or on a Beckman Acculab 7 infrared spectrophotometer.

2.4.4. Thermal analyses

Simultaneous TG-DTA of the samples were carried out under static air conditions, either on a Stanton Redcroft TR-OI thermobalance or on a Derivatograph (Mom OD-102 model) using 50 or 100 mg of finely powdered samples at a heating rate of 8 ^{o}C/min. Finely powdered α-alumina was used as the reference substance.

CHAPTER 3

COMPLEXES OF EMBELIN WITH SOME TRANSITION METALS

3.1. Complexes with Some Divalent 3d-Metals

Studies on the analytical application of embelin have led to the isolation of some of its divalent metal complexes (140-142). These studies relate mainly to the estimation of metal ions using conventional precipitation techniques. Different pH conditions were used to separate the various metal ions. However, the validity and significance of these methods for the quantitative estimation of metal ions are yet to be examined. Furthermore, the polymeric nature and the presence of coordinated water molecules, usually observed for the chelates with several hydroxyquinoid ligands, are expected to give only lower values for the metal content during analytical estimations (34).

The infrared spectra and thermal behaviour of the divalent metal complexes of 2,5-dihydroxy-1,4-benzoquinone have been studied by several authors (34,35). However, attempts to establish their stereochemistries on the basis of magnetic and electronic spectral data have not been reported so far. Complexes of embelin with manganese(II), cobalt(II), nickel(II), copper(II), zinc(II) and cadmium(II) have been synthesised and characterised by elemental analysis, spectral (infrared and electronic), thermal and magnetic studies.

3.1.1. Experimental

Materials

The divalent metal salts used for preparation of the complexes are listed in Chapter 2. Preparation of the ligand is also described there.

Preparation of the complexes

Aqueous ethanolic solutions of the corresponding metal acetates and ethanolic solutions of the ligand in 1:1 molar ratio (with the metal salt in slight excess) were mixed together and refluxed on a water bath for 20-30 minutes.The metal complexes precipitated out were filtered and washed repeatedly with aqueous ethanol to remove excess metal ions. The complexes were dried in vacuum over P_4O_{10}.

Characterisation

Elemental analysis and physical measurements were carried out by the methods described in Chapter 2. As the complexes were found to be insoluble in most of the common organic solvents, conductance measurements could not be carried out. The complexes were insoluble in camphor and biphenyl and hence molecular weight determinations too(by Rast's method) could not be carried out .

3.1.2. Results and Discussion

All the divalent metal complexes of embelin precipitated immediately on mixing the respective solutions containing the ligand and metal ions. The Copper(II) complex of embelin is formed as a green precipitate in the reaction medium, but immediately changes to brownish black,probably due to distortions leading to the transformation from a six-coordinated to a four-coordinated geometry. Colours of all other metal complexes remained the same throughout the preparation.

Analytical data (Table 1) indicate a metal to ligand ratio of 1:1 for all the complexes. All of them except the copper(II) complex contain water as a part of the coordination sphere.

The insolubility of the complexes in most of the common organic solvents indicates a polymeric nature. All the complexes are mildly hygroscopic and hence the experimentally determined values of the metal content (Table 1) are slightly lower than those theoretically expected for a 1:1 complex. Such variations in analytical data were also observed earlier for the metal complexes of 2,5-dihydroxy-1,4-benzoquinone(34).

Infrared spectra

The important infrared frequencies of the ligand and of the metal complexes are presented in Table 2. The O-H stretching frequency is observed as a strong band at 3300 cm^{-1} for embelin. The disappearance of this band in the spectra of all the complexes indicates that phenolic hydrogens present in the ligand molecule are lost on chelation. Changes in the spectra caused by the participation of phenolic oxygen in coordination have been observed for several other complexes (34,35).

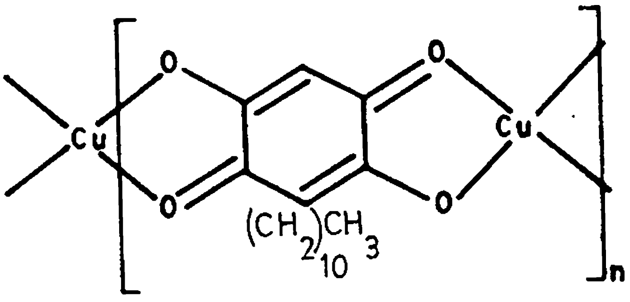
The broad medium intense peak occurring between 3300 and 3400 cm^{-1} in the spectra of manganese(II), cobalt(II), nickel(II), zinc(II), and cadmium(II) may be attributed to the O-H stretching frequency of coordinated water molecules. The O-H bending frquency is observed as a weak band at 1650 cm^{-1} for manganese(II), cobalt(II), nickel(II), zinc(II) and cadmium(II) complexes. Both these bands are absent in the spectrum of copper(II) complex indicating the absence of any water molecules. Vibrational bands in the 880-650 cm^{-1} region, characteristic of coordinated water molecules (179) could not be located owing to strong ligand absorptions in this region.

The carbonyl stretching frequency is observed as a strong peak at 1610 cm^{-1} for embelin. Upon complexation, this has been found to be shifted to 1520 cm^{-1} in the spectra of manganese(II), cobalt(II), nickel(II), zinc(II), and cadmium(II), and to 1460 cm^{-1} in the case of the copper(II) complex. The copper(II) complex of 2,5-dihydroxy-1,4-benzoquinone is known to exhibit a similar enhanced shift for the carbonyl stretching frequency (34). The absence of any absorption in the carbonyl region on the high frequency side of the uncomplexed carbonyl band is a confirmatory evidence for oxygen coordination (8).

The amount of shifting of the carbonyl frequency is generally regarded as an indication of the metal-oxygen bond strength. The lowering of the carbonyl group frequency, upon coordination, has been compared for the chelate polymers of various dihydroxyquinoid ligands(35). The copper(II) complex of 2,5-dihydroxy-1,4-benzoquinone exhibited the lowest lying carbonyl group frequency among this group.

The copper(II) complex of embelin showed a shift in ν C=O by ~ 150 cm^{-1} whereas for other metal complexes, it is lowered only by 90 cm^{-1} and hence this complex can be regarded as having the maximum strength for its metal-oxygen bond.

On the basis of the observed infrared spectral bands, embelin could be regarded to act as a tetradentate ligand coordinating through its carbonyl and phenolic oxygens as indicated below.



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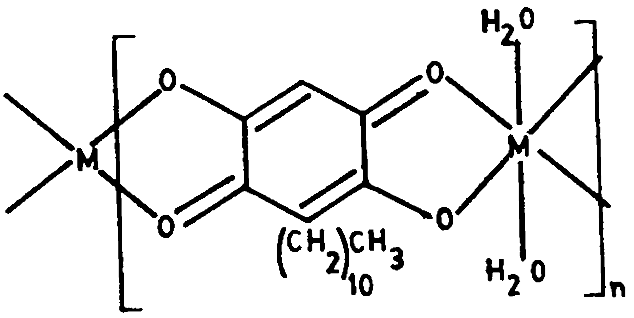


M= Mn,Co,Ni,Zn or Cd.

Magnetic behaviour

The magnetic susceptibilities were determined by the Gouy method at ambient temperature (28 ± 2 °C). The room temperature magnetic moments of the complexes are presented in Table 2.

Manganese(II) complex

The room temperature magnetic moment of 5.84 B.M. for the manganese(II) complex is very close to the spin only value of 5.92 B.M. Compounds of divalent manganese are known in both high spin(S = 5/2) and low spin(S = 1/2) configurations. The high spin compounds are expected to exhibit magnetic moments very close to the spin only value for a d^5 ion, independent of temperature and irrespective of whether the ligand arrangement is of octahedral, tetrahedral or lower symmetry (4). Room temperature magnetic moments in the range 5.7-6.0 B.M. for a large number of octahedrally coordinated manganese(II) complexes have been reported (180). Hence the observed moment of 5.84 B.M. indicates an octahedral environment for the metal ion.

Cobalt(II) complex

The magnetic moment of the cobalt(II) complex is 5.6 B.M. and is much higher as compared to the spin only value of 3.89 B.M for 3 unpaired electrons. In high spin octahedral cobalt(II) complexes,(a d^7 ion), a large orbital contribution to the magnetic moment is expected, because of the three fold orbital degeneracy of the $^4T_{1g}$ ground state. Mixing of a singlet excited state lowers the moment but generally values ranging from 4.7-5.2 B.M. are expected (4,5). Moments lower than 5.2 B.M. may result if the symmetry of the ligand field departs from octahedral. Magnetic moments in the range 4.7 to 5.9 B.M. have been reported for several octahedral cobalt(II) complexes(4). Thus it seems quite probable for the $[Co(em)(H_2O)_2]$ to have an octahedrally coordinted cobalt(II) ion with a large orbital contribution from the ground state.

Nickel(II) complex

The nickel(II) complex has a μeff value of 3.2 B.M. and is higher than the spin only value of 2.83 B.M. for three unpaired electrons.In an octahedral field the d orbitals are split up into a doublet, e_g and a triplet, t_{2g} and the d^8 ion has a ground state electronic configuration of $t_{2g}^6 e_g^2$. The two e_g electrons are spin parallel and since there is no resultant orbital angular momentum, once the degeneracy of the d orbitals is lifted, μeff should be close to the spin only value of 2.83 B.M. However, the first excited triplet level $^3T_{2g}$ has essentially the configuration $t_{2g}^5e_g^3$; there are three possible ways of arranging the five t_{2g} electrons and the d_{yz} and d_{zx} orbitals retain their rotational properties with respect to the Z-axis. This level has therefore orbital angular momentum and the spin orbital coupling of nickel(II) is large enough to allow mixing of this level with the lowest level to produce the true ground state. The effective result is that the orbital angular momentum is not completely quenched by the ligand field, and magnetic moments normally found for the octahedral complexes of nickel(II) are in the range 3.0-3.3 B.M. (181). In tetrahedral fields, however large orbital contribution to the magnetic moment is expected, because of the three fold degeneracy of the $^3T_1$ ground state. Magnetic moments in the range 3.7-4.1 B.M. are frequently observed for the tetrahedral complexes of nickel(II) (2). Square planar complexes of nickel(II) are usually diamagnetic. The observed moment of 3.2 B.M. thus suggests the presence of an octahedrally coordinated nickel(II) ion with an orbital contribution arising from the second order process.

Copper(II) complex

The observed room temperature moment of the copper complex of embelin is 2.12 B.M. Magnetic moments, strictly, can not be used to distinguish between the stereochemistries of copper(II) complexes. Distortions in d^9 system are especially subjected to Jahn-Teller effects and copper(II) complexes in general have μeff. values ranging between 1.75-2.2 B.M. Nevertheless, lower magnetic moments (1.93 B.M.) are frequently attributed to square planar configurations(4). Although a room temperature moment of 2.2 B.M. has been predicted for copper(II) in a tetrahedral environment(182), distortions can appreciably lower it if the low symmetry ligand fields produced are large compared to spin orbit coupling (4). Magnetic behaviour of several pseudo-tetrahedral complexes have been investigated (183-185). Dependence of magnetic moment values on distortions from planar structure has been discussed by Gruber and co-workers (186). The room temperature magnetic moment of some bi - and tri-nuclear copper complexes of tetradentate salicylaldimines were shown to have an increasing trend towards higher values with an increasing distortion away from planar configuration. This trend is compatible also with the increasing -N--R--N-- chain length (ie. the length of the carbon chain(R) joining the adjacent nitrogen atoms in the Schiff base ligand) and is also expected from the steric requirement of the ligands.

Since tetrahedral distortions are expected to lead to increased magnetic moments, the observed μeff. value of 2.12 B.M. supports a tetrahedrally distorted planar stereochemistry for the copper complex of embelin. Furthermore, the steric hindrance caused by the bulky embelin molecules is expected to favour such distortions from planar configuration.

Zinc(II) and cadmium(II) complexes

Zinc(II) and cadmium(II) complexes of embelin were found to be diamagnetic as expected for complexes with a d^{10} configuration.

Electronic spectra

Absorption maxima for the observed spectral bands of the complexes are given in Table 2. Ligand absorption and charge transfer transitions complicate the assignment of bands observed in the ultraviolet region.

Manganese(II) complex

For a manganese(II) ion (d^5 ion), the free ion ground state term ^6S becomes ^6A in a weak ligand field. All the excited states of this d^5 ion have different spin multiplicities.

The absence of any other sextet term implies that all the ligand field transitions from $^6A_1$ ground term are spin-forbidden as well as Laporte-forbidden. Hence the d-d transitions of manganese(II) complexes have very low intensities (6). The observed bands of manganese(II) complex of embelin are very weak and they indicate the following transitions. The band at 19230 cm^{-1} could be assigned to the $^6A_{1g} \longrightarrow {}^4T_{2g}$(G) transition and that at 23800 cm^{-1} to the $^6A_{1g} \longrightarrow {}^4E_g$ (G), $^6A_{1g} \longrightarrow {}^4A_{1g}$(G) doublet. The $^6A_{1g} \longrightarrow {}^4T_{1g}$(G) transition, expected around 17000 cm^{-1} is probably obscured by the fairly strong ligand absorption at ~ 17800 cm-1. The observed spectral bands of manganese(II) complex and their assignments thus suggest an octahedral symmetry (6,187).

Cobalt(II) complex

Cobalt(II) is a d^7 ion with a ^4F ground state. Under the influence of an octahedral field the ^4F ground state will be split into $^4T_{1g}$ ground state and into $^4T_{2g}$ and $^4A_{2g}$ excited states. The spin allowed transitions from the ground state $^4T_{1g}$(F) are those to the $^4A_{2g}$(F), $^4T_{2g}$(F) and $^4T_{1g}$(P). The visible region of the absorption spectrum of cobalt(II) is generally dominated by the highest energy transition $^4T_{1g}$(F)

$\longrightarrow {}^4T_{1g}(P)$ for the octahedral complexes. Since the ground state ${}^4T_{1g}(F)$ is derived mainly from a $t_{2g}^5\ e_g^2$ electronic configuration and the excited state ${}^4A_{2g}$ is derived from a $t_{2g}^3\ e_g^4$ configuration, the ${}^4T_{1g}(F) \longrightarrow {}^4A_{2g}$ transition is essentially a two electron process and for this reason it should be weaker than all other transitions. Further more this transition is usually very close to the transition ${}^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P)$ and hence results in the transition being mostly unobserved (2). The observed band at 8300 cm^{-1} for cobalt(II) complex of embelin could be attributed to the transition ${}^4T_{1g}(F) \longrightarrow {}^4T_{2g}(F)$ and the absorption band at 20400 cm^{-1} may be due to the ${}^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P)$ transition. Interpretation of the other two weak bands observed in the visible region (at 15380 cm^{-1} and 17540 cm^{-1}) of the spectrum are complicated. It is not quite clear whether these bands are due to vibrational phenomena, spin orbit coupling, low symmetry splitting of the ${}^4T_{1g}(P)$ term, transitions to the ${}^4A_{2g}$ level or transitions to the doublet states, derived from the free ion ${}^2G$ and ${}^2H$ terms. Similar complications in the spectral assignments, frequently observed for the cobalt(II) complexes, are discussed in detail by Lever (6). However, on the basis of the observed bands for the highest and lowest energy transitions, cobalt(II) complex of embelin could be envisaged to have a octahedral geometry (7,188,168).

Nickel(II) complex

The absorption bands for the nickel(II) complex in the visible region of the spectrum are observed at 17240 cm^{-1} and 25000 cm^{-1} and are assigned to the spin allowed transitions $^3A_{2g}(F) \longrightarrow {}^3T_{1g}(F)$ and $^3A_{2g}(F) \longrightarrow {}^3T_{1g}(P)$ respectively. This is in conformity with the expected d-d transitions for octahedrally coordinated nickel(II) complexes (2). Spectral assignments of the absorption bands in the visible region for several other octahedral nickel(II) complexes have been reported (6,7).

Copper(II) complex

In the case of the copper(II) complex, the d-d transition bands are seen to undergo a red shift and are located at 11460 cm^{-1} and 14700 cm^{-1} and an asymmetric and weak ligand field band is observed at 20000 cm^{-1}. This suggests a tetrahedrally distorted planar configuration, especially in view of the steric hindrance caused by the bulky embelin molecules. Copper complexes with other bulky ligands too have been known to exhibit similar spectral behaviour (189-191). The complexes of copper(II) with N-isopropyl and N-sec-butylsalicylideneamines have been established by X-ray measurements to possess a pseudotetrahedral structure in contrast with N-n-alkyl salicylideneamine complexes which are planar (17). Sacconi and Ciampolini examined the electronic spectra of a number of these complexes. They found that the planar complexes have a single broad band in the range 14000-16000 cm^{-1} whereas the pseudo-tetrahedral complexes have bands at ~ 8700-10000 cm^{-1} and at ~ 12800-13800 cm^{-1}. Gruber and co-workers have also reported the deviations from planar to tetrahedral symmetries for the bi-and tri-nuclear copper complexes of tetradentate salicylaldimines (186). It has been shown for some of these copper complexes, that increasing distortion from planar to tetrahedral symmetry causes a steady shift to lower energy (as -N--R--N-- chain length increases ie. as the length of the carbon chain joining the adjacent nitrogen atoms in the Schiff base ligand increases) of the main ligand field band which is near 17000 cm^{-1}. West and Hartley had also reported the red shift of the d-d bands for tetrahedrally distorted planar configurations of some copper(II) complexes (192-194). The bands observed in the ultraviolet region are mainly due to charge transfer transitions (195).

Zinc(II) and cadmium(II) complexes

Since no ligand field transition is expected for a d^{10} configuration, the observed bands in the spectrum of the zinc complex and cadmium complex are due to ligand absorptions and/or charge transfer transitions.

Thermal behaviour

Thermal studies on embelin as well as on the metal complexes of embelin were carried out under static air conditions. Thermoanalytical data obtained from simultaneous TG, DTG and DTA curves and independent pyrolysis are presented in Table 3. The TG, DTG and DTA curves of the ligand and complexes are presented in the figures 1-7.

The ligand embelin is found to decompose in four stages between 200°C and 680°C. 60% of the ligand decomposition takes place in three stages and is mainly endothermic in nature. The fourth stage in which the remaining 40% of the ligand decomposition takes place starts only after 470°C. The last stage of the ligand decomposition is exothermic in nature. The exotherm in the DTA of the ligand (~470°C) may be due to its oxidative decomposition and the endothermic effect (at ~ 265 ~ and 340°C) may be due to vaporisation with decomposition. 2,5-Dihydroxy-1,4-benzoquinone, a structurally similar ligand, is also known to exhibit such endothermic effects due to vaporisation with decomposition (35). Apart from these endothermic and exothermic decomposition stages of the ligand, an additional sharp endothermic peak which does not correspond to any weight loss in the thermogram is observed at 140 °C. This endotherm corresponds to melting of the ligand.

The thermograms of manganese(II), cobalt(II),zinc(II) and cadmium(II) complexes of embelin are largely similar and indicate two clear cut stages: the first corresponding to the dehydration of the coordinated water molecules and the second to the decomposition process. In the case of the nickel(II) complex, the dehydration step is seen to merge with the decomposition process resulting in a single extended stage. The temperature range for the dehydration step, in this case has, therefore, been deduced from the DTG curve and the percentage mass loss corresponding to this range has been attributed to the loss of water molecules. Slight variations in the experimental and theoretical values for the percentage mass loss during the dehydration of some of the complexes of embelin may be attributed to the presence of absorbed water. Such variations have been reported for other coordination polymers too (34,35). Copper(II) complex of embelin shows only a single decomposition stage, being devoid of any water molecules. Most of the copper(II) complexes of hydroxyquinoid ligands have been shown to decompose in a single stage because of their anhydrous nature (118).Dehydration peaks in the DTG for manganese(II) cobalt(II), nickel(II), zinc(II) and cadmium(II) complexes are paralleled by corresponding endothermic DTA peaks.

The procedural decomposition temperatures for the metal complexes of embelin were taken as those temperatures at which the decomposition of the ligand portion of the complex started after the dehydration stages. On the basis of procedural decomposition temperatures, the complexes are seen to follow the stability sequence Cd ~ Zn > Ni ~ Co > Mn > Cu. A similar order for the thermal stability has been observed for the coordination polymers of 2,5-dihydroxy-1,4-benzoquinone (34). Usually the stability order for metal complexes with various hydroxyquinoid ligands does not follow a regular pattern (102).

Several authors (35,118) have compared the thermal stability of the coordination polymers to their thermodynamic stability as indicated by the amount of shift in carbonyl frequency in the infrared spectra. The complex of embelin with copper(II) exhibits the lowest thermal stability among the group as indicated by the procedural decomposition temperature. However, the increased shift in carbonyl frequency of this complex suggests an increased stability which could also be related to the initial stability range of the complex in the

TG curve. A similar relationship for the stability has been reported for the copper(II) complexes of 2,5-dihydroxy-1,4-benzoquinone and 5,8-dihydroxynaphthoquinone (35). However, the copper(II) complex of 3,6-dichloro-2,5-dihydroxy-1,4-benzoquinone has been shown to exhibit the lowest lying carbonyl peak, but with the highest thermal stability among a group of metal complexes with the same ligand (118). The thermal stability and thermodynamic stability of the coordination polymers are not comparable in certain aspects. The extent of carbonyl peak shift is related to the metal-oxygen bond strength and consequently the breaking of metal-oxygen bond becomes a more important criteria for thermodynamic stability whereas it can be the breaking of the metal-oxygen bond or one of the several bonds within the ligand portion which determines the thermal stability (35).

It is quite well known that coordination increases the thermal stability of the ligand (105,106). On the basis of the procedural decomposition tempeeratures, metal complexes of embelin are also seen to exhibit similar enhanced thermal stabilities.

The thermal decomposition for all the metal complexes of embelin are completed at 500^{o}C (except Zn and Cd). Zinc(II) and cadmium(II) complexes require still higher temperatures for their complete decomposition. This seems quite reasonable, because zinc and cadmium have fixed oxidation states of two, while manganese, nickel, cobalt and copper have several oxidation states and could give rise to catalytic effects in the decomposition of their complexes. A similar explanation has been suggested to account for the unusual thermal stability of several thiopicolinamido chelate polymers of zinc as compared to those of copper and nickel (196).

Exothermicity of the decomposition peaks for metal complexes of embelin may be attributed to the concomitant oxidation reactions of the ligand. Final residues of the independent pyrolysis (upto 700 °C) of the complexes were subjected to chemical analyses (174), and were found to have metal contents corresponding to the compositions of Mn_2O_3, CoO, NiO, CuO, ZnO and CdO. The experimental values for the percentage mass loss from TG and independent pyrolysis after the final stage of decomposition are fairly comparable with the theoretically expected values.

Table 1

Analytical data of the divalent transition metal complexes of embelin.

Complexes	colour	% metal		% carbon		% hydrogen	
		found	calcd.	found	calcd.	found	calcd.
$[Mn(em)(H_2O)_2]$	grey	14.30	14.35	54.11	53.27	7.84	7.31
$[Co(em)(H_2O)_2]$	brownish black	14.95	15.23	53.26	52.72	7.68	7.23
$[Ni(em)(H_2O)_2]$	green	14.90	15.20	53.42	52.75	7.56	7.24
$[Cu(em)]$	brownish black	17.10	17.86	58.16	57.38	6.95	6.75
$[Zn(em)(H_2O)_2]$	bluish violet	15.70	16.60	52.55	51.86	7.58	7.12
$[Cd(em)(H_2O)_2]$	bluish violet	25.31	25.52	48.90	46.37	6.80	6.36

em = $C_{17}H_{24}O_4^{=}$

Table 2

<u>Magnetic and spectral data of embelin and its divalent transition metal complexes.</u>

Compound	μ_{eff}	electronic spectra	<u>assignments of important IR bands</u>				
	(B.M.)	max (cm^{-1})	νO - H phenolic (cm^{-1})	νO - H coord water (cm^{-1})	νO - H phenolic (cm^{-1})	νO - H coord water (cm-1)	νC = O (cm^{-1})
Embelin	--	17800 28570 33330	3300	--	1640	--	1610
$[Mn(em)(H_2O)_2]$	5.84	19230 23800 28570 33330	--	3400	--	1650	1520
$[Co(em)(H_2O)_2]$	5.90	8300 15380 17540 20400	--	3400	--	1650	1520
$[Ni(em)(H_2O)_2]$	3.20	17240 25000 33330	--	3400	--	1650	1520
$[Cu(em)]$	2.12	11460 14700 20000 22720 33330	--	--	--	--	1460
$[Zn(em)(H_2O)_2]$	--	16660 28570 33330	--	3400	--	1650	1520
$[Cd(em)(H_2O)_2]$	--	17200 30000 33330	--	3400	--	1650	1520

em = $C_{17}H_{24}O_4^{=}$

Thermo-analytical data of the divalent transition metal complexes of embelin

Complex	stability range in TG from ambient upto (°C)	pdt (°C)	peak temp. (°C)		dehydration and decomposition temp. ranges (°C)		% mass loss* from TG curve		% mass loss** from independent pyrolysis
			DTG	DTA	DTG	DTA	after dehydration	after final stage	
$[Mn(em)(H_2O)_2]$	170	260	210 395	220 endo 400 exo	170-250 260-500	160-250 endo 260-500 exo	8.85 (9.39)	79.4	79.39 (79.38)
$[Co(em)(H_2O)_2]$	140	270	180 340	180 endo 340 exo	140-220 270-560	140-220 endo 270-560 exo	10.00 (9.30)	81.02	81.18 (80.64)
$[Ni(em)(H_2O)_2]$	180	270	210 385	220 endo 400 exo	190-270 270-560	180-280 endo 280-550 exo	9.40 (9.30)	81.11	81.36 (80.68)
$[Cu(em)]$	250	250	350	360 exo	250-500	260-500 exo	-	76.91	77.90 (77.64)
$[Zn(em)(H_2O)_2]$	120	300	160 390	170 endo 400 exo	120-290 300-480	120-270 endo 290-550 exo	9.20 (9.15)	75.10	79.88 (79.30)
$[Cd(em)(H_2O)_2]$	200	300	230 425	220 endo 420 exo	200-300 300-600	200-300 endo 300-600 exo	8.30 (8.17)	64.03	71.12 (70.80)

* theoretical value in parenthesis.

** theoretical value based on metal oxide composition in parenthesis.

pdt - procedural decomposition temperature.

em = $C_{17}H_{24}O_4$

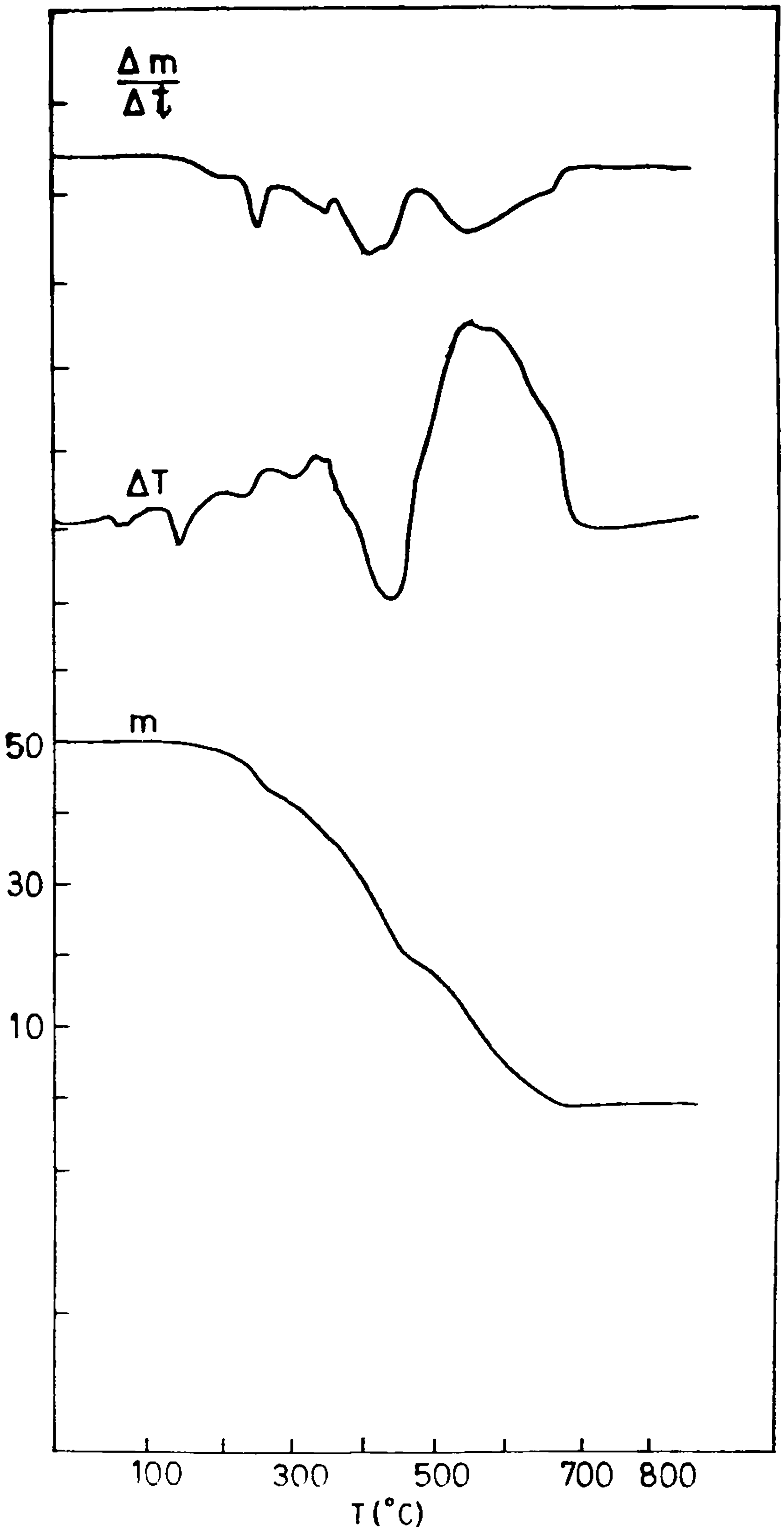


Fig.1. TG, DTG and DTA curves of embelin

m = mass of the sample remaining in the crucible (mg)

$\frac{\Delta m}{\Delta t}$ = change of mass with respect to time mg. min^{-1}

ΔT = differential temperature (°C)

T = temperature (°C)

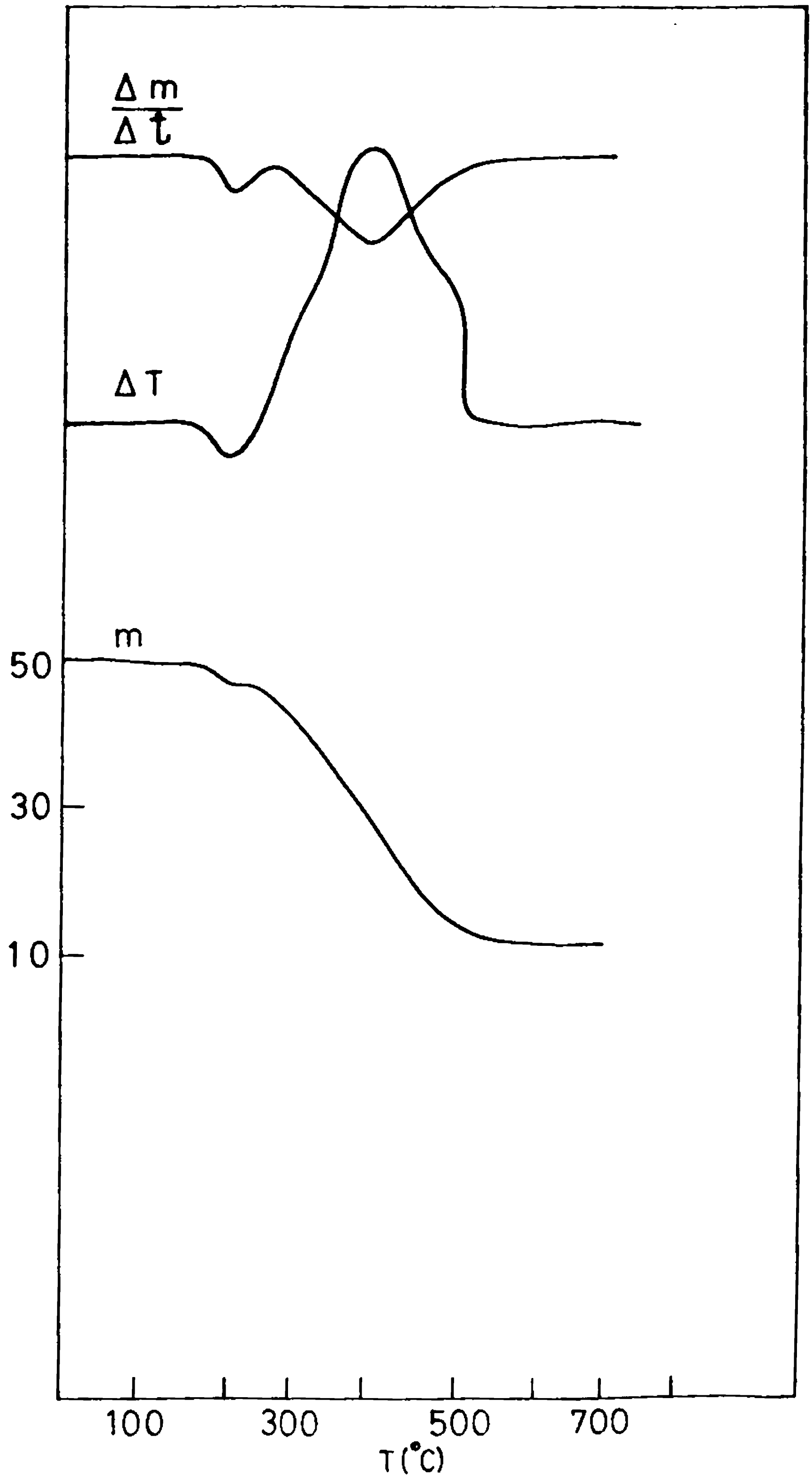


Fig.2. TG, DTG and DTA curves of $[Mn(em)(H_2O)_2]$

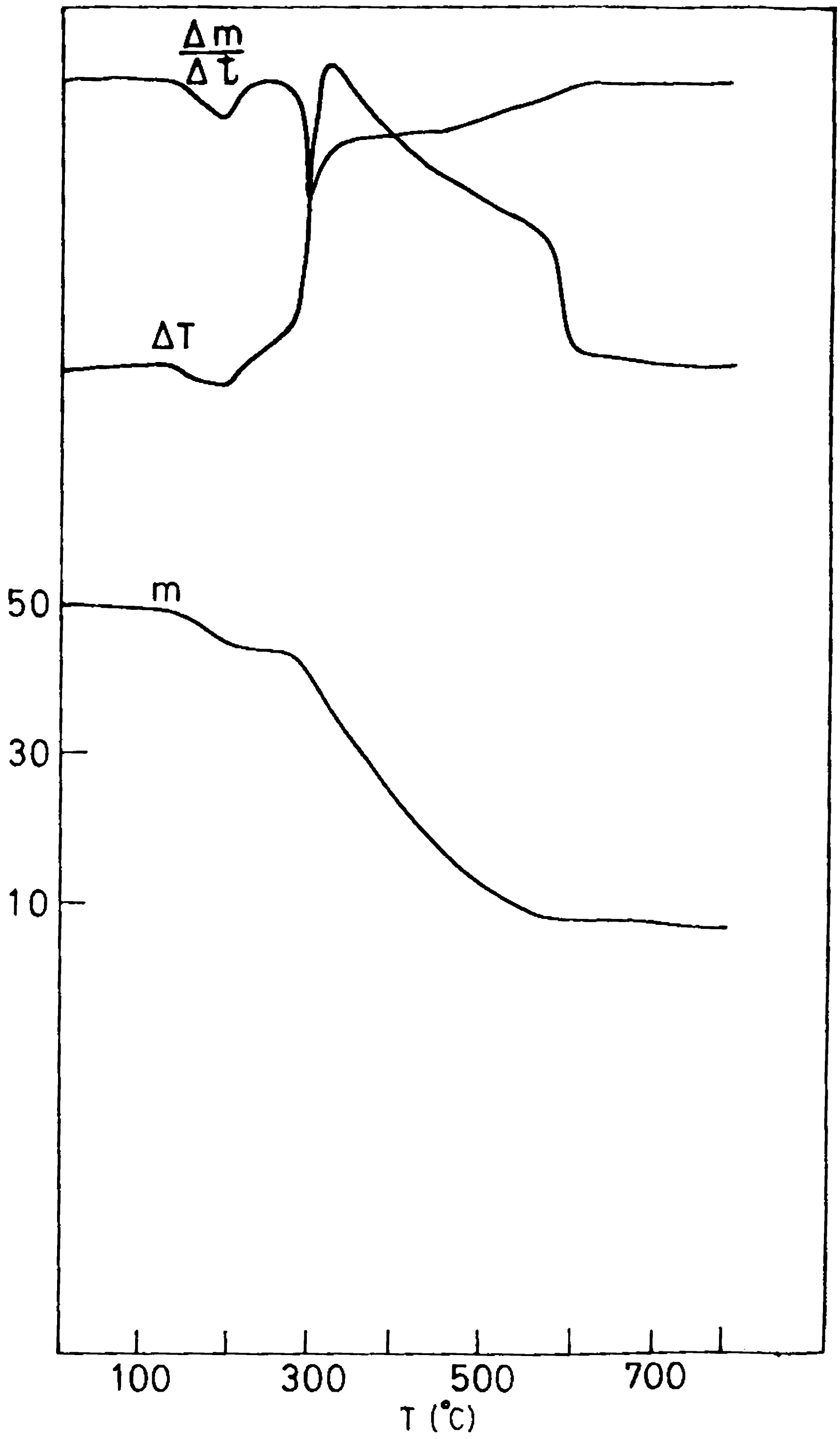


Fig.3. TG, DTG and DTA curves of $[Co(em)(H_2O)_2]$

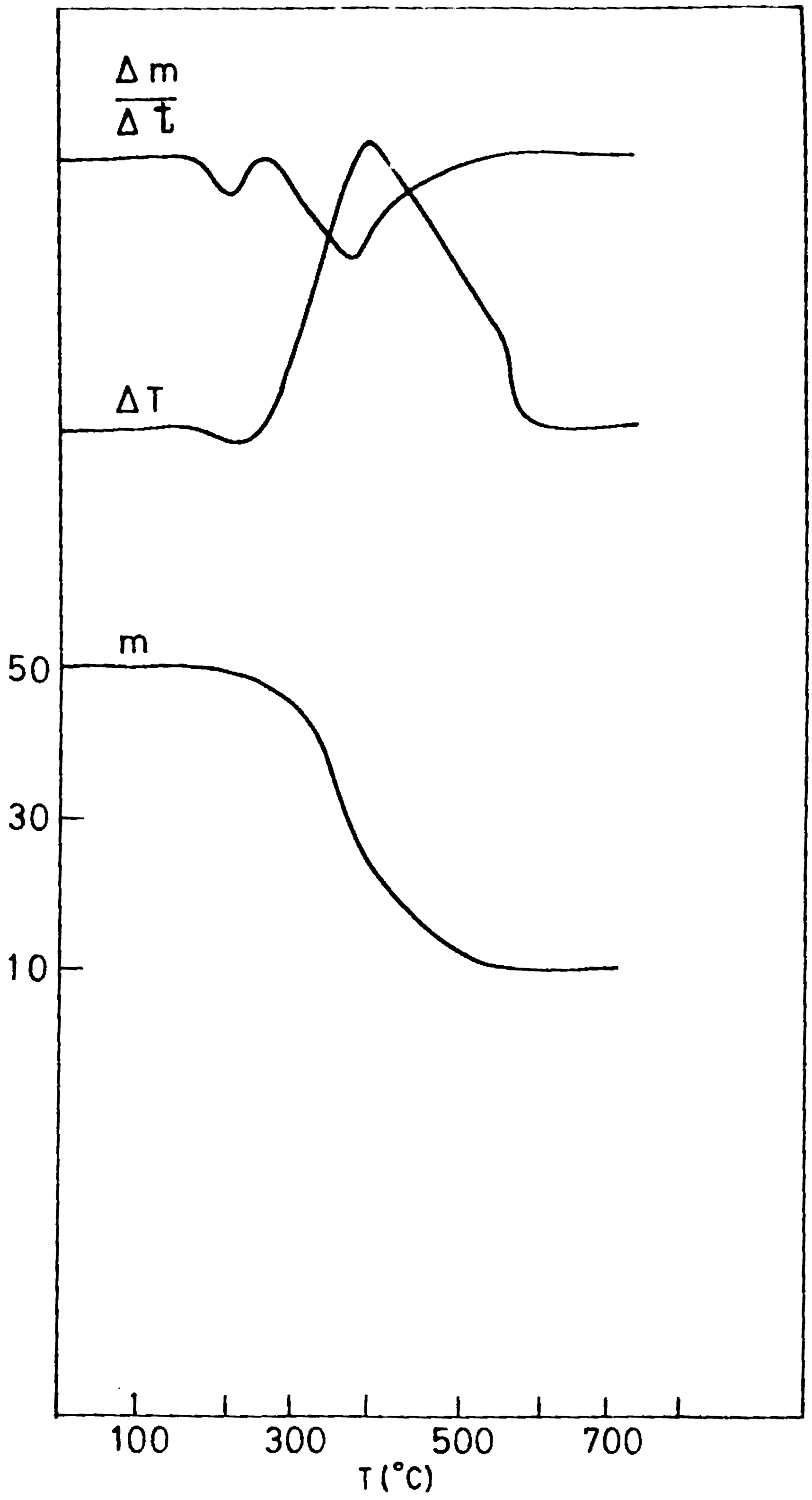


Fig.4. TG, DTG and DTA curves of $[Ni(em)(H_2O)_2]$

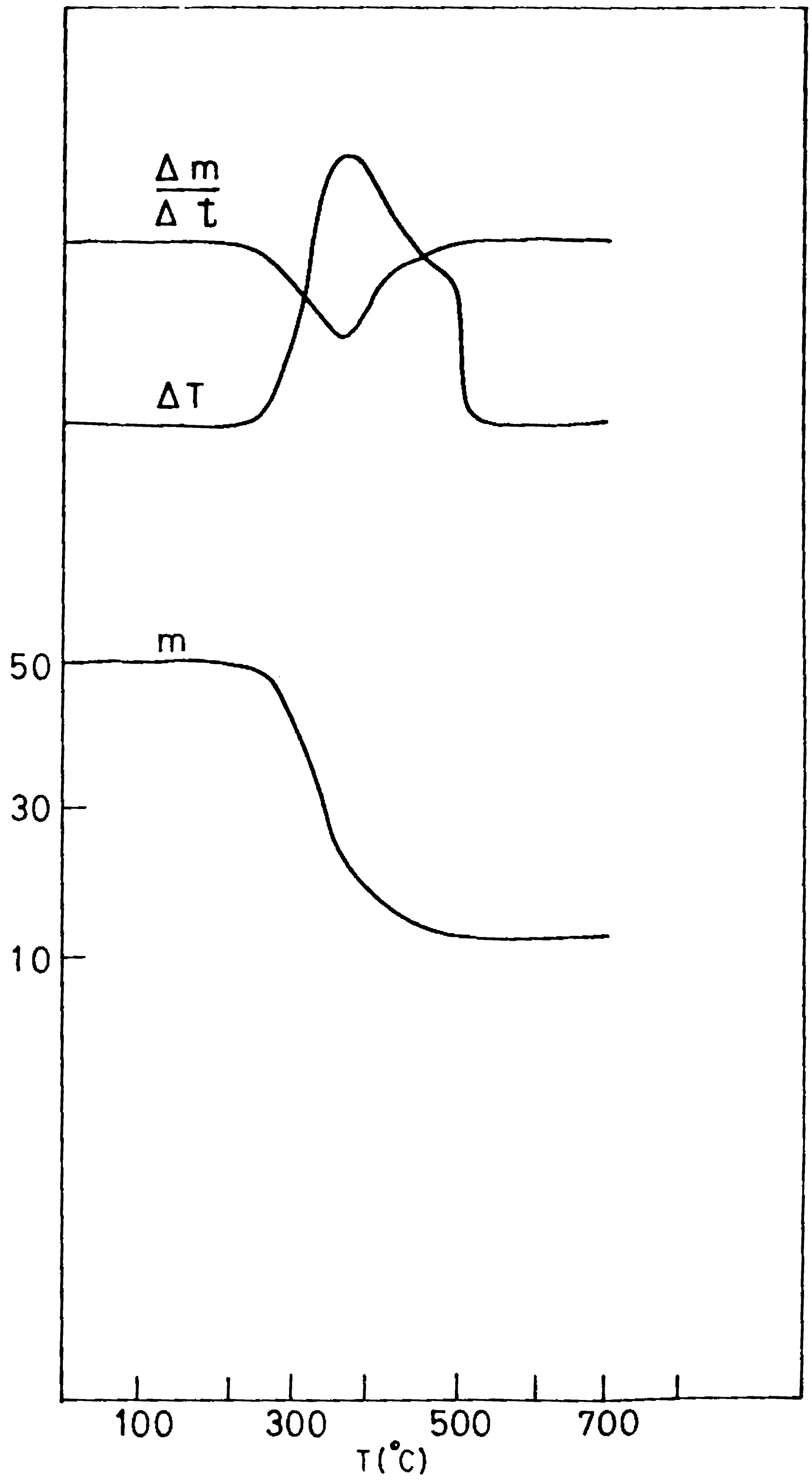


Fig.5. TG, DTG and DTA curves of [Cu(em)]

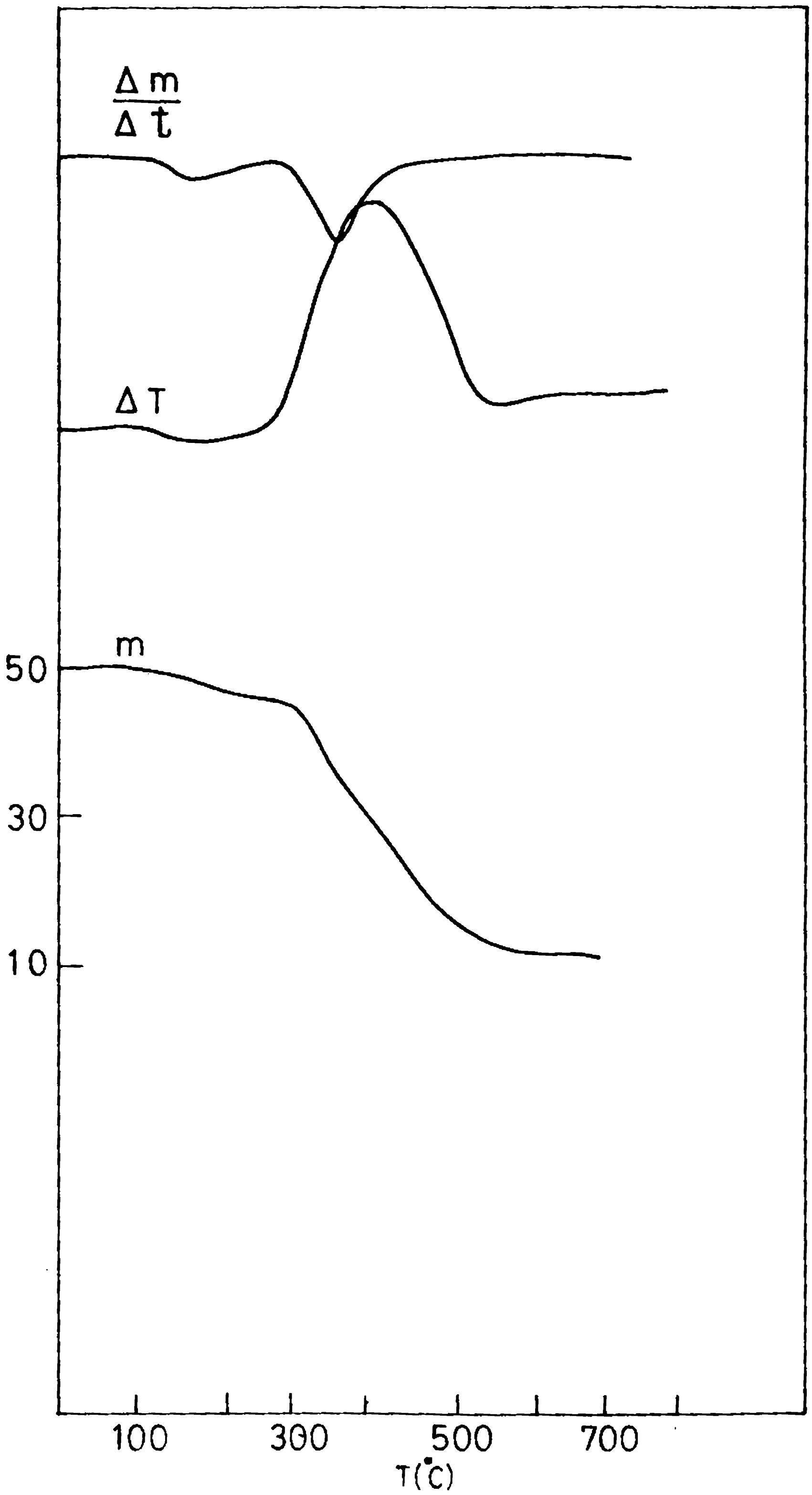


Fig.6. TG, DTG and DTA curves of $[Zn(em)(H_2O)_2]$

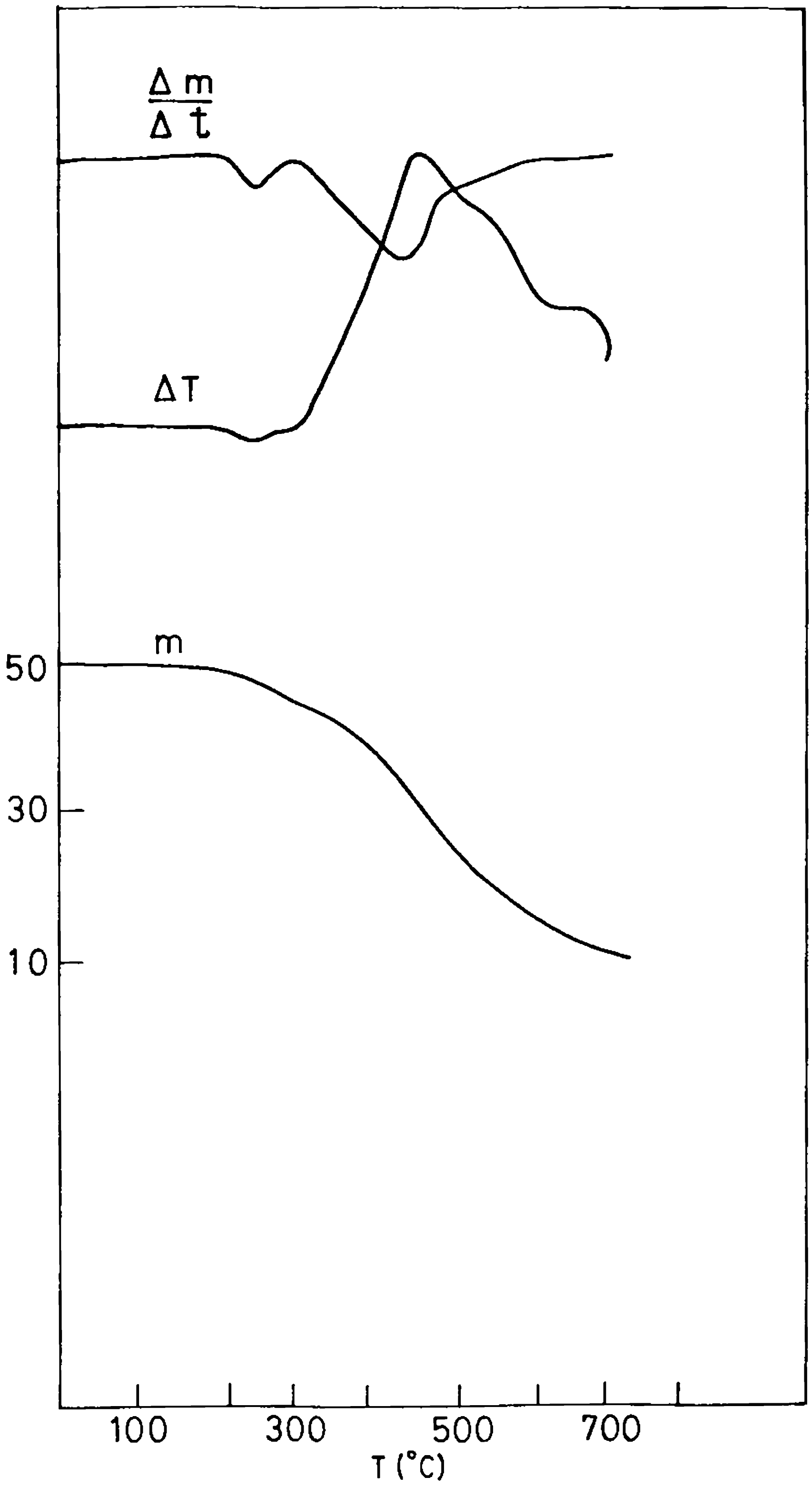


Fig.7. TG, DTG and DTA curves of $[Cd(em)(H_2O)_2]$

3.2. Complexes of Embelin with Chromium(III) and Iron(III).

The coordination chemistry of iron and chromium have received much attention (2,14,13) owing to their industrial and biological importance. Iron is an essential element and the biochemistry of this element is often discussed as a typical example of the possibilities available for absorption, storage, handling and usage of an essential metal. Iron-containing proteins participate in two main processes in living systems viz. oxygen transport and electron transfer (143). Although iron is an abundant element in the earth's crust, it is not readily absorbed by plants. The chelated form of iron is prepared for administration to plants(3). Chromium is also believed to be an essential trace element and is expected to have biological functions in sugar metabolism (3,197). However chromium is often regarded as a potential pollutant, since amount used industrially is large, compared to the normal biological levels. For example, chromium compounds are used extensively in catalyst and pigment manufacturing processes (172,14).

Characterisation of iron(III) and chromium(III) complexes with some biologically important ligands have been reported in literature. Complexes of the broad spectrum antibiotic cycloserine with trivalent chromium(198) and iron(158,159) have been studied in detail. Mossbauer spectra of the complexes of iron(III) with 2,5-dihydroxy-1,4-benzoquinone have been reported in literature (199). However the coordination chemistry of hydroxyquinones with chromium(III) has not been reported so far.

Stereochemical aspects of the complexes of embelin with chromium(III) and iron(III) have been studied herewith for the first time. Complexes of embelin with chromium(III) and iron(III) have been synthesised and characterised by elemental analysis, infrared and electronic spectra as well as by thermal and magnetic studies

3.2.1. Experimental

Materials

The trivalent metal salts used for complex preparation and the method of preparation of the ligand are mentioned in Chapter 2.

Preparation of the complexes

Aqueous ethanolic solutions of the corresponding metal acetates (slightly acidified with acetic acid) and ethanolic solutions of the ligand in 2:3 molar ratio (with the ligand in slight excess) were mixed together and refluxed on a water bath for 20-30 minutes. The metal complexes precipitated out were filtered and washed repeatedly with aqueous ethanol to remove the adhering impurities. The complexes were dried in vacuum over P_4O_{10}.

Characterisation

Elemental analysis and physical measurements were carried out by the methods described in Chapter 2. As the complexes were found to be insoluble in most of the common organic solvents, conductance measurements could not be carried out. Owing to the poor and inadequate solubility of these complexes in camphor and biphenyl, molecular weight determination by Rast's method could not be carried out either.

3.2.2. Results and Discussion

The iron(III) complex of embelin is precipitated immediately after mixing the aqueous ethanolic solutions of the ferric salt and the ligand. But the complete precipitation of chromium(III) complex takes place only after digesting the mixture for 10-20 minutes.

Analytical data of the complexes (Table 4) suggest an M_2L_3

composition for the iron(III) and chromium(III) complexes. The insolubility of the complexes in most of the common organic solvents indicates a polymeric nature. A similar polymeric nature had been reported for the divalent metal complexes also (101).

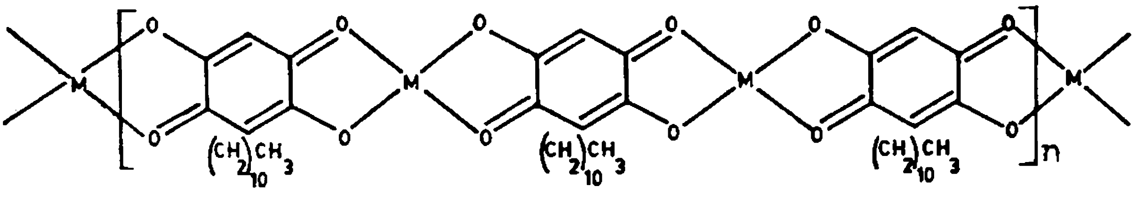
Infrared spectra

The important infrared frequencies of the iron(III) and chromium(III) complexes are presented in Table 5. The O-H stretching frequency is observed as a strong band at 3300 cm^{-1} for embelin. The disappearance of this band in the complexes indicates that phenolic hydrogens are lost on chelation.

The absence of the broad medium intense peak occurring between 3300-3400 cm^{-1} indicates the absence of water molecules which had been observed for some divalent transition metal complexes of embelin (101).

The carbonyl stretching frequency observed as a strong peak at 1610 cm^{-1} for the ligand is found shifted to 1510 cm^{-1} and 1490 cm^{-1} for the iron(III) and chromium(III) complexes respectively. Some hexa-coordinated divalent metal complexes of embelin exhibited ν C=O at 1520 cm-1 whereas the four-coordinated copper complex exhibited νC=O at 1460 cm^{-1} Since the amount of shifting of the carbonyl group frequency towards the lower side is regarded as an indication of the metal-oxygen bond strength (35), chromium(III) and iron(III) complexes may be assumed to have slightly higher M-O strength than the hexa-coordinated divalent metal complexes.

An extra stability for iron(III) complex is indicated by the lowest lying carbonyl group frequency for it as compared to that of chromium(III) complex. On the basis of infrared studies,it could be concluded that embelin acts as a tetradentate ligand coordinating through its carbonyl and phenolic oxygens as indicated below.



M=Cr or Fe.

Magnetic properties

The room temperature magnetic moments of chromium(III) and iron(III) complexes are presented in Table 5.

Chromium(III) complex

The magnetic moment of 3.68 B.M. (at 28 ± 2 ^{o}C) for the chromium(III) complex is very close to the spin only value for 3 unpaired electrons. Although d^3 ion in a tetrahedral environment with a $^4T_1(F)$ ground term is expected to have orbital contributions towards the magnetic moment (5),lower than expected values of magnetic moments have been reported for other four coordinated complexes. (eg. chromium(III) with a sterically demanding alkoxo ligand, bis(t-butyl) methoxide has a μeff of 3.2 B.M.(200)).

Iron(III) complex

For the iron(III) ion, the free ion ground state is ^6S, becoming $^6A_1$ in a weak ligand field. For ions with a $^6A_1$ ground state ($t_{2g}^3 e_g^2$) configuration and S=5/2) there is no orbital contribution to the magnetic moment and thus the observed moments are usually close to 5.92 B.M. as predicted by the spin only formula for five unpaired electrons(5). As there are no other states with the same spin multiplicity, large deviations cannot occur due to the mixing in of excited states into the ground state (as is usually noted in the case of A or E ground states) although high order perturbations are probably responsible for slight deviations frequently noted (201). The room temperature magnetic moment of the iron(III) complex of embelin is 5.8 B.M. and generally μ_{eff} value in the range 5.1 to 6.0 B.M. are frequently observed for iron(III) complexes irrespective of whether the ligand arrangement is octahedral or tetrahedral (4). Hence it is not possible to distinguish between tetrahedral and octahedral coordination on the basis of magnetic measurements. However, tetrahedral iron(III) complexes of few halides and cycloserine derivatives have been known to exhibit magnetic moments in the range 5.1 to 6.0 B.M. (201, 158).

Electronic spectra

Absorption maxima for the observed spectral bands of the complexes are given in Table 5. Ligand absorptions and charge transfer transitions complicate the assignment of the bands observed in uv region.

Chromium(III) complex

The observed bands at 8300 cm^{-1} and 15000 cm^{-1} could be attributed to the transitions $^4T_1(F) \longrightarrow {}^4A_2$ and $^4T_1(F) \longrightarrow {}^4T_1(P)$ levels. Among the four-coordinated complexes, square planar complexes of chromium(III) are unknown, and tetrahedral coordination has been reported only in very few complexes (6). Chromium(III) is believed to have tetrahedral coordination in tungstochromic acid and has bands in the region at 8300 and 16000 cm^{-1}. Tetrahedrally coordinated complex of chromium(III) with a sterically demanding alkoxo ligand, bis(t-butyl) methoxide has shown only a single band in the visible region at 14500 cm^{-1} (200). Octahedral chromium(III) complexes are expected to show three bands for the d-d transitions in the visible region(6). The spectral assignments for the observed absorption bands, therefore suggests a tetrahedrally coordinated structure for the chromium(III) complex of embelin, especially in view of the steric hindrance caused by the bulky embelin molecules (200).

Iron(III) complex

In a weak crystal field, the ^{6}S free ion term for iron(III) transforms as $^{6}A_{1}$. There are no other sextuplet states which lie above the ground state. All the excited states of the d^{5} ion have a spin multiplicity different from that of the ground state, and transitions to them are spin forbidden. Hence the absorption bands due to d-d transitions are extremely weak and frequently obscured by the charge transfer bands tailing into the visible region of the spectrum. Since there is no centre of symmetry in a tetrahedral molecule, somewhat intense absorptions than those in the octahedral complexes are often obtained for d-d transitions in tetrahedral complexes (6,7). Tetrahedral iron(III) complexes such as FeX (X = halides) give a more detailed spectrum with fairly narrow bands (202). Assignments for the absorption bands of tetrahedrally coordinated complexes of iron(III) with cycloserine derivatives and benzoxazole-2-thione have been reported in literature (158,203). The observed bands for iron(III) complex of embelin at 14290 cm^{-1} and 16390 cm^{-1} may be attributed to the transitions $^{6}A_1 \longrightarrow {}^{4}T_1(G)$ and $^{6}A_1 \longrightarrow {}^{4}E(G)$, $^{6}A_1 \longrightarrow {}^{4}A_1(G)$ doublet respectively. The next transition at 18690 cm^{-1} may be due to the transition $^{6}A_1 \longrightarrow {}^{4}E(^{4}D)$ while the remaining transition at 24100 cm^{-1} may be due to the transition to the ^{4}F sublevel. These bands are in conformity with a tetrahedral coordination for the iron(III) complex.

Thermal studies

Thermal studies of the complexes were carried out under static air conditions. Thermoanalytical data obtained from TG, DTG and DTA curves and independent pyrolysis are presented in Table 6. Some of the salient features of the thermal decomposition of embelin and some of its divalent transition metal complexes have already been discussed (101). It would be interesting here to compare the thermal behaviour of complexes of iron(III) and chromium(III) with those of the divalent transition metals. The TG,DTG and DTA curves of the chromium(III) and iron(III) complexes are presented in figures 8 and 9.

The absence of a dominant endotherm upto 220^{o}C indicate the absence of coordinated water molecules for chromium(III) and iron(III) complexes. Copper(II) complex of embelin is also characterised by the absence of such an endotherm (101).

The decomposition of the complexes is mainly exothermic with an endothermic shift at 360^{o}C. This endothermic shift is not observed for the divalent metal complexes of embelin. Furthermore, these decompositions are extended over a broad range between 220^{o}C and 850^{o}C. The observed trends in thermal behaviour may be mainly due to the increased ligand to metal ratio in these complexes in contrast to the divalent metal complexes of embelin. Chromium and iron could also assume various oxidation states and it is expected that these metal ions should also give rise to catalytic effects in the decomposition of their complexes (196). However on the basis of temperature ranges for decompositions, the divalent metal complexes of embelin, except zinc and cadmium, were found to decompose completely, much earlier (at 550^{o}C) as compared to iron(III) and chromium(III) complexes, probably due to the enhanced catalytic effects of these divalent metal ions for the oxidative decompositions of their complexes. It might also be mentioned that the observed trends in these catalytic oxidative decompositions, particularly, in the extent of temperature ranges for the decompositions, could possibly be an indication of the effects due to ligand field stabilisation energies of various metal ions in these complexes. The potential power of crystal field models for predicting the catalytic activities for the oxidation of carbon monoxide and hydrocarbons has been reported (204, 205). The oxides of manganese(III), cobalt(III), nickel(II), and copper(II) were found to have enhanced catalytic activities for these oxidation reactions in contrast to the oxides of chromium(III) and iron(III). Furthermore, it has been tentatively suggested that the variations in catalytic effects could be due to the variations in crystal field stabilisation energies.

The procedural decomposition temperatures of $Fe_2(em)_3$ and $Cr_2(em)_3$ complexes are slightly lower than that of the divalent transition metal complexes. Hence divalent metal complexes of embelin can be regarded to have more thermal stability than the iron(III) and chromium(III) complexes. $Fe_2(em)_3$ exhibits higher procedural decomposition temperature (from TG) and increased shift in carbonyl absorption frequency than $Cr_2(em)_3$ thus indicating more thermal and thermodynamic stability for the iron(III) complex.

Independent pyrolysis carried out on the complexes gave final mass loss comparable to the values obtained from the thermograms. Final residues of the pyrolysis of all the complexes (up to 900 °C) were subjected to chemical analysis (174) and were found to have metal contents corresponding to the compositions of Fe_2O_3 and Cr_2O_3. The complexes undergo complete decomposition at 900 °C giving the respective stable oxides.

Table 4

Analytical data of Fe(III) and Cr(III) complexes of embelin.

Complex	colour	% metal		% carbon		% hydrogen	
		found	calcd.	found	calcd.	found	calcd.
$[Cr_2(em)_3]$	dull black	10.21	10.61	62.62	62.44	7.48	7.35
$[Fe_2(em)_3]$	dull black	11.12	11.35	62.81	61.94	7.92	7.30

em = $C_{17}H_{24}O_4^{=}$

Table 5

Magnetic and spectral data of Fe(III) & Cr(III) complexes of embelin.

Complex	μ_{eff} B.M.	electronic spectra (cm^{-1})	important IR bands νC = 0 (cm^{-1})
$[Cr_2(em)_3]$	5.80	8330 15000 28570 33330	1510
$[Fe_2(em)_3]$	3.68	14290 16390 18690 24100 28550 33300	1490

em = $C_{17}H_{24}O_4^{=}$

Table 6

Thermo-analytical data of the Fe(III) and Cr(III) complexes of embelin.

Complex	pdt*	peak temp.		decomp. temp. range		% mass loss after decomposition**	
	from TG	DTG	DTA	DTG	DTA	from TG	from independent Pyrolysis
$[Cr_2(em)_3]$	220	320	340 exo	220-360	220-360 exo	85.00	84.86
		400	390 endo	360-420	360-420 endo	(84.49)	(84.49)
		440	440 exo	420-850	420-850 exo		
$[Fe_2(em)_3]$	230	280	260 exo	230-300	230-330 exo	84.50	84.10
		400	430 endo	340-460	360-450 endo	(83.81)	(83.81)
		500	500 exo	450-850	450-850 exo		

* procedural decomposition temperature

** theoretical value in parenthesis.

$em = C_{17}H_{24}O_4$

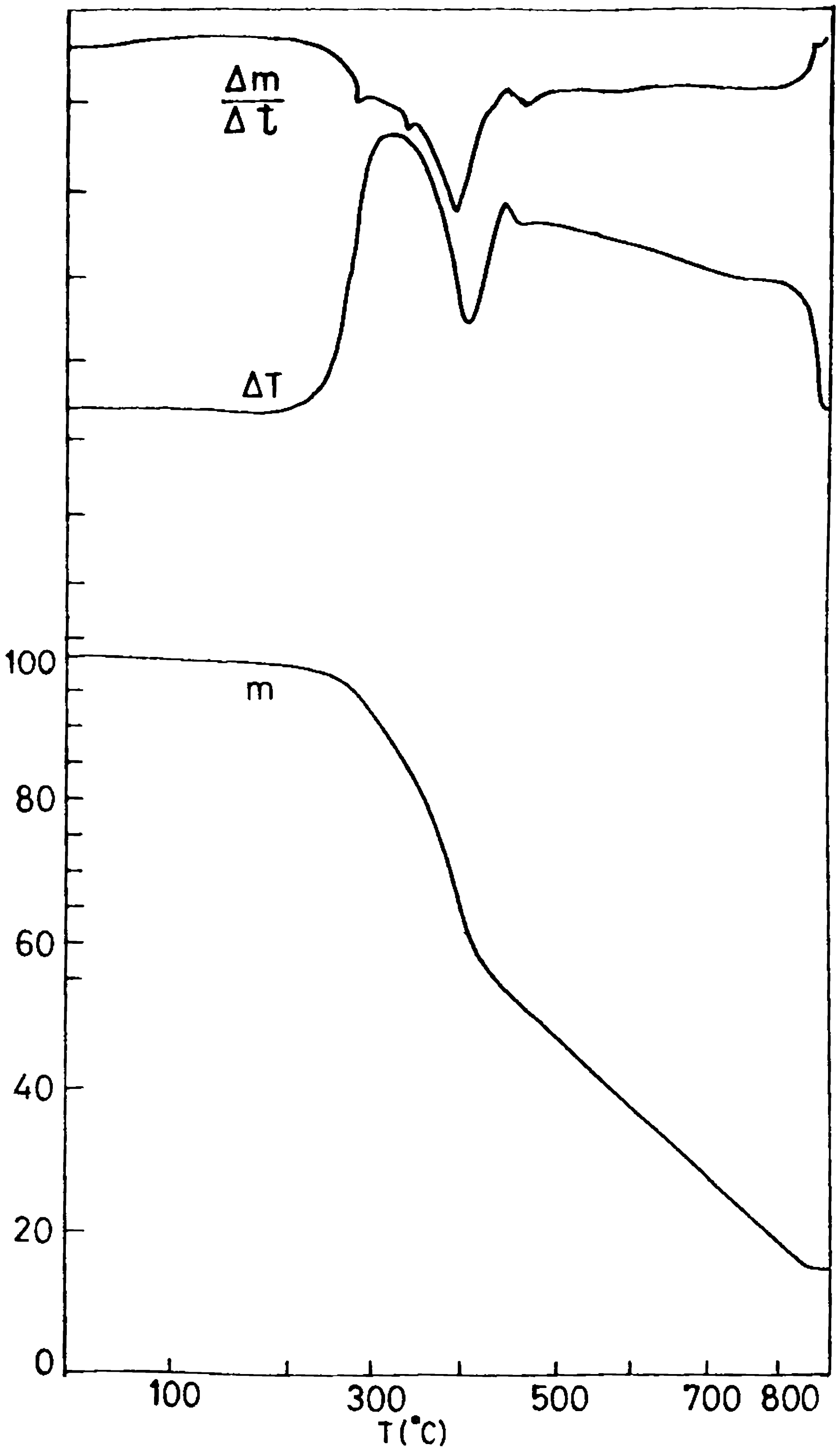


Fig.8. TG, DTG and DTA curves of $[Cr_2(em)_3]$

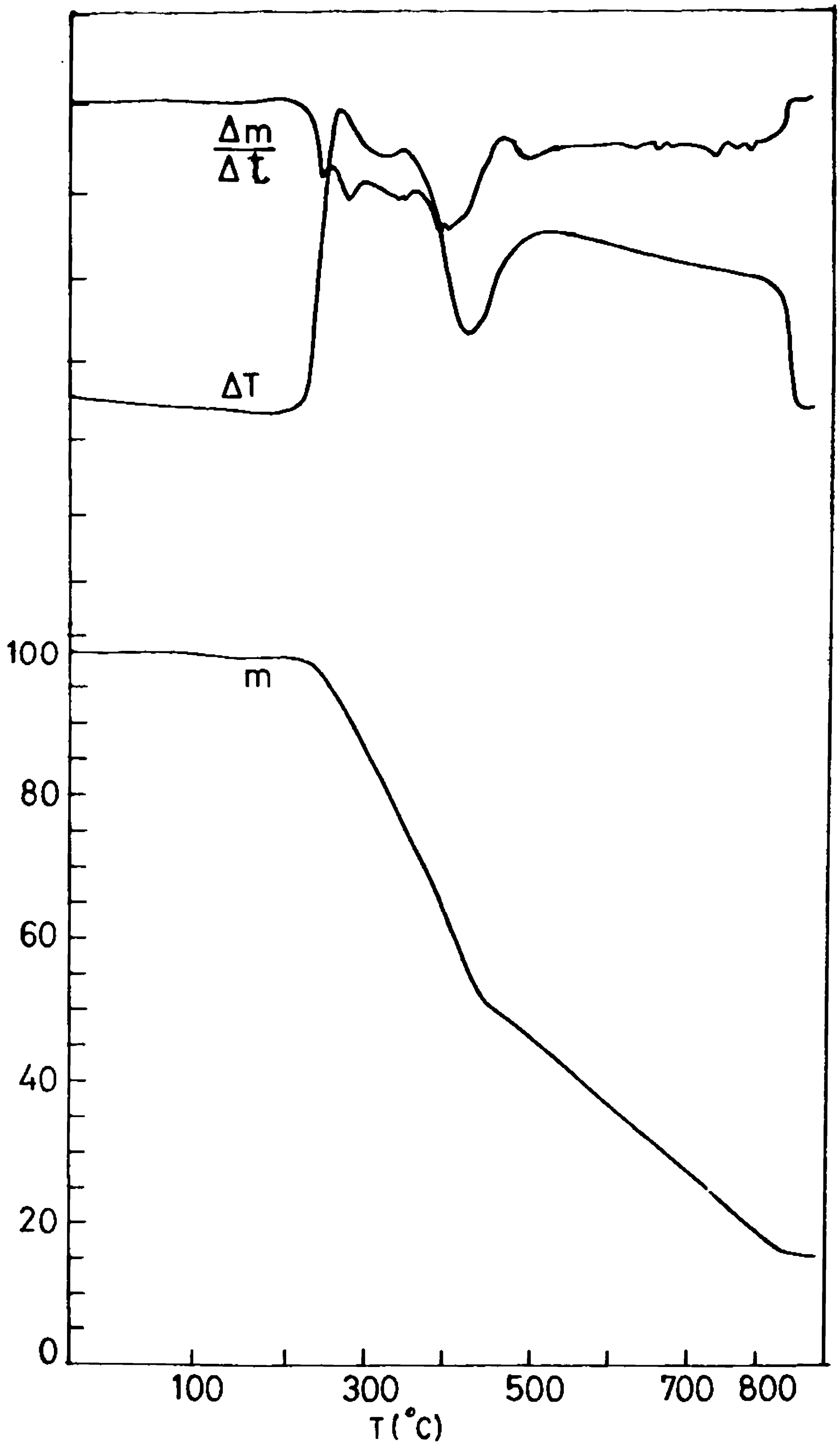


Fig.9. TG, DTG and DTA curves of $[Fe_2(em)_3]$

CHAPTER 4

LANTHANIDE AND ACTINIDE COMPLEXES OF EMBELIN

Complexes of lanthanides and actinides with oxygen donor ligands have been reviewed by several authors (61,62,206). Studies on some of the 3d-transition metal complexes of embelin have provided confirmatory evidences for the participation of carbonyl and phenolic oxygens in coordination. Several examples of lanthanide and actinide complexes can be cited for the participation of carbonyl and phenolic oxygens in coordination (*vide* Chapter I). Embelin, being a tetradentate oxygen donor ligand, is expected to form very stable complexes with lanthanides and actinides.

Complexes of embelin with lanthanum(III), praseodymium(III), neodymium(III), samarium(III), gadolinium(III), dysprosium(III), yttrium(III), thorium(IV), and uranium(VI) have been synthesised and characterised by elemental analysis, vibrational and electronic spectra as well as by thermal and magnetic studies.

4.1. Experimental

Materials

Preparation of lanthanide acetates from the pure rare earth oxides, the metal salts used, and the preparation of the ligand are given in Chapter 2.

Preparation of the complexes

Aqueous ethanolic solutions of the lanthanide acetates (acidified with a few drops of acetic acid) and ethanolic solutions of the ligand in 2:3 molar ratio (with the ligand in slight excess) were mixed together and refluxed on a water bath for 20 - 30 minutes. Thorium nitrate and the ligand in 1:2 molar ratio and uranyl nitrate and the ligand in 1:1 molar ratio were mixed similarly. The complexes which precipitated out were filtered and repeatedly washed with aqueous ethanol to remove any excess ligand. They were then dried in vacuum over P_4O_{10}.

Characterisation

Elemental analysis and physical measurements were carried out by the methods described in Chapter 2. As the complexes were found to be insoluble in most of the common organic solvents, conductance measurements could not be carried out. These complexes were also insoluble in camphor and biphenyl and hence molecular weight determinations by (Rasts method) could not be carried out.

4.2. Results and Discussion

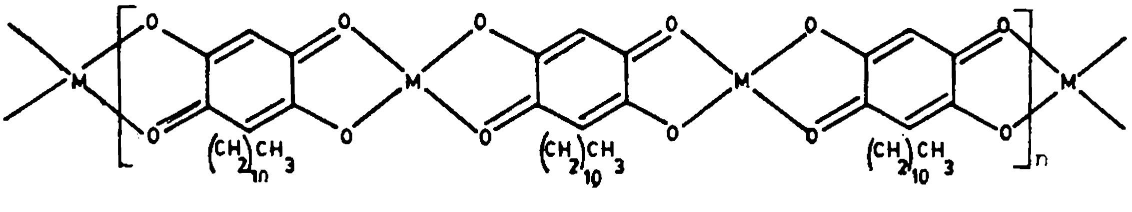
Lanthanide and actinide complexes were precipitated immediately on mixing aqueous ethanolic solutions of the corresponding metal salts and the ligand. But for ensuring completion of the reaction, they were digested on the water bath for 20 - 30 minutes.

All the lanthanide and yttrium(III) complexes have a dull greyish violet colour. The thorium(IV) complex is green and the uranium(VI) complex is orange. Analytical data of the complexes (Table 7) suggest an $M_2L_3.4H_2O$ composition for the lanthanides, $ThL_2.2H_2O$ and $UO_2L.2H_2O$ for the actinides. The insolubility of the complexes in most of the common organic solvents possibly indicates a polymeric nature. All the complexes showed a high tendency to absorb moisture and hence the experimentally determined values of the metal content are slightly lower than the theoretically expected values. On drying these chelates at $50^{o}C$ under vacuum for ~ 16 hours, mass loss corresponding to four water molecules for the lanthanides and two water molecules for the actinides has been observed. Hence water molecules in these chelates may be regarded as crystalline water (38).

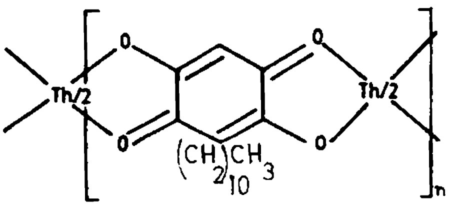
Infrared spectra

The important infrared frequencies of the lanthanide and actinide complexes of embelin are presented in Table 8. The O-H stretching frequency is observed as a strong band at 3300 cm^{-1} for embelin. The disappearance of this band indicates that the phenolic hydrogens are lost on chelation. The broad medium intense peak occurring between 3300 and 3400 cm^{-1} in the spectra of lanthanide and actinide complexes may be attributed to the O-H stretching frequency of the water molecules (8).

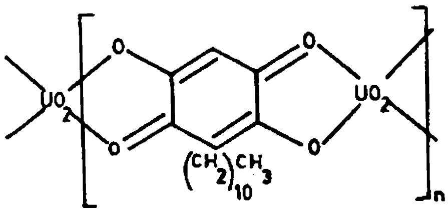
The absorption bands for the O-H bending frequency of the water molecules, expected around 1650 cm^{-1}, are overlapped by the bands due to the ligand. Embelin shows absorptions in the region 1600-1640 cm^{-1} (Table 1).However the absorptions in this region were extremely negligible for the divalent and trivalent 3d-metal complexes of embelin. The carbonyl stretching frequency observed as a strong band at 1610 cm^{-1} for embelin is found shifted to 1500-1520 cm^{-1} in the spectra of all the complexes (Table 8). Shifts of C=O stretching frequencies towards lower frequencies have been observed in all the complexes of the lanthanides with ligands containing this group (62). The decrease in the C=O stretching frequency in the complexes can be taken as an indication of the strength of the metal-oxygen bond strength and hence of the stability of the complexes. In the present case the shifts (90 - 100cm^{-1}) are almost the same for all the lanthanide complexes and is indicative of the similarity among the 4f-elements. Analogous behaviour has been observed in the case of other lanthanide complexes (207 - 212). It may be mentioned here that the complexes of lanthanides, actinides and trivalent transition metals, exhibit almost similar ν C=O shifts towards lower frequencies upon complexation. The infrared spectral data, therefore suggest that embelin, in these complexes, behaves as a tetradentate ligand coordinating through its carbonyl and phenolic oxygens as indicated below.



M= La,Pr,Nd,Sm,Gd,Dy or Y.



THORIUM COMPLEX



URANYL COMPLEX

Magnetic studies

The magnetic susceptibilities were determined by the Gouy method at ambient temperature 28± 2 °C. The experimentally determined magnetic moments are presented in Table 8.

Lanthanum(III), yttrium(III), thorium(IV) and uranium(VI) complexes are diamagnetic as is to be expected in view of the noble gas configuration of these ions. All other complexes were found to be paramagnetic. The measured susceptibilities were corrected for the diamagnetism of the rest of the molecule using Pascal's constants (4,5). A correction for the diamagnetism due to the completely filled orbitals of the lanthanide ion was also applied. Since these complexes represent magneticaly dilute systems, the Weiss constant could be neglected (4,5). The moments were calculated using the Curie law formula $\mu_{eff} = 2.84\sqrt{\chi'_M T}$ where χ'_M= corrected magnetic susceptibility, M = molecular weight and T = temperature.

Theoretical magnetic moments were calculated using the formula $\mu = g\sqrt{J(J+1)}$. (J is the total angular momentum of the ground state given, according to the LS coupling). This equation is valid when splitting of ground state caused by spin orbit coupling is large compared to kT. Appreciable contribution to the magnetic moment is expected from this coupling. Furthermore, in this equation g is independent of the stereochemical environment and the amount of magnetic dilution. This type of behaviour exists in the lanthanide complexes in which the inner 4f orbitals are well shielded from the external ligand fields by the $5s^2p^6$ octet. Moreover these ions behave very much like gaseous ions. Hence the g factor (applicable only to gaseous ions) used in the equation for the theoretical magnetic moment is given by the relation.

$$g = 1 + \frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)}$$

Besides these theoretical values calculated on the basis of simple spin-orbit coupling model, the values obtained by Van Vleck and Frank from more refined calculations (213) are also included in Table 8 for comparison.

The measured magnetic moments agree well with the theoretical values calculated from the Van Vleck formula (213) except in the case of samarium. In the case of samarium, the observed moment is almost double the simple model theoretical value. The reason for this is that in samarium(III), the first excited J state ${}^6H_{7/2}$ is sufficiently close to the ground state ${}^6H_{5/2}$. The separation between these states is only 1000 cm^{-1}. Consequently this permits an appreciable population in the excited state, thus causing an increase in the magnetic moment (4,5).

Electronic Spectra

Electronic spectra of the complexes were recorded in the solid state by the mull technique (178) in the range 200-900 nm. Ligand absorptions and charge transfer transitions complicate the assignment of the bands observed in the uv and visible regions. The electronic spectrum of the ligand shows absorption maxima at 17800, 28570 and 33330 cm^{-1}. All the complexes show absorption maxima at 15600, 25000 and 28000 cm^{-1} respectively. Most of the absorption bands due to f-f transitions of lanthanide ions in the uv and the visible regions are obscured in the present complexes by the very strong ligand absorptions in this region.

Thermal behaviour

Thermal studies on the metal complexes were carried out under static air conditions. Thermoanalytical data as well as TG, DTG and DTA curves are presented in Table 9 and in figures 10-18. The complexes exhibit dehydration and decomposition stages. A broad endothermic peak extending between 50 ^{o}C and 180 ^{o}C was observed indicating the loss of crystalline water molecules. All the lanthanide and actinide complexes are hygroscopic and hence the mass loss corresponding to the dehydration are slightly higher than the theoretical value. Such variations had been reported for the transition metal complexes too (101). Dehydration for the divalent transition metal complexes (Table 3) starts only after 120°C. However about 90% of the mass loss corresponding to the dehydration of the lanthanide and actinide complexes of embelin are observed between 50 and 100°C in the TG curves and only < 10% was observed between 100°C and 180°C. Vacuum drying at ~ 50°C was observed to yield completely dehydrated lanthanide and actinide complexes. Loss of water molecules at temperatures less than 100°C have been attributed to loss of crystalline water in the case of some iron(III) complexes also(199). Therefore the water molecules in these chelates may be regarded as crystalline water.

The decomposition of the complexes is mainly exothermic in nature with a slight endothermic shift at 340 - 380°C for all the complexes. This endothermic shift during complex decomposition may be due to the increased ligand to metal ratio in these complexes in contrast to the divalent metal complexes(101). The decomposition of the complexes is extended over a wide range, and is completed only at 800°C to give the respective stable oxides. For some divalent metal complexes of embelin, mass loss is completed at 550°C.

Some of the lighter lanthanides are expected to assume varying oxidation states and were found to have catalytic activities for some oxidation reactions (42). However their tripositive ions exhibit more resemblance to the dipositive alkaline earth metal ions and therefore the catalytic effects of these 4f metal ions for the oxidative decompositions of their complexes could be much lesser as compared to those of the 3d-metal ions. Furthermore, the catalytic effects due to crystal field stabilisation energy (204,205) could not be expected for these decompositions, as it is too low for the lanthanides.

On the basis of procedural decomposition temperatures, lanthanide and actinide complexes were found to have lower thermal stabilities than the transition metal complexes. However the complex formation has increased the thermal stability of the ligand which is evident from the procedural decomposition temperatures.

Exothermicity of the decomposition of the complexes could be attributed to the concomitant oxidation reactions of the ligand. Independent pyrolysis carried out on all the complexes gave the final mass loss comparable to the values obtained from the thermograms. Final residues of the pyrolysis of all the complexes (upto 800 °C) were subjected to chemical analyses and were found to have metal contents corresponding to the compositions of Ln_2O_3 (Pr_6O_{11} for Pr(III) complex), U_3O_8 and ThO_2. All the complexes undergo complete decomposition at ~ 800 ^{o}C giving the respective stable oxides.

The present studies indicate that the lanthanide complexes could be envisaged to be four- coordinated, whereas the thorium complex could be eight-coordinated and uranyl complex could be six - coordinated. Higher coordination stereochemistries are often observed for the lanthanide and the actinide complexes (59,2). However three-coordinated and four- coordinated complexes with sterically demanding ligands have been reported (59,214). Steric hindrance of the bulky embelin molecules may be favouring a four - coordinated geometry for the lanthanide complexes. The chromium(III), iron(III) and copper(II) complexes with embelin were also showing four- coordinated geometries due to the steric requirements of the ligand .

Among the various techniques employed for studying the complexes, infrared spectroscopy has been widely used for the characterisation of lanthanide complexes. X-ray powder diffraction methods are employed frequently for the limited purpose of finding out whether a series of lanthanide complexes is isomorphous. But useful structural data are mostly obtained from single crystal X-ray diffraction studies.

Although,stereochemistry of the lanthanide and actinide complexes of embelin cannot be confirmed from the present studies, spectral and thermal data provide convincing evidences for the stoichiometry of the complexes and for the coordination behaviour of the ligand.

Table 7

Analytical data of the lanthanide and actinide complexes of embelin.

Complex	% metal		% carbon		% hydrogen	
	found	calcd.	found	calcd.	found	calcd.
$[La_2(em)_3].4H_2O$	20.21	22.76	51.11	49.93	6.80	6.53
$[Pr_2(em)_3].4H_2O$	20.90	22.91	51.81	49.76	6.85	6.50
$[Nd_2(em)_3].4H_2O$	21.40	23.33	48.91	49.49	6.25	6.46
$[Sm_2(em)_3].4H_2O$	24.40	24.08	50.20	49.01	6.36	6.41
$[Gd_2(em)_3].4H_2O$	24.11	24.91	47.76	48.48	6.32	6.34
$[Dy_2(em)_3].4H_2O$	23.62	25.53	48.21	48.08	6.30	6.28
$[Y_2(em)_3].4H_2O$	15.00	15.80	53.54	54.36	7.34	7.10
$[Th(em)_2].2H_2O$	26.14	27.23	49.61	47.89	5.94	6.16
$[UO_2(em)].2H_2O$	38.20	39.80	35.20	34.11	5.30	4.68

$em = C_{17}H_{24}O_4^{=}$

Magnetic and spectral data of lanthanide and actinide complexes of embelin.

Complex	μeff B.M. experi-mental	μeff* B.M.	μeff** B.M.	IR bands ν O-H (cm^{-1})	IR bands ν C=O (cm^{-1})
$[La_2(em)_3].4H_2O$	-	0	0	3400	1520
$[Pr_2(em)_3].4H_2O$	3.8	3.62	3.58	3400	1520
$[Nd_2(em)_3].4H_2O$	3.8	3.68	3.62	3360	1500
$[Sm_2(em)_3].4H_2O$	1.96	1.55 1.65	0.85	3400	1510
$[Gd_2(em)_3].4H_2O$	7.94	7.94	7.94	3380	1505
$[Dy_2(em)_3].4H_2O$	10.74	10.60	10.64	3380	1515
$[Y_2(em)_3].4H_2O$	-	-	-	3380	1495
$[Th(em)_2].2H_2O$	-	-	-	3400	1510
$[UO_2(em)].2H_2O$	-	-	-	3400	1500

em = $C_{17}H_{24}O_4^{=}$

* theoretical value based on spin orbit coupling model.

** Van Vleck values.

Thermo analytical data of lanthanide and actinide complexes of embelin.

Complex	stability range in TG from ambient upto(°C)	pdt (°C)	peak temp DTG (°C)	peak temp DTA (°C)	dehydration and decomposition temp. ranges DTG (°C)	dehydration and decomposition temp. ranges DTA (°C)	% mass loss* from TG curve after dehydration	% mass loss* from TG curve after final stage	% mass loss from independent pyrolysis.
$[La(em)_3].4H_2O$	50	220	broad peak	broad endo	50-200	50-200 endo			
			280	300 exo	220-320	220-320 exo	6.0	71.0	73.4
			350	350 endo	320-380	320-400 endo	(5.87)	(73.42)	
			400	390 exo	380-830	390-830 exo			
$[Pr(em)_3].4H_2O$	50	240	broad	broad endo	50-160	60-170 endo			
			280	300 exo	220-310	220-350 exo	6.0	76.0	74.8
			355	370 endo	330-400	350-400 endo	(5.85)	(72.31)	
			440	440 exo	420-780	420-780 exo			
$[Nd(em)_3].4H_2O$	50	240	broad	broad endo	50-160	60-160 endo			
			270	270 exo	220-330	220-310 exo	6.0	76.0	73.2
			325	340 endo	310-400	310-390 endo	(5.82)	(72.70)	
			425	430 exo	400-780	380-780 exo			
$[Sm(em)_3].4H_2O$	50	250	broad	broad endo	50-200	50-200 endo			
			290	300 exo	220-300	220-320 exo	7.0	71.0	72.6
			350	350 endo	300-380	320-420 endo	(5.77)	(72.08)	
			430	430 exo	400-740	420-740 exo			
$[Gd(em)_3].4H_2O$	60	240	broad	broad endo	60-200	60-200 endo			
			260	280 exo	220-300	220-320 exo	6.0	71.0	71.5
			350	370 endo	310-400	340-400 endo	(5.70)	(71.28)	
			400	440 exo	420-730	400-730 exo			
$[Dy(em)_3].4H_2O$	50	250	broad	broad endo	50-200	50-200 endo			
			300	315 exo	240-415	250-325 exo	7.0	73.0	71.1
			360	375 endo	315-400	325-400 endo	(5.65)	(70.70)	
			400	440 exo	400-780	400-780 exo			
$[Y(em)_3].4H_2O$	50	250	broad	broad endo	50-180	60-190 endo			
			280	300 exo	240-310	240-310 exo	7.0	81.0	
			360	370 endo	320-410	330-420 endo	(6.40)	(79.94)	79.89
			440	440 exo	410-780	420-780 exo			
$[Th(em)_2].2H_2O$	60	260	broad	broad endo	60-240	60-240 endo			
			290	300 exo	260-310	240-320 exo	4.0	70.0	
			350	350 endo	310-370	330-370 endo	(4.22)	(69.01)	69.80
			430	410 exo	400-800	400-800 exo			
$[UO_2(em)].2H_2O$	50	250	broad	broad endo	50-200	50-200 endo			
			280	300 exo	240-320	240-320 exo	6.0	55.0	
			360	380 endo	320-400	320-400 endo	(6.02)	(53.06)	53.50
			400	420 exo	400-700	400-700 exo			

pdt procedural decomposition temperature
* theoretical value in parenthesis

$em = C_{17}H_{24}\overset{=}{O}_4$

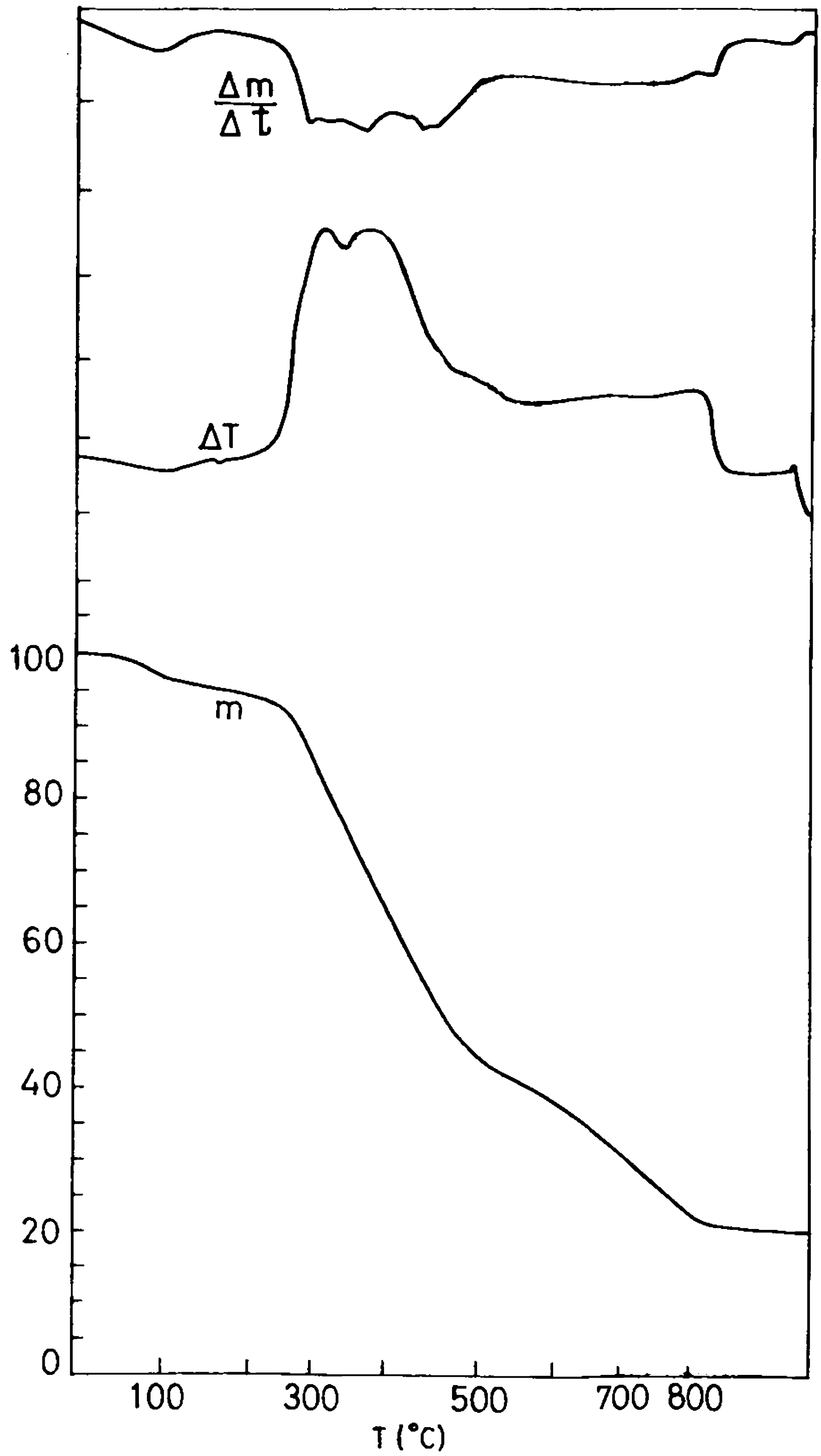


Fig.10. TG, DTG and DTA curves of $[La_2(em)_3 .4H_2O]$

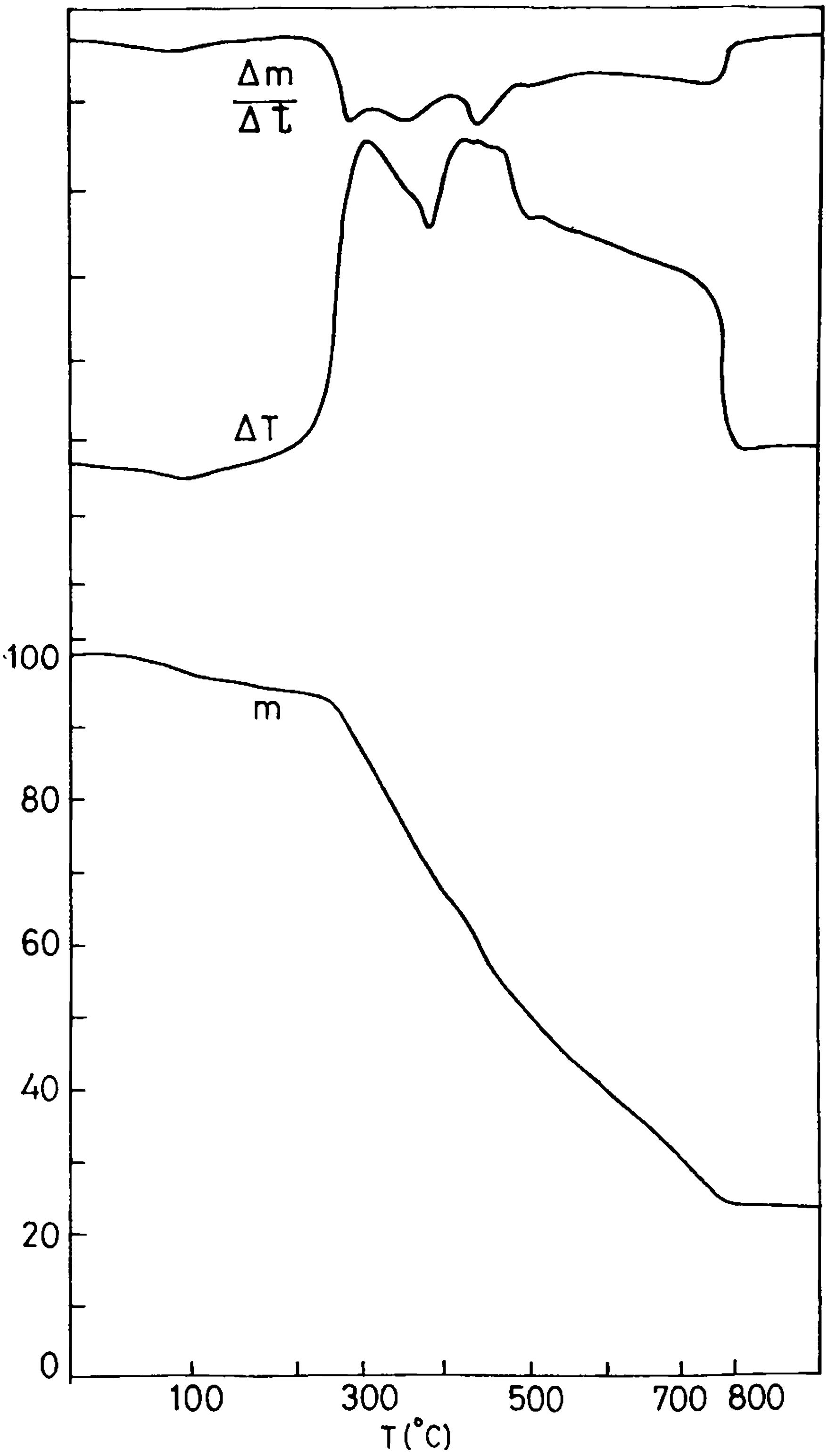


Fig.11. TG,DTG and DTA curves of [$Pr_2(em)_3$].$4H_2O$

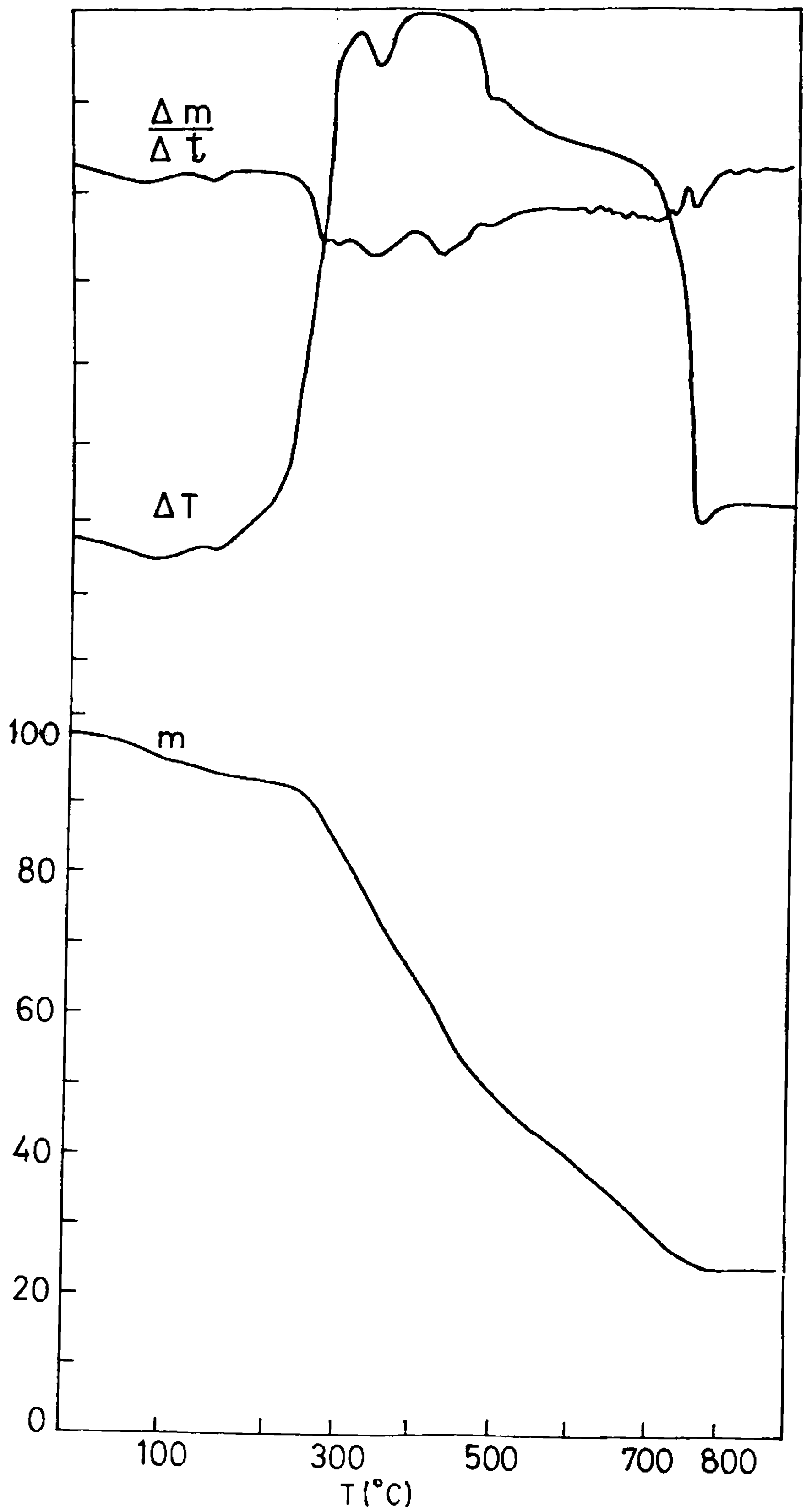


Fig.12. TG, DTG and DTA curves of $[Nd_2(em)_3] . 4H_2O$

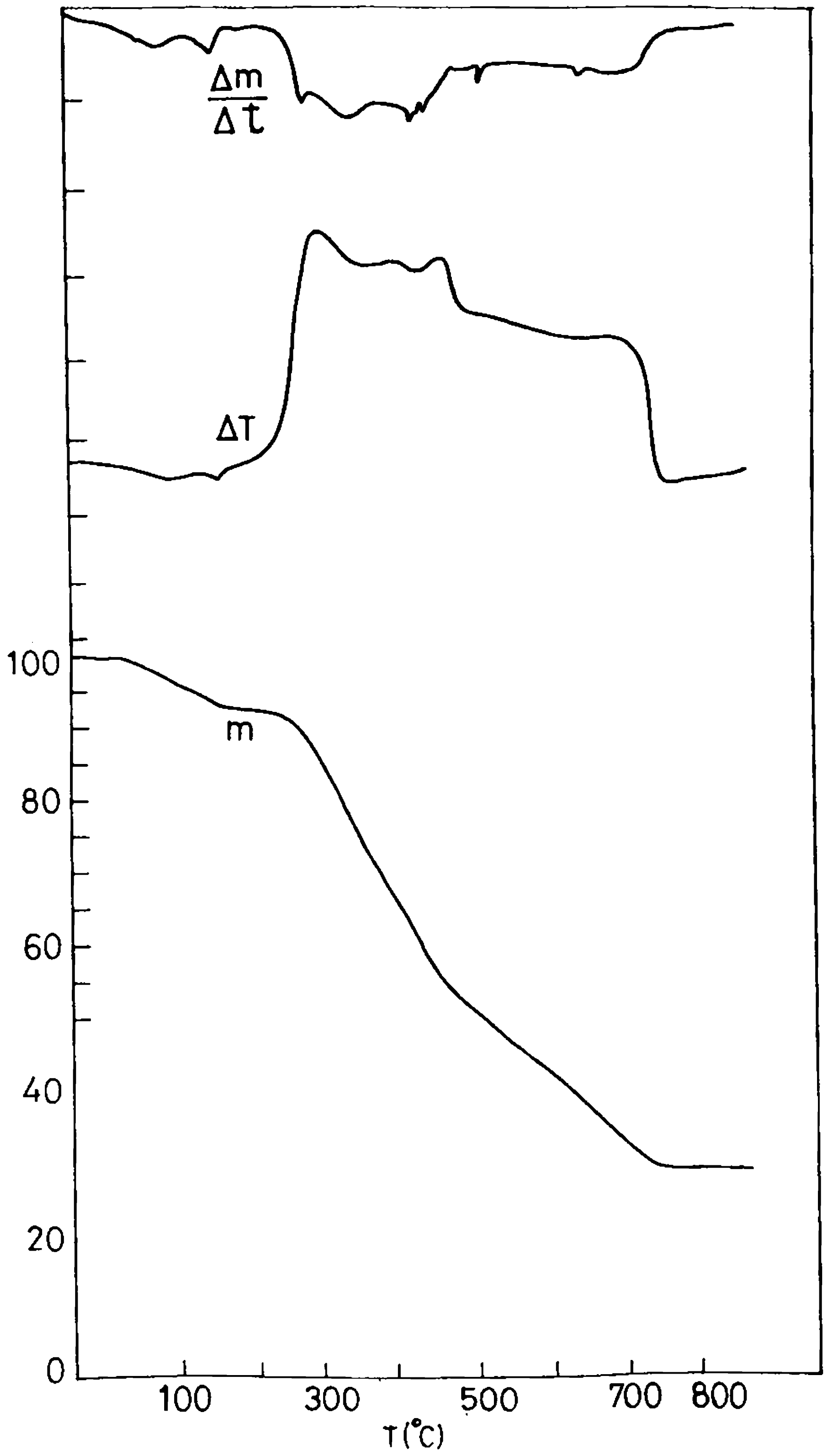


Fig.13. TG, DTG and DTA curves of $[Sm_2(em)_3].4H_2O$

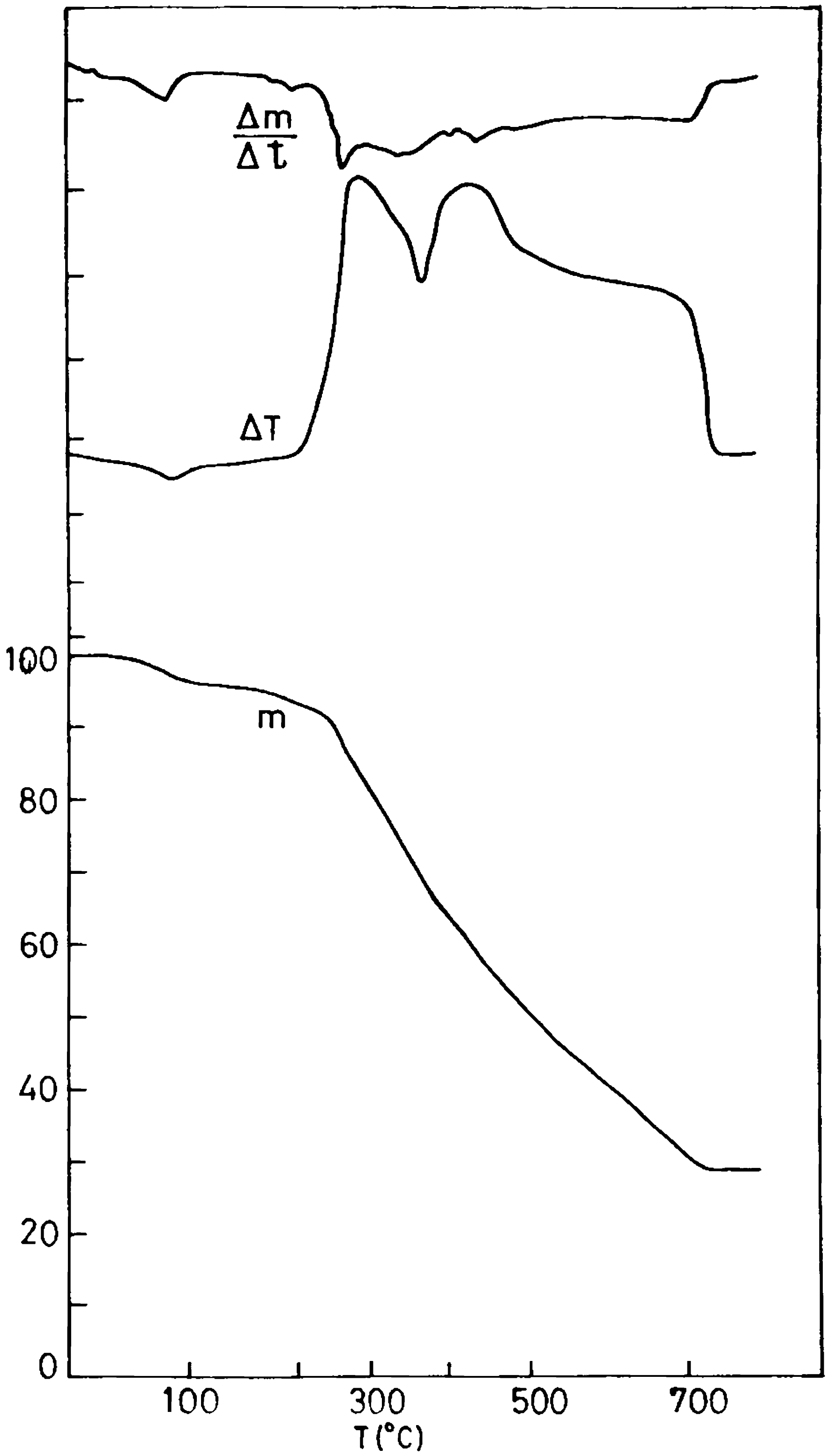


Fig.14. TG, DTG and DTA curves of$[Gd_2(em)_3].4H_2O$

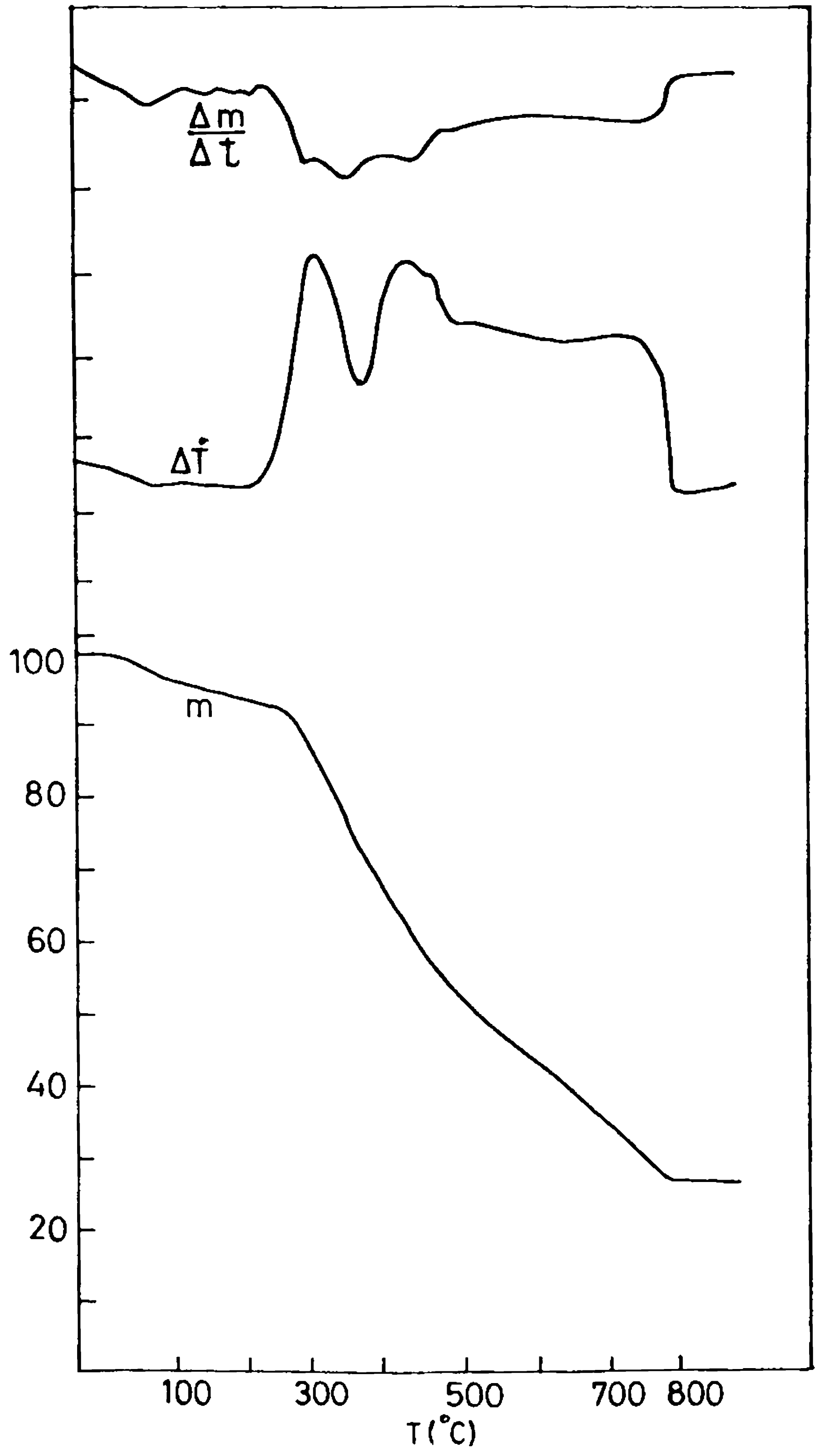


Fig.15. TG, DTG and DTA curves of $[Dy_2(em)_3].4H_2O$

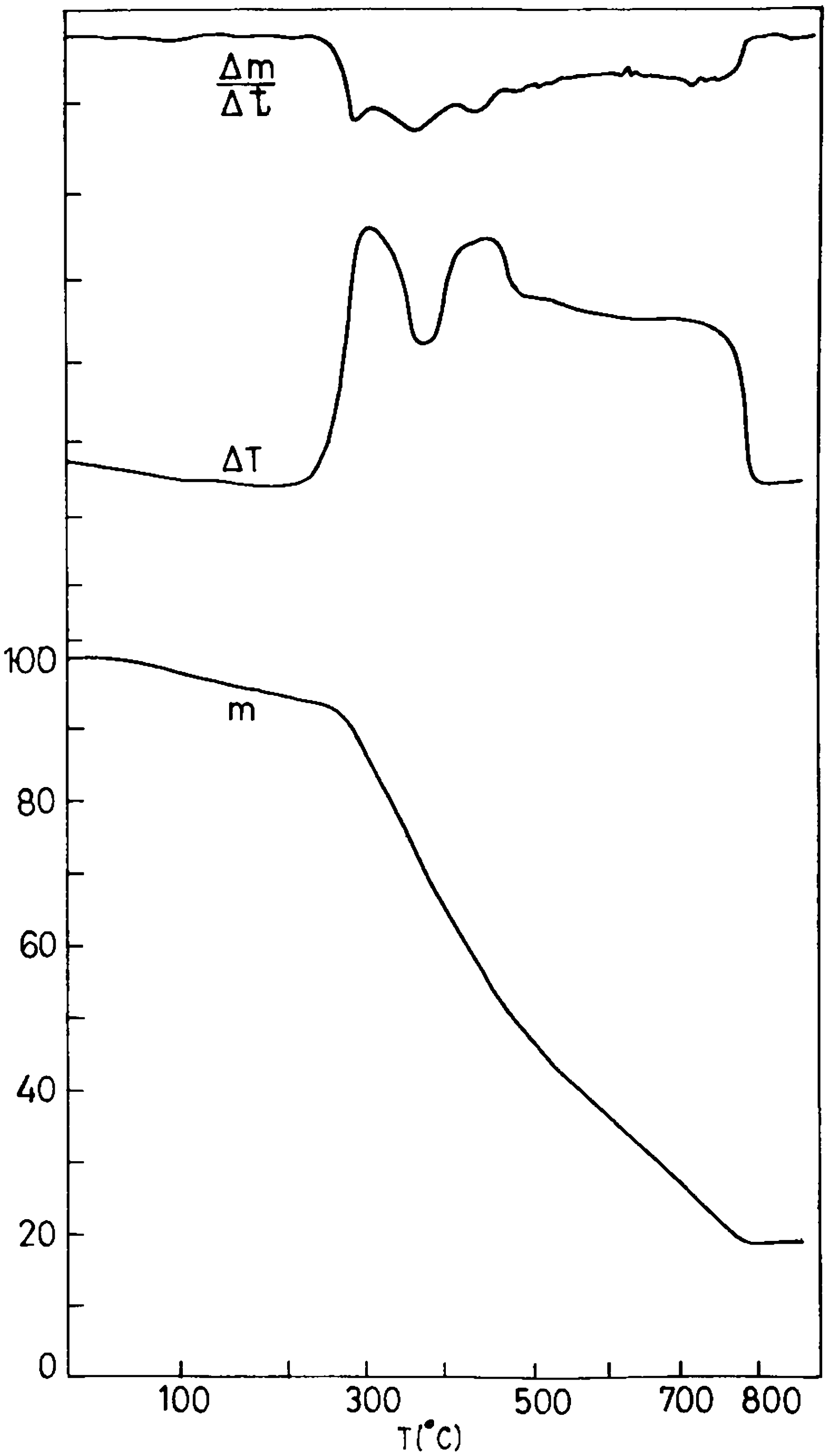


Fig.16. TG, DTG and DTA curves of $[Y_2(em)_3].4H_2O$

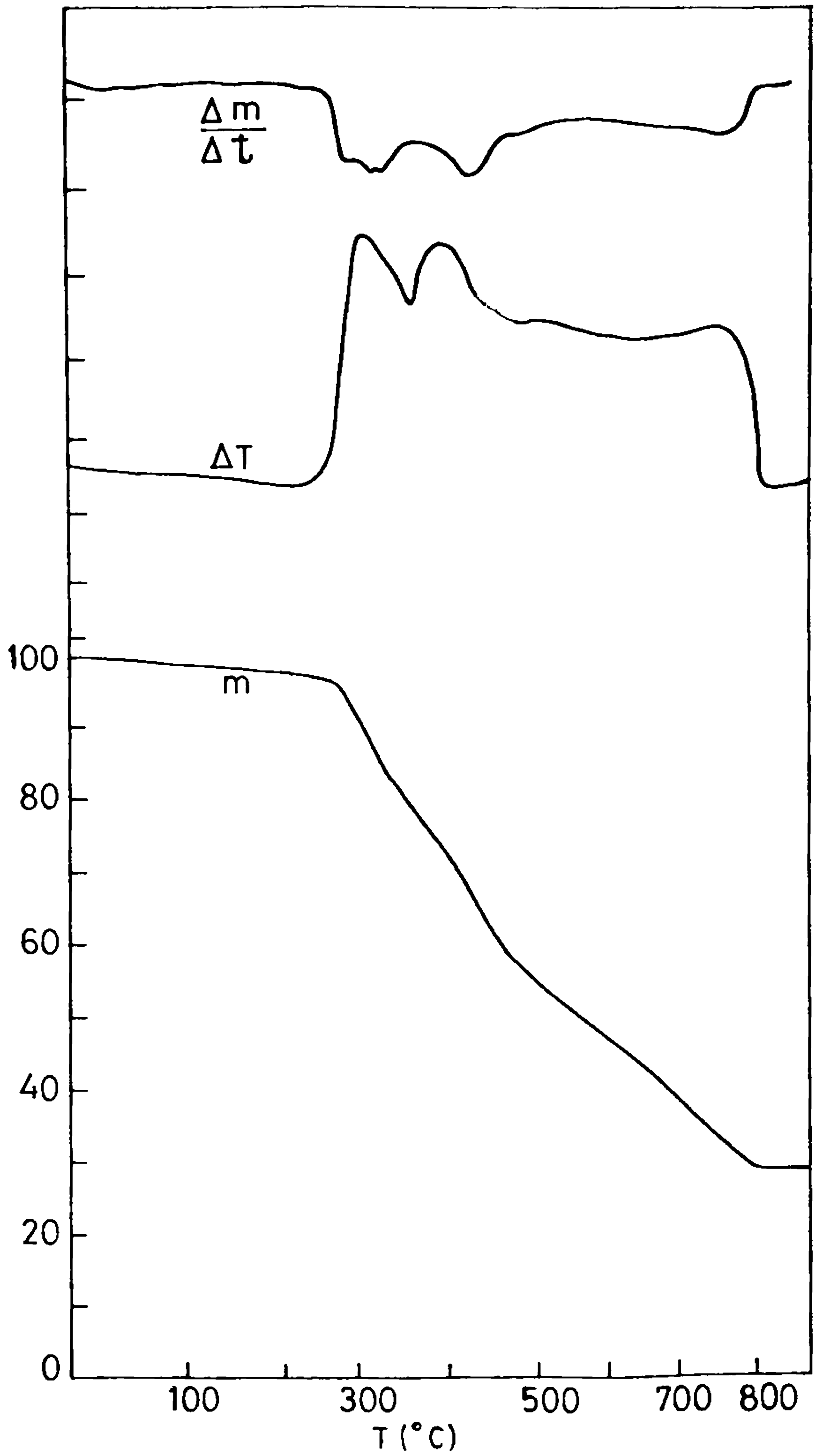


Fig.17. TG, DTG and DTA curves of $[Th(em)_2] \cdot 2H_2O$

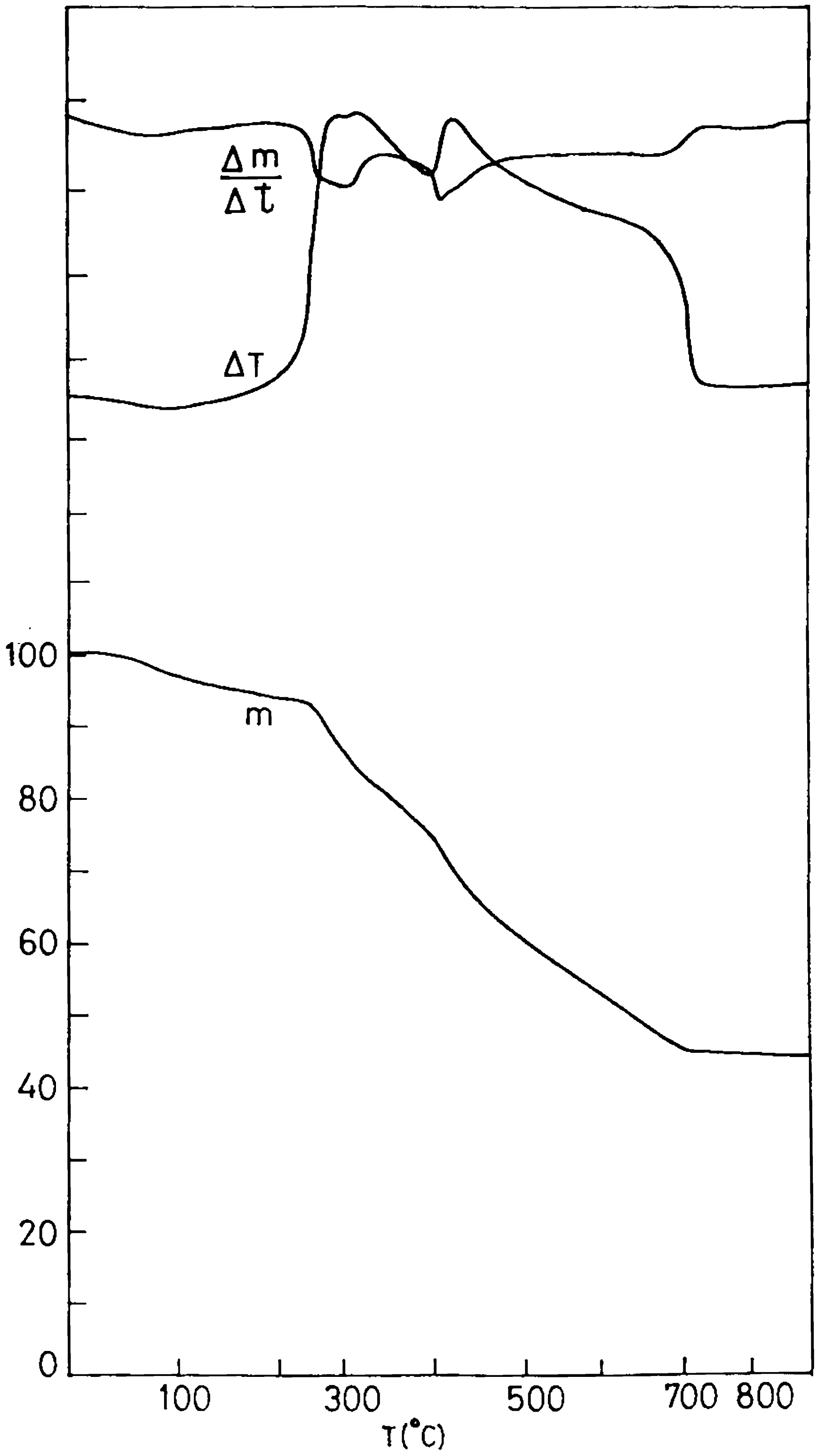


Fig.18. TG, DTG and DTA curves of $[UO_2(em)]\cdot 2H_2O$

SUMMARY

Analytical data of the metal complexes of embelin indicated a metal to ligand ratio of 1:1 in the manganese(II), cobalt (II), nickel(II), copper(II), zinc(II), cadmium(II) and uranium(VI) complexes. The chromium(III), iron(III) and the lanthanide complexes exhibited an M:L ratio of 2:3. A ratio of 1:2 was observed for the thorium(IV) complex.

Infrared spectral data indicated that embelin behaved as a tetradentate ligand in all these complexes, coordinating through its carbonyl and phenolic oxygens.

Electronic spectra and magnetic studies indicated a tetrahedrally distorted planar coordination for copper(II) complex and tetrahedral coordination for chromiun(III) and iron (III) complexes. Four-coordinated structures have been proposed for the lanthanide complexes. Thus the manganese(II), cobalt(II), nickel (II), zinc(II), and cadmium(II) complexes were octahedral; thorium(IV) complex was eight-coordinated and uranyl complex was six-cordinated.

On the basis of procedural decomposition temperatures (from thermoanalytical data) all the metal chelates investigated were shown to have enhanced thermal stabilities upon complexation. However, the divalent metal complexes of embelin were found to be thermally more stable than the iron (III), the chromium(III), the lanthanide and the actinide complexes.

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