STUDIES ON SOME NEW 3d-TRANSITION METAL COMPLEXES OF LIGANDS DERIVED FROM BENZIMIDAZOLE AND TRIAZOLE

A thesis submitted to the
Cochin University of Science and Technology
in partial fulfilment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

in

CHEMISTRY

under the Faculty of Science

by

N. SARAVANAN, M.Phil

DEPARTMENT OF APPLIED CHEMISTRY
COCHIN UNIVERSITY OF SCIENCE AND TECHNOLOGY
KOCHI - 682 022, INDIA

AUGUST, 1996

21-8-1996

Dr. K. K. Mohammed Yusuff
Professor of Inorganic Chemistry

CERTIFICATE

This is to certify that the thesis bound herewith is an authentic record of research work carried out by Shri. N. Saravanan under my supervision in partial fulfilment of the requirements for the degree of Doctor of Philosophy of Cochin University of Science and Technology, Kochi - 682 022.

(K. K. Mohammed Yusuff)

PREFACE

Triazole and benzimidazole compounds have wide applications in diverse areas like medicine, agriculture and industry. The present thesis deals with the studies on some new 3d-transition metal complexes of ligands derived from benzimidazole and triazole: 1-nitrobenzyl-2-nitrophenylbenzimidazole (NBPBI), 2-phenyl-1,2,3-triazole-4-carboxalidene-2-aminophenol (PTCAP), indole-3-carboxalidene-3-amino-1,2,4-triazole (ICAT) and 2-phenyl-1,2,3-triazole-4-carboxalidene-3-amino-1,2,4-triazole (PTCAT).

The thesis is divided into eight Chapters. Chapter I of the thesis is a brief review on the metal complexes of triazole and benzimidazole based compounds. Details regarding the analytical procedures and instrumental techniques employed in the present study are given in Chapter II. The instrumental methods employed include C, H, N micro analysis, molar conductance, magnetic susceptibility measurements, cyclic voltammetry and electronic, infrared, electron paramagnetic resonance, Mössbauer, NMR and mass spectroscopy.

Chapter III of the thesis deals with the synthesis and characterization of the NBPBI ligand and its metal complexes with cobalt(II) and copper(II).

Studies on the synthesis and characterization of some new polymer supported Schiff base complexes of cobalt(II) and copper(II) derived from NBPBI are presented in Chapter IV. The structural changes effected on supporting the complexes on the polymer matrix are also discussed in this Chapter. Chapter V of the thesis deals with the studies on some new complexes of iron(III), cobalt(II), nickel(II) and copper(II) with PTCAP.

Iron(III), cobalt(II), nickel(II) and copper(II) complexes of the ICAT have been synthesized and characterised. The results of these studies are presented in Chapter VI. Chapter VII of the thesis deals with the preparation and characterization of the complexes of PTCAT with cobalt(II), nickel(II) and copper(II).

Chapter VIII deals with the studies on the applications of some of the synthesized complexes. This Chapter comprises of two sections, section A and section B. Antibacterial activity studies of these complexes are presented in section A. Section B of this Chapter is based on the catalytic activity studies of both simple and polymer supported NBPBI complexes of cobalt(II) and copper(II). The simple cobalt(II) and copper(II) complexes have been verified for their catalytic activity in the oxidation of 3,5-di-tertiarybutylcatechol and the polymer supported complexes in the decomposition of hydrogen peroxide.

The work described in this thesis has been published as indicated below.

1. Cobalt(II) and copper(II) complexes of 1-nitro-benzyl-2-nitrophenylbenzimidazole: Synthesis, characterization and antibacterial activity studies, N. Saravanan, K. K. Mohammed Yusuff, P. V. Suresh and G. N. Prabhu, *Synth. React. Inorg. Met.-Org. Chem.* (in press).

2. New complexes of iron(III), cobalt(II), nickel(II) and copper(II) with 2-phenyl-1,2,3-triazole-4-carboxalidene-2-aminophenol, N. Saravanan and K. K. M. Yusuff, *Trans. Met. Chem.*, 21, 1 (1996).

CONTENTS

CHAPTER I

INTRODUCTION

Aromatic nitrogen heterocycles represent an important class of compounds which can act as ligands towards metal ions[1]. Azoles belong to this class, and are five-membered heterocyclic ligands containing two or more heteroatoms, one of which must be nitrogen. These compounds have been paid considerable attention due to their wide applicability in medicines[2-7]. Unlike the azines, which are π-acceptor six-membered nitrogen heterocycles, the azoles are π-donors. Azoles can also exist as anionic ligands by deprotonation of acidic N-H groups in the free ligand, and thus can act as strong σ donors. Metal-ligand interactions in the complexes of the latter are governed by the specific metal, the substituents on the ligand and pH of the medium allowing for the synthesis of complexes of varied structural features[1,8].

Synthesis of the azole ligands and information about their acid/base dissociation constants, dipole moments, and its NMR and UV spectra have been presented by Schofield *et al*[9]. Many such ligands are commercially available or can be easily synthesized by a variety of condensation and ring-closure reactions[9-11].

Triazoles are five-membered heterocyclic ligands containing three nitrogen donor atoms in its structure. They find application in various fields like agriculture[12,13] and industry. Some triazole derivatives have been reported to act as antimicrobic or cytostatic agents[14]. A wide range of triazole compounds are known to exhibit activity against phytopathogenic fungi[15,16]. They also find application in photographic process, corrosion control and dye industry. For example, 5-amino-1,2,4-triazole is the precursor of additives used in photography and products with known anticorrosion properties[17,18]. 3-Amino-1,2,4-triazole is used in the synthesis of diazahemicyanine dyes[19]. To prevent leaching of copper from copper pipes in refrigerators, a copper chelating agent like azole is added to polyoxyalkylene glycol lubricating oil used in refrigerators.

Apart from their wide range of applications, the varied structural aspects of their coordination compounds also cause considerable interest in these compounds.

Triazoles and benzimidazoles have attracted the interest of coordination chemists due to the possibility of their complexes mimicking the properties of biological coordination compounds and also due to the enhancement of their biological activity upon coordination.

Described herein are some examples illustrating the coordination behaviour of triazoles and benzimidazoles.

Triazoles are versatile ligands and are known to form mononuclear, binuclear, trinuclear, tetranuclear, pentanuclear or polynuclear complexes and also complexes with chain or layer type structures depending on the nature of chelation of these ligands with the metal ions.

COMPLEXES OF 1,2,4-TRIAZOLES

1,2,4-Triazole is capable of acting as a bridging ligand, either with or without deprotonation[20]. The neutral ligand can coordinate as the 4-H tautomer through N_1 and N_2 in a manner analogous to that of pyrazolate anion, or as the 1-H tautomer through N_2 and N_4 in a configuration similar to that of the imidazolate anion[20]. Similarly the deprotonated 1,2,4-triazolate anion can be involved in N_1, N_2 or N_2, N_4 bridging or even act as a tridentate ligand with coordination to all three nitrogen atoms. All these possibilities are known[20]. Further, it has been reported that 4-H or 4-substituted triazoles can form single or multiple bridges[20]. Various bridging modes of the triazole and triazolate anion are shown in Figure 1.

The first coordination compound with 1,2,4-triazole was described in 1900[21]. Until 1970, most of the papers on this subject dealt with copper compounds of the type, $[CuCl_2(Htrz)]$, $[CuCl(trz)(H_2O)_2]$ and $[Cu(trz)_2]$[22–28], in which trz stands for the deprotonated form of 1,2,4-triazole. After 1970, a large number of papers on coordination behaviour of both substituted and unsubstituted 1,2,4-triazoles have been reported[29–32]. Several binuclear, trinuclear and tetranuclear metal complexes of iron[33,34], cobalt[35–38], nickel[39–42], copper[39,43–45], zinc[46], cadmium[47], ruthenium[48–50] and palladium[51] have been reported and these polynuclear structures have resulted through different bridging mode of chelation. X-ray crystal structure

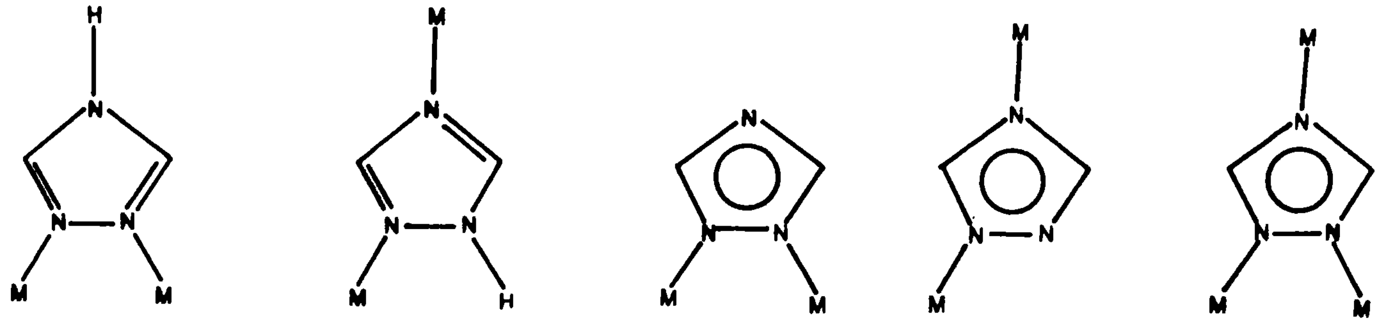


Figure 1. Bridging modes of 1,2,4-triazole and 1,2,4-triazolate

studies of a number of such complexes have been appeared in the literature[36,37,52-59].

Because of the interesting chelating possibilities, some novel mixed ligand complexes, organometallic complexes and heteronuclear complexes, involving 1,2,4-triazole derivatives have been synthesised. Table I shows a list of some transition metal complexes of 1,2,4-triazole ligands with different type of structures arising due to various chelating possibilities.

Mixed ligand phosphine complexes of Pd^0 and Pt^0 with 1,2,4-triazole-3(S)-thiol were prepared and characterized[60]. Mixed ligand complexes of bivalent metal ions with 4-amino-5-mercapto-3-methyl-1,2,4-triazole and glycine or alanine[61] were also reported. 4-Amino-3,5-bis(pyridin-2-yl)-1,2,4-triazole (APT), acts as an ambidentate ligand and forms two bidentate coordination isomers of $Ru(CO)_2Cl_2$, which in one case is coordinated to a pyridyl ring and an adjacent triazole ring, and in other case to a pyridyl ring and the amino nitrogen atom. Both isomers of $Ru(CO)_2Cl_2(APT)$ were crystallographically characterized. Bromo and iodo analogues were also isolated and characterized[62].

The heteronuclear complexes with 1,2,4-triazole ligands have been first reported[37] by Groeneveld *et al.* They have prepared the heterotrinuclear Zn^{II}-Co^{II}-Zn^{II} and Co^{II}-Co^{II}-Zn^{II} complexes with 4-t-butyl-1,2,4-triazole. Recently, another heterotrinuclear

Mn^{II}-Ni^{II}-Mn^{II} complex was synthesised using 3-methyl-4-phenyl-1,2,4-triazole with the anion species, tetrafluoroborate or perchlorate. This compound was claimed to be the first linear heterotrinuclear compound. In this compound, the terminal M^{II} ions are in a different chemical environment compared to the central one and this has been attributed to a significant difference in the ionic radius of the metal involved and consequent unequivalent coordination sites. This unequivalency of coordination sites has been reported to be the criterion for the formation of pure and stable heteronuclear compounds. Mn^{II} and Ni^{II} were found to be the best combinations for this purpose. The combinations of other M^{II} transition metal salts also yielded linear trinuclear mixed metal compounds. However, only in the case of Ni^{II} and Mn^{II} combination, sufficiently pure samples were obtained. These type of heteronuclear compounds may work as precursors for new magnetic materials. Thermal decomposition of mixed metal (Fe^{3+}-Co^{2+}) complexes of 3-amino-1,2,4-triazole has yielded new ferromagnetic material[63]. The oxide product formed during the thermal decomposition of the iron(III) complex of 3-amino-1,2,4-triazole (on heating to a temperature above 500 ^{o}C) was also found to be ferromagnetic.

Exchange interactions are possible when triazole units bridge paramagnetic metal ion. Such interactions lead to interesting magnetic behaviour. Evidences for antiferromagnetic interactions are observed in a number of cases[64-76]. In all these complexes, 1,2,4-triazoles act as bridging ligands.

Complexes with spin-crossover behaviour are also known in the case of 1,2,4-triazole ligands. An iron(II) complex of 4-ethyl-1,2,4-triazole was reported to exhibit such a phenomenon[77]. Furthermore, a spin transition system with thermal hysteresis at room temperature has been found to occur with the complex, $[Fe(Htrz)_{2.85}(4\text{-}NH_2trz)_{0.15}](ClO_4)_2$. In this case, the spin transition is accompanied by a dramatic change of colour: the complex is violet in the S = 0 state and white in the S = 2 state. Both these states were reported to be stable at room temperature[78].

Table I

Complexes of 1,2,4-triazoles

Complex	Ligand	Nature	Ref.
$[MnL(H_2O)_2]_2$	1-(α-hydroxy-naphthyl-2,3'-methyl-5'-mercapto-1',2',4'-triazole)-2-azaethane	octahedral	13
$[Mn_3L_6(H_2O)_6]X_6(H_2O)_x$ X = ClO_4 or BF_4	3-methyl-4-ethyl-1,2,4-triazole	octahedral (bridging)	37
$[Mn_2L_5(NCS)_4]$	4-allyl-1,2,4-triazole	octahedral (bridging)	36

Complex	Ligand	Nature	Ref.
$[MnL_2(SCN)_2]_n$	3,5-diamino-1,2,4-triazole	octahedral (bridging)	54
$[FeL_2(TCNQ)_2]$	3,5-bis(pyridin-2-yl)4-amino-1,2,4-triazole	octahedral	53
$[FeL_2(SeCN)_2]$	4,4-bi-1,2,4-triazole	octahedral	79
$[Fe_2L_5(NCS)_4]$	4-allyl-1,2,4-triazole	octahedral (bridging)	36
$[Fe_3L_6(H_2O)_6]$	3-methyl-4-ethyl-1,2,4-triazole	octahedral (bridging)	37
$[CoL(H_2O)_2]_2$	1-(α-hydroxy-naphthyl-2,3'-methyl-5'-mercapto-1',2',4'-triazole)-2-azaethane	octahedral	13
$[Co_3L_8(NCS)_4](NCS)_2(H_2O)_9$	4-t-butyl-1,2,4-triazole	octahedral	37
$[Co_3L_4(NCS)_6](H_2O)_2$	4-t-butyl-1,2,4-triazole	octahedral/tetrahadral	37
$[Co_3L_6(H_2O)_6]X_6(H_2O)_x$ (X = ClO_4 or BF_4)	3-methyl-4-ethyl-1,2,4-triazole	octahedral (bridging)	37
$[Co_3L_6(H_2O)_6]_2$	3-methyl-4-ethyl-1,2,4-triazole	octahedral (bridging)	80–82

Complex	Ligand	Nature	Ref.
$[Co_3L_8(H_2O)_4]CF_3(SO_3)_{12}\cdot(H_2O)_{12}$	3-methyl-4-ethyl-1,2,4-triazole	octahedral (bridging)	80-82
$[Co_2L_4(H_2O)(NCS)_4](H_2O)_2$	4-allyl-1,2,4-triazole	octahedral (bridging)	36
$[CoL_2(H_2O)_2]X_2$ (X = Cl or Br)	3-acetyl-amino-1,2,4-triazole	octahedral	83
$[CoL_2(TCNQ)_2]$	3,5-bis(pyridin-2-yl)-4-amino-1,2,4-triazole	octahedral	53
$[NiL_2(TCNQ)_2]$	3,5-bis(pyridin-2-yl)-4-amino-1,2,4-triazole	octahedral	53
$[NiL_2(H_2O)_2]Cl_2$	3-acetyl-amino-1,2,4-triazole	octahedral	83
$[Ni_2L_4(H_2O)(NCS)_4](H_2O)_2$	4-allyl-1,2,4-triazole	octahedral (bridging)	36
$[Ni_3L_6(H_2O)_6]X_6(H_2O)_x$ (X = ClO_4 or BF_4)	3-methyl-4-ethyl-1,2,4-triazole	octahedral (bridging)	37
$[NiL(H_2O)_2]_2$	1-(α-hydroxy-naphthyl-2,3'-methyl-5'-mercapto-1',2',4'-triazole)-2-azaethane	octahedral	13

Complex	Ligand	Nature	Ref.
$[Cu_3L_6Cl_4]Cl_2$	4-amino-3,5-bis-(hydroxy-1,2,4-triazole)	octahedral (bridging)	70
$[Cu_3L_9(H_2O)_3](CF_3SO_3)_6 \cdot (H_2O)_x$	4-ethyl-1,2,4-triazole	octahedral	73,74, 56
$[Cu_3L_9(H_2O)_3](CF_3SO_3)_6$	4-ethyl-1,2,4-triazole	octahedral	73,74, 56
$[\{Cu(dien)_3\}_2L](ClO_4)_3$	5,5'-diamino-3,3'-bis-1,2,4-triazole	planar	84
$[CuL(H_2O)(OH)]$	3-amino-1,2,4-triazole	octahedral (solution)	85
$[Cu(HL)L(OH)(H_2O)]$ and $[CuL(NO_3)]$	3-amino-1,2,4-triazole	polymeric	85
$[CuL_2(H_2O)_2]X_2$ (X = Cl or Br)	3-acetyl-amino-1,2,4-triazole	octahedral	83
$[CuL(H_2O)_2]_2$	1-(α-hydroxy-naphthyl-2,3'-methyl-5'-mercapto-1',2',4'-triazole)-2-azaethane	octahedral	13
$[CuL_2(NCS)_2]$	3-acetyl-amino-1,2,4-triazole	octahedral	83

Complex	Ligand	Nature	Ref.
$[CuL_2(H_2O)_2](SO_4)(H_2O)_5$	3-acetyl-amino-1,2,4-triazole	octahedral	86, 83
$[Cu(HL)_2(H_2O)_2]$	3-amino-5-carboxy-1,2,4-triazole	octahedral	87
$[CuL_2(TCNQ)_2]$	3,5-bis(pyridin-2-yl)-4-amino-1,2,4-triazole	octahedral	53
$[CuLCl]$	1,3-bis[3-(5-amino-1,2,4-triazolyl)-triazene	planar	88
$[ZnL_2(NCS)_2]$	4-t-butyl-1,2,4-triazole	tetrahedral	88
$[ZnL_2(H_2O)_2](ClO_4)_2$	3,5-di-(2-pyridyl)-4-amino-1,2,4-triazole	octahedral	89

COMPLEXES OF 1,2,3-TRIAZOLES

The coordination chemistry[90] of 1,2,3-triazole appears to be quite different from that of 1,2,4-triazoles. This section covers ligands containing the 1,2,3-triazole ring systems. These include, in addition to the parent triazole, various N- and C- substituted triazoles and benzotriazoles. All of these molecules, with exception of the N-substituted triazoles, are capable of coordinating in anionic as well as neutral form. 1,2,3-Triazole, first prepared by von Pechmann in 1888[62], is a weak acid (pK_a = 9.26)[91] and exists as a mixture of tautomeric forms. Benzotriazole, first correctly formulated by Ladenburg in 1876[92], is also a weak acid[91] (pK_a = 8.38) and displays similar tautomerism. The use of 1,2,3-triazoles, notably benzotriazole and naphthotriazole, as corrosion inhibitors for copper and as quantitative precipitating agents for copper and the platinum group metals[93] has contributed substantially to the interest in the coordination chemistry of these ligands. Moore and Robinson reviewed complexes of 1,2,3-triazoles with some transition metal ions[94]. A list of some transition metal complexes of benzotriazoles (btaH), deprotonated benzotriazoles (bta) and 1,2,3-triazoles (taH) with different chelation possibilities are given in Table II.

Table II

Complexes of 1,2,3-triazoles

Complex	Mode of chelation	Reference
$[MnCl_2(btaH)_2]$	monodentate	95
$[Fe(CN)_5(btaH)]^{3-}$	monodentate	96
$[Fe(taH)(C_5H_5)(CO)_2](HSO_4)$	monodentate	97
$[CoCl_2(btaH)_2]$	monodentate	98
$[NiCl_2(btaH)_2]$	monodentate	98
$[Cu(bta)_2(H_2O)]_n$	bridging	99
$[ZnCl_2(btaH)_2]$	monodentate	100
$[Mo_2(btaH)_3(CO)_6]$	bridging	101
$[AgNO_3(btaH)_2]$	mono/bridging	102
$[CdCl_2(btaH)_2]_2$	monodentate	95
$[OsH(bta)(btaH)(CO)(PPh_3)_2]$	mono/bidentate	103
$[Ir(CO)(PPh_3)_2(bta)]$	monodentate	104
$[HgMe(bta)]_2$	bridging	105

btaH = benzotriazole; bta = deprotonated benzotriazole and taH = 1,2,3-triazole

COMPLEXES OF SCHIFF BASES DERIVED FROM TRIAZOLE COMPOUNDS

Schiff bases (imines) are the compounds formed by the condensation of carbonyl compounds with amines[106]. Metal ions contribute to the formation of Schiff bases by creating stable complexes, thus producing a favourable overall free energy of reaction[107]. Throughout the years, Schiff bases have played a central role as chelating ligands for a large variety of metal ions. Both synthesis and properties of Schiff base complexes are very often intimately related to the associated metal ions. Apart from the obvious implications for synthetic coordination chemistry, aspects of the topic are of relevance to those whose interests include organic synthesis in the presence of metal ions, areas of metal-ion catalysis, and biochemical reactions involving Schiff bases. Further, a literature survey reveals that there are only few Schiff base complexes of triazoles, and the existing references are given in Table III.

Table III

Schiff base ligands and their complexes
derived from triazole compounds

Ligand	Metal	Reference
Terephthalidene-4-amino-3-hydrazino-5-mercapto-1,2,4-triazole	Ni, Cu and Zn	108
Terephthalidene-4-amino-3-hydrazino-5-hydroxy-1,2,4-triazole	Ni and Zn	108
Pyridine-2-carboxalidene-3-amino-1,2,4-triazole	Co, Ni and Cu	109

Ligand	Metal	Reference
Mesterolone-3-amino-1,2,4-triazole	Co and Ni	110
5-Mercapto-4-salicylalidene-amino-3-trifluromethyl-*s*-triazole	Co, Ni, Cu, Zn and Cd	111
5-Mercapto-4-salicylalidene-*s*-triazole	Co, Ni,Cu, Zn and Cd	112
4-(2-Hydroxy-1-naphthalmethylene-amino-5-2-mercapto-*s*-triazole	Co, Ni,Cu, Zn and Cd	112
4-(*p*-Dimethyl-amino-benzylidene-amino)-5-mercapto-*s*-triazole	Co, Ni, Zn and Cd	112
Salicylalidene-3-amino-1,2,4-triazole	Mn, Co, Ni and Cu	113
Hydroxybenzylidene-3-amino-1,2,4-triazole	Mn, Co and Cu	113
4-Hydroxy-3-methoxy-benzylidene-3-amino-1,2,4-triazole	Mn, Co, Ni and Cu	113
Salicylalidene-4-amino-3-ethyl-5-mercapto-*s*-triazole	Co, Ni, Cu, Zn and Cd	114
2-Hydroxy-1-naphthalidene-4-amino-3-ethyl-5-mercapto-*s*-triazole	Co, Ni, Cu, Zn and Cd	114
Phenyl-1,2,3-triazole-4-carboxalidene-aniline	Cu	115, 116
2-Phenyl-1,2,3-triazole-4-carboxalidene-2-aminophenol	Fe, Co, Ni and Cu	117

METAL COMPLEXES OF BENZIMIDAZOLES

Benzimidazoles play a significant role in determining the function of a number of biologically important metal complexes[118]. Benzimidazole is a planar molecule, as expected for an aromatic system. The resonance energies of benzimidazole and naphthalene are comparable. The benzimidazoles contain a phenyl ring fused to an imidazole ring. These compounds have a hydrogen atom attached to nitrogen and can readily tautomerise.

Imidazole and benzimidazole are amphoteric in nature. They are moderately strong organic bases capable of accepting protons at N-3 as well as weak acids capable of losing a proton from N-1. Therefore, in neutral solutions the unprotonated molecule usually functions as a unidentate ligand through the unshared pair of electrons on N-3. The probability of participation of the pair of electrons on N-1 in coordination is very small, because these electrons are delocalized throughout the π-system. However, neutral imidazole undergoes deprotonation at N-1 in strongly basic solution, and the resulting aromatic imidazolate ion possesses two equivalent sites for coordination[119,120].

Fusion of benzene ring at position 4 and 5 in benzimidazole does not perturb the electronic configuration of the heterocyclic ring or alter the properties considerably from that of imidazole. However, due to the increased size of the ligand, the maximum number of benzimidazole molecules that has been reported to coordinate with a metal ion is four[121]. A very large number of research papers have been published on transition metal complexes of benzimidazole derivatives. While some of the reports are on the applied aspects of these complexes such as their role in the protection of metals from corrosion, their use as antifungal, antibacterial, antiviral and antifouling agents etc., a few number of articles describe with agrochemicals such as fungicides and bactericides. Metal complexes of pyridylbenzimidazole are uv absorbers which are resistant to degradation by uv-light and useful in plastics for providing long-term protection against uv-light, which are important from an industrial point of view. Further, a large number of papers deal with the syntheses and structural studies of these complexes.

A detailed review of literature on the benzimidazole complexes of iron, cobalt, nickel and copper have been published[122]. This review (till 1989) elaborates some of the structural properties of these complexes revealed by magnetic susceptibility measurements, electronic, infrared, and electron proton resonance, and crystal structure determinations, and the biological importance of such complexes. The Table IV presents a list of some of the recent references on the complexes of benzimidazoles.

Table IV

Complexes of benzimidazoles

Ligand	Metal	Reference
Tris(2-benzimidazolylmethyl)amine	Manganese	123
N-(Benzimidazole-2-ylmethyl)salicylalimine	Iron	124
Benzimidazol-2-yl-methyl (2-hydroxy-benzyl)amine	Iron	124
Benzimidazol-2-ylmethyl-(2-hydroxy-5-nitrobenzyl)amine	Iron	124
Bis-(benzimidazol-2-ylmethyl-amine)	Iron	124
Tris[(N-ethylbenzimidazol-2-yl)-methyl]amine	Iron	125
Tris(2-benzimidazolimethyl)amine	Iron	126
Bis-[2,6-bis(1'-methylbenzimidazol-2'-yl)-pyridine	Cobalt	127
2-Methylbenzimidazole	Cobalt	128
1,2,4,5-Tetrakis(benzimidazol-2-yl)benzene	Cobalt	129
2-Methylbenzimidazole	Cobalt	130
Tris(2-benzimidazolimethyl)amine	Cobalt	126

Ligand	Metal	Reference
Tris(2-benzimidazol-imethyl)amine	Nickel	126
2,6-Bis(2-benzimidazolyl)-pyridine	Copper	131
Bis(2-benzimidazolyl-methyl)-amine	Copper	132
N-(2-Hydroxyethyl)-bis-(2-benzimidazolylmethyl)-amine	Copper	132
Bis[bis(benzimidazol-2-yl-methyl)amine]	Copper	133
Bis(benzimidazolyl)-tetra-thioether	Copper	134
Bis(benzimidazolyl)-penta-thioether	Copper	134
N,N',N"-Tris-s-(2-benzothiazolyl-methylamine)	Copper	135
2-Methylbenzimidazole	Copper	136
1-(2-Hydroxyphenyl)-2-aza-3,5-bis(benzimidazol-2-yl)-pentane	Copper	137
1-(2-Hydroxy-5-bromophenyl)-2-aza- 3,5-bis (benzimidazol-2-yl)-pentane	Copper	137

Ligand	Metal	Reference
N,N,N',N'-Tetrakis-[(2-benzimidazolyl)-2-hydroxy-1,3-diaminopropane]	Copper	138
1,2,4,5-Tetrakis(benzimidazol-2-yl)benzene	Copper	139
2-[Bis(2-benzimidazolylmethylamino]-methyl-4-methyl-6-[2-benzimidazolylmethyl)-(benzyl)-amino]-methylphenol	Copper	140

SCOPE OF THE PRESENT INVESTIGATION

The fast moving and expanding development in the chemistry of coordination compounds is due to their applicability in various fields of current interest, mainly in medicine, agriculture and chemical industry. A number of reports on the triazoles and benzimidazoles have appeared in the scientific literature because of their remarkable bioactivity which has been shown to be related to their metal complexing ability. Further, such type of compounds are part of many biological coordination compounds, which are so complex that the function of metal ions can be understood only by studying simple model compounds.

The quest for the model compounds has been the focus of attention of a very large number of coordination chemists. Whatever be measure of success of the numerous model compounds synthesized in mimicking the properties of the natural compounds, these studies have yielded at least very interesting coordination compounds.

The objectives of the present study include the following:

1. The synthesis and characterization of metal complexes with ligands containing a large number of potential donor sites have always been a challenging problem to the coordination chemists. Triazoles and benzimidazoles have more than one potential donor sites and these sites can be further increased by including them as a part of the Schiff base ligands. The ligands selected for the present study are 1-nitrobenzyl-2-nitrophenyl-benzimidazole (NBPBI), 2-phenyl-1,2,3-triazole-4-carboxalidene-2-aminophenol (PTCAP), indole-3-carboxalidene-3-amino-1,2,4-triazole (ICAT) and 2-phenyl-1,2,3-triazole-4-carboxalidene-3-amino-1,2,4-triazole (PTCAT). A search through the literature has revealed some untouched aspects about the complexes of these ligands. It was therefore thought worthwhile and interesting to synthesise some new transition metal complexes with these ligands and characterize them using various physicochemical techniques like elemental analyses, molar conductance, magnetic susceptibility measurements, cyclic voltammetry and UV-visible, infrared, and electron paramagnetic resonance and thermal studies.

2. Most of the benzimidazoles and triazoles exhibit biological activity. Furthermore, there are reports that such activity will be

further enhanced on complexation. A study was therefore planned to know the antimicrobial activity of cobalt(II) and copper(II) complexes of NBPBI.

3. Some of the complexes reported herein have vacant coordination sites. It was therefore thought that such complexes would act as catalysts. A study was therefore undertaken to screen the catalytic activity of the complexes of cobalt(II) and copper(II) derived from NBPBI.

4. More often the heterogeneous catalysts are used for industrial purposes. Ease of the separation procedure and hence cost of production involving such catalysts would be lower, when compared to the production cost involving homogeneous catalysts. Thus, there is a greater enthusiasm among the chemists for the development of heterogenized catalysts. A catalytic study involving heterogenized (polymer supported) metal complexes has also been included as a part of the present study.

REFERENCES

1. J. Reedjik, in G. Wilkinson, R. D. Gillard and J. A. McCleverty (Eds.), "*Comprehensive Coordination Chemistry*", Vol. 2, Pergamon Press, Oxford, p. 73, 1987.

2. D. Sanglard, K. Kuchler, F. Ischer, J. C. Pagani, M. Monod, J. Bille, *Antimicrobial agents and chemotherapy*, 39, 2378 (1995).

3. M. A. Ghannoum, Y. Fu, A. S. Ibrahim, C. A. Mortara, M. C. Shafiq, J. E. Edwards, and R. S. Criddle, *Antimicrobial agents and chemotherapy*, 39, 2459 (1995).

4. J. E. Sjostorm, J. Fryklund, T. Kuhler and H. Larsson, *Antimicrobial agents and chemotherapy*, 40, 621 (1996).

5. F. C. Odds, G. Dams, G. Just and P. Lewi, *Antimicrobial agents and chemotherapy*, 40, 588 (1996).

6. E. M. Narcisi and W. E. Secor, *Antimicrobial agents and chemotherapy*, 40, 1121 (1996).

7. F. Z. E. Ablack, M. A. Metwally, *Pak. J. Sci. Ind. Res.*, 36, 77 (1993).

8. E. C. Constable and P. J. Steel, *Coord. Chem. Rev.*, 93, 205 (1989).

9. K. Schofield, M. R. Grimmett and B. R. T. Keene, "*The Azoles*", Cambridge Univeristy Press, Cambridge, 1976.

10. A. Weissberger and E. C. Taylor (Eds.), "*The Chemistry of Heterocyclic Compounds*", Wiley, New York, 1980.

11. K. T. Finley, ref. 10, "*Triazoles*", Vol. 39, Wiley, New York, 1980.

12. G. S. Basarab, M. Pifferitti and M. M. Bolinski, *Pestic. Sci.*, 31, 403 (1991).

13. K. C. Satpathy, A. K. Panda, R. Mishra, A. P. Chopdar and S. K. Pradhan, *Trans. Met. Chem.*, 16, 628 (1991).

14. R. Bohm and C. Karow, *Die Pharmazie*, 4, 243 (1981).

15. S. C. Bahal, B. L. Dubey, N. Nath and J. K. Srivastava, *Inorg. Chim. Acta*, 91, L43 (1984).

16. M. Nadasy, *Magy Kem. Lapja*, 36, 518 (1981).

17. D. L. Cash and A. N. Ferguson, *J. Photogr. Sci.*, 28, 12 (1980).

18. D. L. Smith and H. L. Luss, *Photogr. Sci. Eng.*, 20, 15 (1976).

19. Kirk-Othmer, "*Encyclopedia of Chemical Technology*, 4th Edn., John Wiley & Sons, 8, 590 (1994).

20. P. J. Steel, Coord. Chem. Rev., 106, 227 (1990).

21. O. Hantzsch and O. Silberrad, *Chem. Ber.*, 33, 58 (1900).

22. I. de Paolini and C. Goria, *Gazz. Chim. Ital.*, 62, 1048 (1932).

23. M. Inoue, M. Kishita and M. Kudo, *Inorg. Chem.*, 4, 626 (1965).

24. M. Inoue and M. Kudo, *Inorg. Chem.*, 5, 70 (1966).

25. M. J. Campbell, R. Grzeskowiak and M. Goldstein, *Spectrochim. Acta* (Part A), 24, 1149 (1968).

26. M. Inoue, S. Emori and M. Kudo, *Inorg. Chem.*, 7, 1427 (1963).

27. D. E. Billing, *J. Inorg. Nucl. Chem.*, 31, 137 (1969).

28. K. Hyde, G. F. Kokoszka and G. Gordon, *J. Inorg. Nucl. Chem.*, 31, 1993 (1969).

29. J. G. Haasnoot, G. Vos and W. L. Groeneveld, *Z. Naturforsch.*, Teil B, 32, 533 (1977).

30. L. R. Groeneveld, G. Vos, S. Gorter and J. G. Haasnoot, *Acta Crystallogr.*, B38, 2248 (1982).

31. G. Vos, *Ph. D. Thesis*, State University of Leiden, 1983.

32. G. Vos, J. G. Haasnoot, G. C. Verschoor and J. Reedijk, *Inorg. Chim. Acta* (in press).

33. G. Vos, R. A. le Fêbre, R. A. G. de Graaff, J. G. Haasnoot and J. Reedijk, *J. Am. Chem. Soc.*, 105, 1682 (1983).

34. D. W. Engelfriet and G. C. Verschoor, *Acta Crystallogr.*, B37, 237 (1981).

35. R. J. Rietmeijer, G. A. van Albada, R. A. G. de Graaff, J. G. Haasnoot and J. Reedijk, *Inorg. Chem.*, 24, 3597 (1985).

36. G. Vos, J. G. Haasnoot, G. C. Verschoor and J. Reedijk, *Inorg. Chim. Acta*, 102, 187 (1985).

37. L. R. Groeneveld, R. A. le Fêbre, R. A. G. de Graaff, J. G. Haasnoot, G. Vos and J. Reedijk, *Inorg. Chim. Acta*, 102, 69 (1985).

38. W. Vreugdenhil, S. Gorter, J. G. Haasnoot and J. Reedijk, *Polyhedron*, 4, 1769. (1985).

39. G. A. van Albada, R. A. G. de Graaff, J. G. Haasnoot and J. Reedijk, *Inorg. Chem.*, 23, 1404 (1984).

40. C. W. Reimann and M. Zocchi, *Acta Crystallogr.*, B27, 682 (1971).

41. D. W. Engelfriet, J. G. Haasnoot and W. L. Groeneveld, *Z. Naturforsch.*, Teil A, 32, 783 (1977).

42. D. W. Engelfriet, W. den Brinker, G. C. Haasnoot and S. Gorter, *Acta Crystallogr.*, B35, 2922 (1979).

43. M. G. B. Drew, P. C. Yates, F. S. Esho, J. T. Grimshaw, A. Lavery, K. P. McKillop, S. M. Nelson and J. Nelson, *J. Chem. Soc., Dalton Trans.*, 2995 (1988).

44. M. G. B. Drew, P. C. Yates, J. T. Grimshaw, K. P. McKillop and S. M. Nelson, *J. Chem. Soc., Chem. Commun.*, 262 (1985).

45. J. F. Geldard and F. J. Lions, *Org. Chem.*, 30, 318 (1965).

46. D. W. Engelfriet, W. den Brinker, G. C. Verschoor and S. Gorter, *Acta Crystallogr.*, B35, 2922 (1979).

47. L. R. Groeneveld, G. Vos, G. C. Verschoor and J. Reedijk, *J. Chem. Soc., Chem. Commun.*, 620 (1982).

48. L. A. Oro, M. T. Pinillos, C. Tejel, C. F. Foces and F. H. Cano, *J. Chem. Soc., Dalton Trans.*, 2193 (1986).

49. L. A. Oro, M. T. Pinillos, C. Tejel, C. F. Foces and F. H. Cano, *J. Chem. Soc., Chem. Commun.*, 1687 (1984).

50. L. A. Oro, M. T. Pinillos, C. Tejel, C. F. Foces and F. H. Cano, *J. Chem. Soc., Dalton Trans.*, 1087 (1986).

51. A. Tiripicchio, F. J. Lahoj, L. A. Oro, M. T. Pillinos and C. Tejel, *Inorg. Chim. Acta*, 100, L5 (1985).

52. M. B. Cingi, A. M. M. Lanfredi, F. Ugozzoli, J. G. Haasnoot and J. Reedjik, *Inorg. Chim. Acta*, 209, 219 (1993).

53. J. P. Cornelissen, J. H. van Diemen, R. L. Groeneveld, J. G. Haasnoot, A. L. Spek and J. Reedijk, *Inorg. Chem.*, 31, 198 (1992).

54. A. C. Fabretti, A. Giusti and R. Sessoli, *Inorg. Chim. Acta,* 205 53 (1993).

55. Y. Pei, A. Lang, P. Bergerat, O. Kahn, M. Fettouhi and L. Ouahab, Inorg. Chem., 35, 193 (1996); P. J. van Koningsbruggen, J. M. Hal, R. A. G. de Graaff, J. G. Haasnoot and J. Reedijk, *J. Chem. Soc., Dalton Trans.*, 2163 (1993).

56. G. Vos, J. G. Haasnoot, G. C. Verschoor, J. Reedijk and P. E. L. Schaminee, *Inorg. Chim. Acta*, 105, 31 (1985).

57. A. K. Sen, S. N. Dubey and P. J. Squatterito, *Acta Cryst.*, C52, 865 (1996).

58. G. Net, J. C. Bayon, P. Esteban, P. G. Rasmussen, A. A. Larena and J. F. Piniella, *Inorg. Chem.*, 32, 5313 (1993).

59. A. L. Rheingold, P. Saisuwan and N. C. Thomas, *Inorg. Chim. Acta*, 214, 41 (1993).

60. R. N. Pandey, A. N. Sahay and S. K. Singh, *Orient. J. Chem.*, 9, 146 (1993).

61. R. R. Jha, D. K. S. Sircar and J. Usa, *Asian J. Chem.*, 6, 464 (1994).

62. H. Von Pechmann, *Chem. Ber.*, 21, 2751 (1888).

63. A. L. Spek and G. Vos, *Acta Crystallogr.*, C39, 990 (1983).

64. D. W. Engelfriet and D. C. Verschoor, *Acta Crystallogr.*, B37, 237 (1981).

65. D. W. Engelfriet and W. L. Groeneveld, *Z. Naturforsch.*, Teil A, 33, 848 (1978).

66. D. W. Engelfriet, W. L. Groeneveld and G. M. Nap, *Z. Naturforsch.*, Teil A, 35, 852 (1980).

67. D. W. Engelfriet, W. L. Groeneveld, H. A. Groeneveld, J. J. Smit and G. M. Nap, *Z. Naturforsch.*, Teil A, 35, 115 (1980).

68. D. W. Engelfriet, W. L. Groeneveld and G. M. Nap, *Z. Naturforsch.*, Teil A, 35, 1387 (1980).

69. D. W. Engelfriet, *Ph. D. Thesis*, State University Leiden, 1980.

70. P. J. van Koningsbruggen, J. W. van Hal, R. A. G. de Graaff, J. G. Haasnoot and J. Reedijk, *J. Chem. Soc. Dalton Trans.*, 2163 (1993).

71. D. W. Engelfriet, G. C. Verschoor and W. den Brinker, *Acta Crystallogr.*, B36, 1554 (1980).

72. D. W. Engelfriet, G. C. Verschoor and W. J. Vermin, *Acta Crystallogr.*, B35, 2927 (1979).

73. G. Vos, J. H. Haasnoot and W. L. Groeneveld, *Z. Naturforsch.*, Teil B, 36, 802 (1981).

74. G. Vos, A. J. de Kok and G. C. Verschoor, *Z. Naturforsch.*, Teil B, 36, 809 (1981).

75. M. Inoue and M. Kubo, *Coord. Chem. Rev.*, 21, 1 (1976).

76. D. J. Mackey and R. C. Martin. *J. Chem. Soc., Dalton Trans.*, 702 (1978).

77. G. Vos, R. A. G. de Graaff, J. G. Haasnoot, A. M. vander Kraan, P. de Vaal and J. Reedijk, *Inorg. Chem.*, 23, 2905 (1984).

78. K. Jonas, C. Epiphane, K. Olivier, G. Francoise and J. Charlotte, J. Am. Chem. Soc., 115, 9810 (1993).

79. A. K. Powell, *Coord. Chem. Rev.*, 134 (Part 1), 100 (1994).

80. W. Vreugdenhil, J. G. Haasnoot, M. F. J. Schoondergang and J. Reedijk, *Inorg. Chim. Acta*, 130, 235 (1987).

81. W. Vreugdenhil, J. G. Haasnoot, M. F. J. Schoondergang and J. Reedijk, Z. Naturforsch., Teil B, 42, 792 (1987).

82. W. Vreugdenhil, J. G. Haasnoot, J. Reedijk and J. S. Wood, *Inorg. Chim. Acta*, 167, 109 (1990).

83. S. Ferrer, J. G. Haasnoot, J. Reedijk, E. Muller, M. B. Cingi, A. M. M. Lanfredi, F. Ugozzoli and C. Foglia, *J. Chem. Soc., Dalton Trans.*, 3029 (1992).

84. M. B. Cingi, A. M. M. Lanfredi, F. Ugozzoli and J. G. Haasnoot, *Inorg. Chim. Acta*, 227, 181 (1994).

85. V. V. Ginzburg, A. N. Glebov, *Zh. Neorg. Khim.*, 38, 866 (1993); Chem. Abstr., 119: 240325d.

86. M. B. Cingi, A. M. M. Lanfredi, A. Tiripicchio, J. P. Haasnoot and J. Reedijk, *Acta Crystallogr.*, C45, 601 (1989).

87. V. V. Ginzburg, A. N. Glebova, D. Yu. Tarasov, *Zh. Neorg. Khim.* 37, 2050 (1992); Chem. Abstr., 118: 115468f.

88. V. Hanot and T. Robert, *J. Coord. Chem.*, 32, 349 (1994); V. Hanot, T. Robert and L. vander Elst, *Synth. React. Inorg. Met.-Org. Chem.*, 24, 1191 (1994).

89. U. Hartmann and H. Vahernkamp, *Inorg. Chim. Acta*, 239, 13 (1995).

90. B. J. Graves and D. J. Hodgson, Inorg. Chem., 20, 2223 (1981).

91. L. D. Hansen, B. D. West, E. J. Baca and C. L. Blank, *J. Am. Chem. Soc.*, 90, 6588 (1968).

92. A. Ladenburg, *Chem. Ber.*, 9, 219 (1876).

93. F. E. Beamish, *Talanta*, 1, 1 (1958); F. E. Beamish, *Talanta*, 8, 85 (1961); F. E. Beamish, *Talanta*, 13, 773 (1966).

94. D. S. Moore and S. D. Robinson, *Advances in Inorg. Chem.*, 32, 171 (1988).

95. I. Sotofte and K. Nielsen, *Acta Chem. Scand.*, 38A, 257 (1984).

96. H. E. Toma, E. Giesbrecht and R. L. Espinoza Rojas, *Can. J. Chem.*, 61, 2520 (1983).

97. M. Y. Antipin, G. G. Aleksandrov, Y. T. Struchkov, Y. A. Belousov, V. N. Babin and N. S. Kochetkova, *Inorg. Chim. Acta*, 68, 229 (1983).

98. D. I. Semenishin, A. V. Yurchak and Z. V. Slobodyan, *Visn. L'viv. Politekh. Inst.*, 149, 7 (1981), Chem. Abstr., 96: 114882b (1982).

99. I. Sotofte and K. Nielsen, *Acta Chem. Scand.*, 38A, 253 (1984).

100. I. Sotofte and K. Nielsen, *Acta Chem. Scand.*, 35A, 739 (1981).

101. G. G. Aleksandrov, V. N. Babin, A. P. Kharchevnikov, Y. T. Struchkov and N. S. Kochetkova, J. Organomet. Chem., 266, 109 (1984).

102. I. Sotofte and K. Nielsen, *Acta Chem. Scand.*, 37A, 891 (1983).

103. M. B. Hursthouse, B. G. Obly, R. L. Short and S. D. Robinson. (unpublished results)

104. L. D. Brown, J. A. Ibers and A. R. Siedle, *Inorg. Chem.*, 17, 3026 (1978).

105. A. L. Spek, A. R. Siedle and J. Reedijk, *Inorg. Chim. Acta*, 100, L15 (1985).

106. W. P. Jencks, *Prog. Phys. Org. Chem.*, 2, 63 (1964); R. B. Martin, *J. Phys. Chem.*, 2, 1369 (1964); T. C. Bruice and S. J. Benkovic, *Bioorganic Mechanisms*, W. A. Benjamin, New York (1966).

107. D. L. Leussing and C. K. Stanfield, *J. Am. Chem. Soc.*, 88, 5726 (1966); K. S. Bai and D. L. Leussing, *J. Am. Chem. Soc.*, 89, 6126 (1967); D. Hopgood and D. L. Leussing, *J. Am. Chem. Soc.*, 91, 3740 (1969); B. E. Leach and D. L. Leussing, *J. Am. Chem. Soc.*, 93, 3377 (1971).

108. S. A. Zabin and C. R. Jejurkar, *Indian J. Chem.*, 34A, 241 (1995).

109. B. Manju and A. I. P. Sinha, *Asian J. Chem.*, 1, 329 (1989).

110. C. Zahid Hussain and A. Shuaib, *Sci. Int.*, 5, 149 (1993).

111. S. N. Dubey, R. N. Handa and B. K. Vaid, *Monatsh. Chem.*, 125, 395 (1994).

112. S. N. Dubey and B. K. Vaid, *Indian J. Chem.*, 31A, 199 (1992).

113. F. S. M. Hassan, A. A. E. Adil, A. A. Gabr and A. A. Gad, *Orient. J. Chem.*, 8, 25 (1992).

114. S. N. Dubey and K. Beena, *J. Indian Chem. Soc.*, 69, 774 (1992).

115. K. K. Mohammed Yusuff and C. Krishnakumar, *Synth. React. Inorg. Met.-Org. Chem.*, 23, 695 (1993).

116. K. K. Mohammed Yusuff and C. Krishnakumar, *React. Kinet. Catal. Lett.*, 49, 437 (1993).

117. N. Saravanan and K. K. Mohammed Yusuff, *Trans. Met. Chem.*, 21, 1 (1996).

118. P. N. Preston, *Chem. Rev.*, 74, 279 (1974).

119. A. D. Mignell and S. Santoro, *Acta Crystallogr.*, 27B, 2084 (1971).

120. L. G. Marzilli and P. A. Marzilli, *Inorg. Chem.*, 11, 457 (1972).

121. R. J. Sundberg and R. B. Martin, *Chem. Rev.*, 74, 471 (1974).

122. R. Sreekala, *Ph. D. Thesis*, Cochin University of Science and Technology, Kochi, India, 1991.

123. A. R. Oki, R. P. Bommarreddy, H. Zhang and N. Hosmane, *Inorg. Chim. Acta*, 231, 109 (1995).

124. R. Viswanathan and M. Palaniandavar, *J. Chem. Soc., Dalton Trans.*, 1259 (1995).

125. S. Wang, Q. Luo, X. Wang, L. Wang and K. Yu, *J. Chem. Soc., Dalton Trans.*, 2045 (1995).

126. Z. Lu, Y. Yin and D. Jin, *Fenzi Cuihua*, 8, 143 (1994); *Chem. Abstr.*, 121: 173730h.

127. V. Shklover, I. L. Eremenko, H. Berke, R. Nesper, S. M. Zakeeruddin, M. K. Nazeeruddin and M. Graetzel, *Inorg. Chim. Acta*, 219, 11 (1994).

128. S. S. Tandon, L. K. Thomson, J. N. Bridson and C. John, *Inorg. Chem.*, 33, 54 (1994).

129.(a) M. Ahmed and N. A. Obeid, *Rev. Inorg. Chem.*, 12, 81 (1993);

(b) G. Narain, S. Naidu, Sufal Kumar and J. K. Jain, *Asian J. Chem.*, 4, 680 (1992).

130. A. C. Dash and N. Dash, *Int. J. Chem. Kinet.*, 22, 1237 (1990).

131. J. G. Lozano, J. S. Carrio, E. Coret, J. V. Folgado, E. Eseriva and R. Ballesteros, *Inorg. Chim. Acta*, 245, 75 (1996).

132. M. J. Young, D. Wahnon, R. C. Hynes and J. Chim, *J. Am. Chem. Soc.*, 117, 9441 (1995).

133. M. Palaniandavar, T. Pandiyan, M. Lakshminarayanan and H.Manohar, *J. Chem. Soc., Dalton Trans.*, 455 (1995).

134. S. Usha and M. Palaniandavar, *J. Chem. Soc., Dalton Trans.*, 2277 (1994).

135. H. N. Pandey and P. Mathur, *Indian J. Chem.*, 34A, 186 (1995).

136. M. Hvastijova, J. Kohout, J. Mrozinski and L. Jaeger, *Pol. J. Chem.*, 69, 852 (1995); Chem. Abstr., 123: 216857r.

137. A. K. Powell, *Coord. Chem. Rev.*, 134 (Part 1), 100 (1994).

138. F. Z. Weng, P. C. Chen, M. M. Sung and H. L. Gene, *Inorg. Chem.*, 35, 2259 (1996).

139. S. S. Tandon, L. K. Thomson, J. N. Bridson and J. C. Dewan, *Inorg. Chem.*, 33, 54 (1994).

140. P. Kamaras, M. C. Cajulis, M. Rapta, G. A. Brewer and G. B. Jameson, *J. Am. Chem. Soc.*, 116, 10334 (1994).

CHAPTER II

EXPERIMENTAL TECHNIQUES

Details regarding the general reagents used, preparation of some starting materials (2-phenyl-1,2,3-triazole-4-carboxaldehyde, indole-3-carboxaldehyde, quinoxaline-2-carboxaldehyde and aminomethylpolystyrene) and various analytical and physico-chemical methods employed for the characterization of the compounds are presented in this chapter. Procedural details of the synthesis of the ligands and their complexes are given in the appropriate chapters.

REAGENTS

The following metal salts were used for the synthesis of the complexes.

Anhydrous iron(III) chloride (Merck, GR), cobalt(II) chloride (Merck, GR), nickel(II) chloride (Merck, GR), copper(II) chloride (BDH, GPR), iron(III) nitrate nonahydrate (Merck, GR), cobalt(II) nitrate hexahydrate (Merck, GR), nickel(II) nitrate hexahydrate (BDH, GPR) and copper(II) nitrate trihydrate (BDH, GPR).

Cobalt(II) bromide and copper(II) bromide salts were prepared from cobaltous carbonate and cupric carbonate (Riedel Chemicals) respectively, by reacting them with HBr. Cobalt(II) iodide was obtained in a similar way by treating cobaltous carbonate with HI.

o-Phenylenediamine (Merck, GR), 3-nitrobenzaldehyde (Merck), 2-aminophenol (Merck), 3-amino-1,2,4-triazole (Aldrich, 95 % pure) and 2 % cross-linked chloromethyl polystyrene (Fluka) were used as the starting materials for the preparation of the ligands.

All other chemicals used were of analytical reagent grade, unless otherwise specified. Solvents employed were either of 99 % purity or purified by known laboratory procedures[1].

PREPARATION OF ALDEHYDES

1. *2-Phenyl-1,2,3-triazole-4-carboxaldehyde*

This aldehyde was prepared[2] by the following procedure:

Phenylhydrazine (20 mL, 0.2 mol) was dissolved in glacial acetic acid (20 mL), and was added to a 20 % aqueous solution of glucose (50 mL). The solution was stirred well and heated on a water bath for 20 minutes. Yellow glucosazone separated out was filtered, washed with water and dried. The osazone (2 g, 0.005 mol) was dissolved in minimum quantity of water and $CuSO_4.5H_2O$ (3 g) was added. The solution was heated under reflux for about 3 h, and was then filtered. The volume of the filtrate was reduced to almost half under vacuum and was kept over night for the complete separation of phenylosotriazole. It was then filtered and recrystallised from hot water. Phenylosotriazole

(2 g, 0.0075 mol) was then dissolved in water (75 mL), and was added to a solution of sodium metaperiodate (7.3 g, 0.03 mol) in water (75 mL). The mixture was stirred for 10 h at 20 ^{o}C and then kept at 5^{o}C for 10 minutes. 2-Phenyl-1,2,3-triazole-4-carboxaldehyde separated out was filtered and dried.
{Yield: 55 %, Melting point: 121 ^{o}C}

2. *Indole-3-carboxaldehyde*

This aldehyde was prepared[3] as per the procedure given below.

Dimethylformamide (2 mL) was taken in a 100 mL beaker and $POCl_3$ was added to it dropwise. The beaker was placed on a crushed ice bath, and indole (1 g) was added to the reaction mixture. The resultant solution was mixed thoroughly and brought to room temperature after the formation of a farry precipitate. After 45 minutes, the solution was poured into ice water. The pale red solution obtained was made alkaline, boiled for 30 minutes, and then allowed to settle. The indole-3-carboxaldehyde formed as a yellow precipitate was filtered, washed with water followed by ethanol, and dried *in vacuo* over anhydrous $CaCl_2$.
{Yield: 80 %}

3. *Quinoxaline-2-carboxaldehyde*

Quinoxaline-2-carboxaldehyde was prepared[4] by adopting the following procedure:

Glacial acetic acid (6 mL), *o*-phenylenediamine (21.6 g, 0.2 mol), hydrazine hydrate (5 mL, 0.1 mol) and a pinch of sodium bicarbonate were added to a solution of D-glucose (36 g, 0.2 mol) in water (54 mL), and the mixture was heated under reflux for 5 h on a boiling water bath. The solution was then cooled in ice, and the precipitated product, 2-(D-arabinotetrahydroxybutyl)quinoxaline, was filtered and washed with water. This product was further purified by recrystallisation from hot water. The recrystallised 2-(D-arabinotetrahydroxybutyl)quinoxaline (5 g, 0.02 mol) was mixed with sodium metaperiodate (13 g, 0.06 mol) in water (300 mL) and glacial acetic acid (10 mL), and the mixture was kept at room temperature with controlled stirring for 16 h. It was then filtered, and the filtrate was neutralized with sodium bicarbonate. The neutral solution was extracted with ether. The ether extract was then dried with anhydrous sodium sulfate, filtered and evaporated to dryness. The resulting residue was recrystallised from petroleum ether to give pure quinoxaline-2-carboxaldehyde.

{Yield: 60 %, Melting point: 107 ^{o}C}

Preparation of aminomethylpolystyrene from chloromethylpolystyrene

Aminomethylpolystyrene was prepared by following the procedure[5] as described below.

Chloromethyl polystyrene (11 g) was suspended in DMF (200 mL), hexamethylene tetramine (11.2 g) and potassium iodide (13.28 g) were added to this suspension, and then refluxed on an oil bath for 12 h at 100 °C with occasional stirring. The resin was filtered, washed several times with DMF, methanol and chloroform, and then dried *in vacuo* over anhydrous $CaCl_2$ to get constant weight {Yield: 9.5 g}. A test portion of the resin on heating with ninhydrin reagent gave a blue colour.

ANALYTICAL METHODS

Estimation of metal ions

A uniform procedure was followed for eliminating the organic part of all the simple complexes. A known weight of the metal complex (0.2–0.3 g) was treated with concentrated sulfuric acid (5 mL) followed by concentrated nitric acid (20 mL). After the reaction had subsided, perchloric acid (5 mL, 60 %) was added. This mixture was maintained at boiling temperature for 3 h on a sand bath. The clear solution thus obtained was evaporated to dryness. After cooling, concentrated nitric acid (5 mL) was added and once again evaporated to dryness on a water bath. The residue was dissolved in water and this solution was used for the estimation of metal ions.

Gravimetric procedures were adopted for the estimation of iron, cobalt and nickel. Iron in the complex was estimated by precipitating the metal with ammonia solution and igniting the resulting hydroxide to ferric oxide. Cobalt was estimated by precipitating it as

$[Co(C_5H_5N)_4](SCN)_2$ using ammonium thiocyanate and pyridine. Nickel was precipitated as nickel dimethylglyoxime complex by the addition of an alcoholic solution of dimethylglyoxime and excess of ammonia solution. Iodimetric method[6] was employed for the estimation of copper in the complex.

In the case of polymer supported complexes, the organic part was eliminated by heating them in aqua regia for 24 h at 100 °C and then the metal ion concentration in the filtered solution was estimated by atomic absorption spectroscopy using a Perkin-Elmer 2380 Atomic Absorption Spectrophotometer.

CHN analyses

Microanalyses for C, H and N were carried out using either Heraeus CHN rapid analyzer, Perkin Elmer 2400 series II CHNS/O elemental analyzer or Perkin Elmer 240-C elemental analyzer.

Estimation of halogens

Halogen content of the simple complexes (Cl, Br or I) was determined by the peroxide fusion of the sample followed by the gravimetric precipitation as silver halide. Further, Volhard's method was employed in few cases for the estimation of chlorides.

For the estimation of chlorine, bromine or iodine in the polymer supported complexes, the following procedure was adopted:

The polymer supported complex (3 g) was digested with pyridine (5 mL) for 2 h at 100 ^{o}C and after cooling to room temperature, the solution was transferred quantitatively to a conical flask containing 50 % acetic acid (30 mL) and concentrated nitric acid (5 mL). To this solution, standard silver nitrate solution was added with stirring and the mixture was allowed to stand for 5 minutes. About 50 mL of water was then added to it followed by toluene (5 mL). The solution was mixed thoroughly using a magnetic stirrer. The excess of silver nitrate was back titrated with standard ammonium thiocyanate solution.

PHYSICO-CHEMICAL METHODS

Conductance measurements

Molar conductance values for the soluble complexes (10^{-3} M) in acetone, DMF or DMSO were measured at room temperature (28 ± 2 ^{o}C) on a Century CC 601 Digital Conductivity Meter with a dip type smooth platinum eletrode.

Magnetic susceptibility measurements

Magnetic susceptibility measurements for the solid complexes were obtained at room temperature on a simple Gouy-type magnetic balance. The Gouy tube was standardised using $Co[Hg(SCN)_4]$ as the calibrant, as recommended by Figgis and Nyholm[7]. The effective magnetic moment was calculated using the equation,

$$\mu_{eff} = 2.84\ (\chi_m'T)^{1/2}\ \text{B.M.}$$

Where, T is the absolute temperature, and χ_m' is the molar susceptibility corrected for diamagnetism of all the atoms present in the complex using Pascal's constants[8-11].

Electronic absorption spectra

The UV-Visible absorption spectra for the ligands and the complexes were recorded in solution or in solid state by nujol mull technique (for the insoluble compounds) following a procedure recommended by Vananzi[12]. The procedure is as given below.

Small filter paper strips were impregnated with a paste of the sample in nujol. These were placed over the entrance to the photocell housing. A nujol treated filter paper strip of similar size and shape was used as the blank.

The spectra of all the compounds were scanned on a Shimadzu UV 160A UV-Visible spectrophotometer in the range 1100-200 nm.

The near-IR spectra of some of the cobalt(II) complexes were obtained with a Hitachi U-3410 spectrophotometer.

Infrared spectra

Infrared spectra of the ligands and the complexes were taken both as nujol paste and as KBr pellets on either Shimadzu 8101 FTIR spectrophotometer in the 4600–400 cm^{-1} region, Perkin Elmer 597 spectrophotometer in the range 4000–200 cm^{-1} or Perkin Elmer 598 spectrophotometer in the 4000–200 cm^{-1} region.

NMR spectra

Proton nuclear magnetic resonance and carbon-13 nuclear magnetic resonance spectra of the soluble ligands (NBPBI and PTCAP) were recorded on a GE NMR OMEGA 400 MHz spectrometer using TMS as an internal standard.

Mass spectra

Electron impact mass spectra for the ligands (NBPBI and PTCAT) were obtained at 70 eV on a Finnigan Mat 8230 GC-Mass spectrometer.

EPR spectra

The room temperature powder EPR spectra of the copper(II) complexes were measured at the X-band frequencies with either Bruker model 200-D EPR spectrophotometer or Varian E-112 X/Q band spectrophotometer. Spectra were calibrated using diphenylpicrylhydrazyl (DPPH) as a field marker and the 'g' values were calculated using Kneubuhl procedure[13].

Mössbauer spectra

Mössbauer spectra of the iron(III) complexes were obtained on a high velocity constant acceleration Mössbauer spectrometer (Wissel, Germany) with a 10 mCi source of ^{57}Co in a rhodium matrix. The calibration was made with a standard iron foil of thickness 25 mm at room temperature, and a multichannel analyzer with 1024 channels was used for the data acquisition.

Cyclic voltammetry

The cyclic voltammograms of the copper(II) and iron(III) complexes were performed on a EG & G Par model 273 potentiostat.

Thermal studies

The thermogravimetric analysis of a few compounds were performed on a Dupont 2000 thermogravimetric analyzer with the sample of 10-20 mg in an air atmosphere.

REFERENCES

1. D. D. Perrin, W. L. F. Armarego and D. R. Perrin, "*Purification of Laboratory Chemicals*", Pergamon Press, Oxford, 1990.

2. W. T. Haskins, R. M. Hann and C. S. Hudson, *J. Am. Chem. Soc.*, 69, 1051 (1947).

3. L. F. Fieser and M. Fieser, "*Reagents for Organic Synthesis*", John Wiley & Sons, Inc., pp. 284, 1967.

4. C. L. Leese and H. N. Rydon, *J. Chem. Soc.*, 303 (1955).

5. K. S. Devaki and V. N. R. Pillai, *Eur. Polymer J.*, 24, 209 (1988).

6. A. I. Vogel, "*A Text-book of Quantitative Inorganic Analysis*" Longmans-Green, London, 1978.

7. B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 4190 (1958).

8. B. N. Figgis and J. Lewis, "*Modern Coordination Chemistry*", J. Lewis and R. G. Wilkins, Eds., Interscience, New York, 1960.

9. P. W. Selwood, "*Magnetochemistry*", Interscience, New York, 1958.

10. A. Earnshaw, "*Introduction to Magnetochemistry*", Academic Press, New York, 1968.

11. B. N. Figgis and J. Lewis, "*Progress in Inorganic Chemistry*", F. A. Cotton, Ed., Interscience, New York, Vol. 4, 1964.

12. G. Dyer, J. G. Hartley and L. M. Venanzi, *J. Chem. Soc.*, 1293 (1965).

13. F. K. Kneubuhl, *J. Chem. Phys.*, 33, 1074 (1960).

CHAPTER III

COBALT(II) AND COPPER(II) COMPLEXES OF 1-NITROBENZYL-2-NITROPHENYLBENZIMIDAZOLE

INTRODUCTION

Recently, the chemistry of benzimidazoles and their metal complexes has created great interest and enthusiasm among the chemists because of their medicinal[1-10] importance such as antibacterial, antifungal, antiviral, anticancer, antiinflammatory, analgesic, antipyretic, antihelmentic, germicidal and immuno-chemical activities. Complex compounds of transition metal ions with imidazole, benzimidazole and substituted compounds of these ligands have been studied extensively[11-15]. Many low-molecular weight complexes of copper(II) containing imidazole ligands have been proposed as models of active site of copper proteins[16-18]. It has been observed that incorporation of a nitro group in the azole compounds contribute to their antiamoebic activity[19]. Furthermore, herbicidal and growth regulating activity[20] of copper(II) complexes, and also their catalytic activity, particularly towards oxidation reactions of substituted phenols, have been reported. Hence, it was considered worthwhile and interesting to synthesise some new transition metal complexes with a derivative of benzimidazole. This derivative, 1-nitrobenzyl-2-nitrophenylbenzimidazole (NBPBI) (Figure 1) is interesting from the structural point of view because of its bulky nature and steric effects. Cobalt(II) and copper(II) complexes of this ligand were synthesized. However, attempts to synthesize the iron(III) and nickel(II) complexes by using this ligand were not successful. The results of our studies on the cobalt(II) and copper(II) complexes of this ligand are presented in this chapter.

EXPERIMENTAL

The materials used for the syntheses of complexes with NBPBI, and the instruments employed for the characterization of NBPBI and its complexes are given in Chapter II.

A three-electrode system consisting of a platinum sphere electrode, a platinum plate, and a reference electrode $Ag(s)/AgNO_3$ was used for the cyclic voltammetric measurement. Tetra-*n*-butylammoniumperchlorate (TBAP) (0.1 M) in DMF was employed as the supporting electrolyte.

Synthesis of the ligand

The ligand, NBPBI was prepared by adopting the procedure reported in the literature[21] with some modifications.

o-Phenylenediamine (10.81 g, 0.1 mol) and 3-nitrobenzaldehyde (30.22 g, 0.2 mol) were separately dissolved in glacial acetic acid (150 mL), and mixed. The mixture was kept aside for 24 h. It was then filtered, and the filtrate was poured into crushed ice. After 3 h, the mother liquor was decanted off. The product formed was washed several times with distilled water by decantation, and was recrystallized from methanol.

{Yield: 45-50 %; Melting point: 126 °C}

Synthesis of the complexes

[CoL_2Cl_2]

A hot ligand solution of NBPBI (3.74 g, 10 mmol dissolved in 75 mL ethanol) was added to a cobalt(II) chloride hexahydrate (1.18 g, 5 mmol dissolved in 5 mL ethanol) and the resulting green coloured solution was refluxed for about 3 h over a water bath. The blue crystals obtained were filtered, washed with hot ethanol and chloroform and dried *in vacuo* over anhydrous $CaCl_2$.

{Yield: 70 %; Decomposition temperature: 320 °C}

[CoL_2Br_2] and [CoL_2I_2].

A solution containing cobalt(II) bromide (1.09 g, 5 mmol) or cobalt(II) iodide (1.56 g, 5 mmol) and NBPBI (3.74 g, 10 mmol) in acetone (20 mL) was refluxed for about 2 h. Then the volume of the solution was reduced to half and the greenish blue crystals formed on cooling were collected, washed with chloroform and dried *in vacuo* over anhydrous $CaCl_2$.

{Yield: 85 % for [CoL_2Br_2] and 70 % for [CoL_2I_2]; Decomposition temperature: 280 °C}

$[CuL_2Cl_2]$ and $[CuL_2Br_2]$

A hot ethanolic solution of the ligand (3.74 g, 10 mmol in 75 mL ethanol) was added slowly to a solution of copper(II) chloride dihydrate (0.85 g, 5 mmol) or copper(II) bromide (1.12 g, 5 mmol in 5 mL ethanol) and the resulting solution was refluxed for about 1 h. The greenish grey crystals obtained in the case of the chloro complex of copper(II) and the greenish yellow ones in the case of the bromo complex were filtered, washed with hot ethanol and chloroform, and dried *in vacuo* over anhydrous $CaCl_2$.
{Yield: 85 % for $[CuL_2Cl_2]$ and 85 % for $[CuL_2Br_2]$; Decomposition temperature: 280 °C}

RESULTS AND DISCUSSION

The elemental analyses (C, H, N) of the ligand, NBPBI, corresponds to the empirical formula $C_{20}H_{14}N_4O_4$. The ^1H NMR spectrum (Figure 2) in DMSO-d_6 was integrated for 12 protons in the aromatic region between δ 7.1 and 9.1 ppm. The benzylic protons (2 H) appear as a singlet at δ 5.8 ppm. Proton decoupled ^{13}C NMR spectrum is also in agreement with the structure shown in Figure 1. Mass spectrum of this compound (Figure 3) exhibits a molecular ion peak at m/e 374 (8 %), which exactly corresponds to the molecular weight of the NBPBI. A base peak at m/e 239 (100 %) (resulted by fragmentation of the benzylic moiety) was also observed.

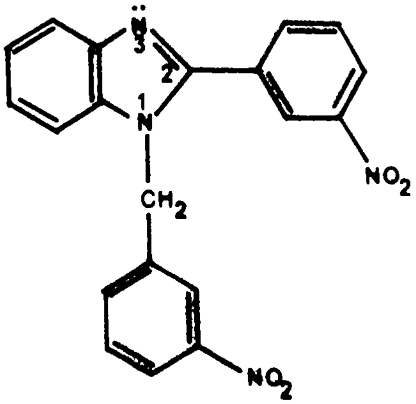


Figure 1. Structure of the NBPBI

All the complexes are crystalline, non-hygroscopic and are stable to aerial oxidation. They are soluble in acetone, DMF and dioxane, and slightly soluble in dichloromethane, and insoluble in ether and ethanol. The analytical (Table I) and molar conductance (Table II) data show that the cobalt complexes have the general formula $[CoL_2X_2]$ (where, L = NBPBI and X = Cl, Br or I) and for the copper complexes, the formula is $[CuL_2X_2]$, (where, X = Cl or Br). Molar conductance values of the complexes suggest that all complexes are non-electrolytes in acetone.

Magnetic susceptibility measurements

The distinction of tetrahedral and octahedral complexes of cobalt(II) from the magnetic moment values is possible to a certain extent. Generally, the magnetic moment value for the cobalt(II) ion[22] falls in the range, 4.1-5.2 B.M. at room temperature. However, the

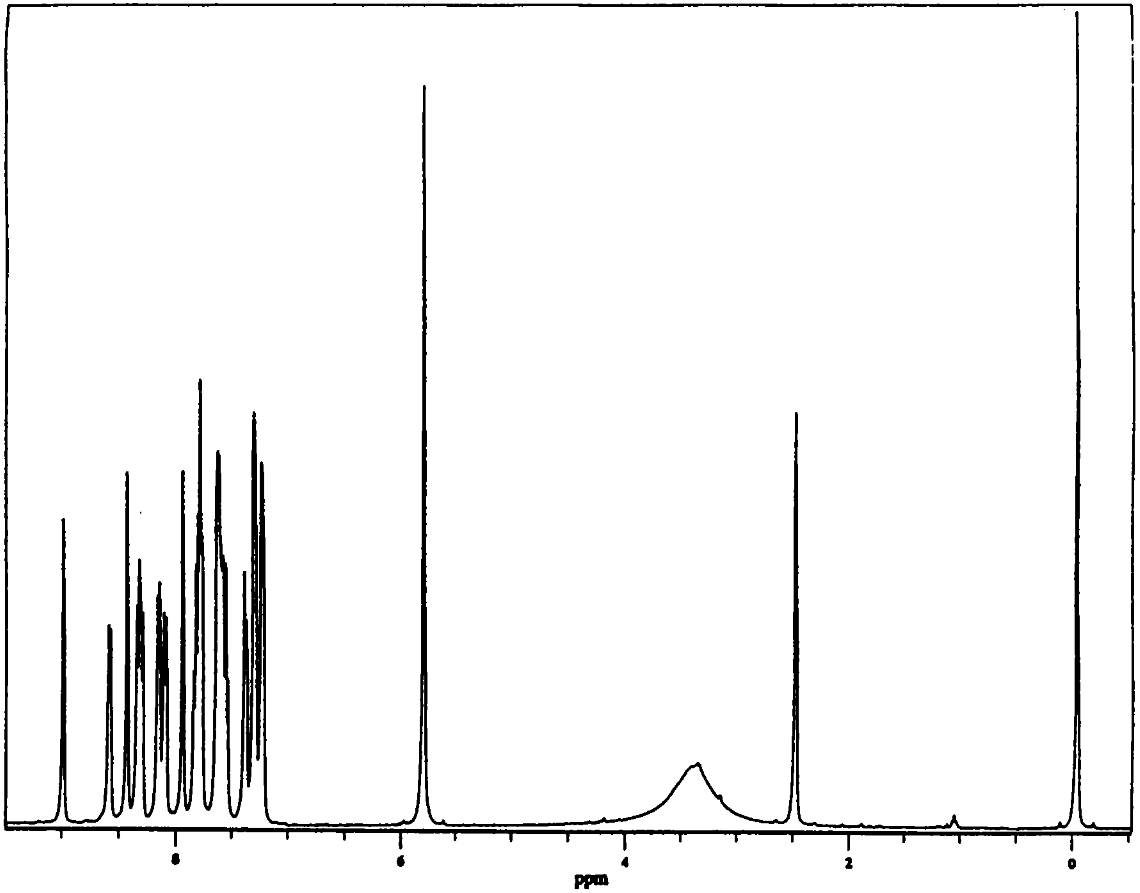


Figure 2. ^{1}H NMR of NBPBI

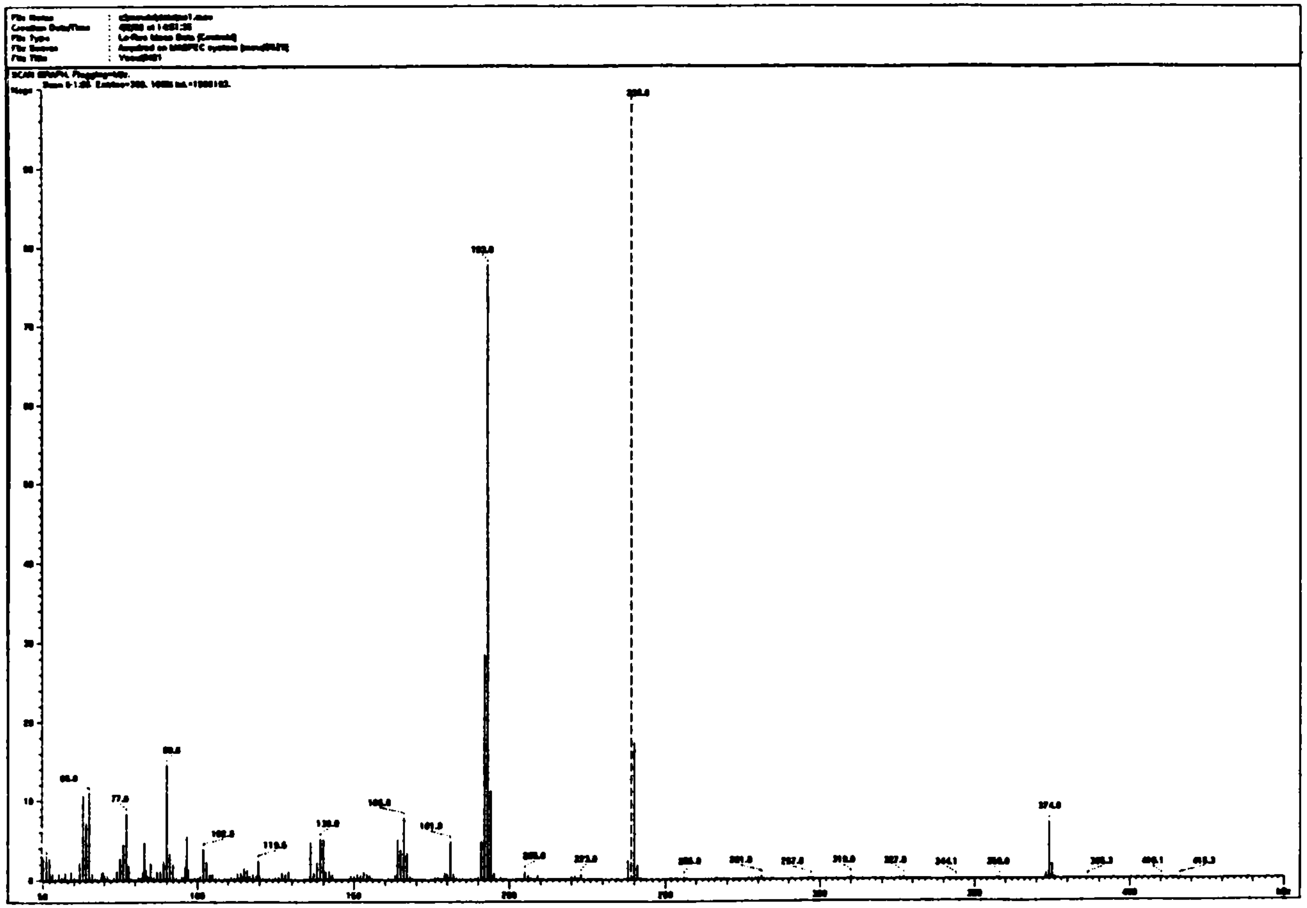


Figure 3. Mass spectrum of NBPBI

Table I

Elemental analyses and colour of the ligand and its complexes

Substance	Colour	Found (Calc.) % C	H	N	M	X
L, Ligand	Yellow	62.88	3.86	15.45	-	-
		(64.17)	(3.74)	(14.97)	-	-
$[CoL_2Cl_2]$	Blue	54.70	3.27	13.00	6.90	7.81
		(54.68)	(3.19)	(12.76)	(6.69)	(8.08)
$[CoL_2Br_2]$	Greenish	51.42	3.02	12.12	6.83	16.74
	blue	(49.66)	(2.89)	(11.58)	(6.07)	(16.53)
$[CoL_2I_2]$	Green	45.24	2.64	10.55	5.53	23.93
		(46.65)	(2.89)	(11.08)	(5.09)	(23.53)
$[CuL_2Cl_2]$	Grey	53.75	3.10	12.51	7.67	8.34
		(54.39)	(3.17)	(12.69)	(7.20)	(8.04)
$[CuL_2Br_2]$	Green	49.60	2.94	11.49	6.26	16.79
		(49.41)	(2.88)	(11.53)	(6.54)	(16.45)

L = 1-Nitrobenzyl-2-nitrophenylbenzimidazole

Table II

Molar conductance and magnetic data for the complexes

Complex	Molar conductance (ohm^{-1} cm^2 mol^{-1})	Magnetic moment (B.M.)
$[CoL_2Cl_2]$	18.5	4.40
$[CoL_2Br_2]$	27.2	4.20
$[CoL_2I_2]$	79.2	4.54
$[CuL_2Cl_2]$	12.5	2.01
$[CuL_2Br_2]$	28.4	2.00

L = NBPBI

magnetic moment values for octahedral high-spin complexes are around 4.8-5.2 B.M.[23], and those for the tetrahedral complexes of cobalt(II) are usually below this range. In the present cases, all the cobalt complexes exhibit μ_{eff} values in the range 4.1 to 4.6 B.M. (Table II) suggesting a tetrahedral geometry for these complexes[24,13].

In practice, moments of magnetically dilute compounds of copper(II) are in the range 1.9-2.2 B.M., with compounds whose geometry approaches octahedral having moments at the lower end, and those with geometries approaching tetrahedral having moments at the higher end.

However, their μ_{eff} values cannot be used diagnostically with safety unless supported by other evidences[23]. For the present copper(II) complexes, the magnetic moment values are around 2.0 B.M. suggesting square planar structures for these complexes[25]. A slightly high magnetic moment value found here may be due to the distortions from the square planar structure.

Infrared spectra

Infrared spectrum (Table III) of the free ligand, NBPBI, shows an intense band at 1475 cm^{-1} which may be attributed to the ν(C=N) stretching vibration. This frequency is lowered in all the complexes indicating the participation of N-3 atom of NBPBI to the metal ion. Similar type of shifts have been reported by earlier workers also[26-29]. Strong characteristic bands due to the nitro group[30,31] are observed at 1522 cm^{-1} and 1350 cm^{-1} in the spectrum of the ligand. In the spectra of the complexes, these bands appear at the same frequency which suggests non-participation of the NO_2 group in coordination to the metal ion. In addition, all compounds show a C-N stretching vibration[32] near 870 cm^{-1}.

All the complexes show a strong band near 380 cm^{-1} in the far IR region, which may be attributed to the M-N (benzimidazole) stretching vibration[29]. The bands observed at 320 cm^{-1} for the cobalt(II), and 300 cm^{-1} for the copper(II) complexes indicate the M-Cl bond. Further, the bands observed near 260 cm^{-1} for the bromo complexes may be due to the M-Br bond. The band seen at 202 cm^{-1} in the spectrum of the iodo complex is due to the ν(Co–I) bond. The above mentioned bands are absent in the spectrum of the ligand.

Table III

Some relevant IR spectral (cm^{-1}) data

I	II	III	IV	V	VI	Tentative assignments
1522	1522	1522	1522	1522	1522	aromatic nitro group
1475	1456	1462	1458	1466	1464	ν(C=N) (benzimidazole)
1350	1350	1350	1350	1350	1350	aromatic nitro group
880	880	880	880	880	880	ν(C–N) stretching
——	380	380	380	380	390	ν(M–N) (ligand) mode
——	320	——	——	300	——	ν(M–Cl) mode
——	——	260	——	——	265	ν(M–Br) mode
——	——	——	202	——	——	ν(Co–I) mode

I=NBPBI; II=$[CoL_2Cl_2]$; III=$[CoL_2Br_2]$;
IV=$[CoL_2I_2]$; V=$[CuL_2Cl_2]$; VI=$[CuL_2Br_2]$

Electronic spectra

Electronic spectral data for all the complexes are shown in Table IV.

All the cobalt(II) complexes exhibit two absorption bands in the region 17500–13450 cm^{-1} which may be assigned to the $^4A_2 \longrightarrow {}^4T_1(P)$ electronic transition. An additional band observed in this region may

Table IV

Electronic spectral data (cm^{-1}) for the complexes

Substance	Absorption maxima	ε_{max} (l cm^{-1} mol^{-1})	Tentative assignments
[CoL$_2$Cl$_2$]	29070	2472	Intraligand transition
	17100	202	$^4A_2 \rightarrow {}^4T_1(P)$
	15480	286	
	7050	73	$^4A_2 \rightarrow {}^4T_1(F)$
[CoL$_2$Br$_2$]	29850	2470	Intraligand transition
	27780	2070	Charge transfer
	16920	400	$^4A_2 \rightarrow {}^4T_1(P)$
	15850	900	
	14990	1267	
	6980	67	$^4A_2 \rightarrow {}^4T_1(F)$
[CoL$_2$I$_2$]	29070	2141	Intraligand transition
	27620	1930	Charge transfer
	16210	198	$^4A_2 \rightarrow {}^4T_1(P)$
	15080	352	
	14290	398	
	13460	285	
	6900	65	$^4A_2 \rightarrow {}^4T_1(F)$
[CuL$_2$Cl$_2$]	30120	2430	Intraligand transition
	24390	302	$^2B_{1g} \rightarrow {}^2E_g$
	21320	650	
[CuL$_2$Br$_2$]	30120	2400	Intraligand transition
	24100	1617	$^2B_{1g} \rightarrow {}^2E_g$
	15240	266	$^2B_{1g} \rightarrow {}^2B_{2g}$

L = NBPBI

be due to spin-orbit coupling of the T state. The band observed in the near-IR region 7200–6900 cm^{-1} may be attributed to the $^4A_2 \longrightarrow {}^4T_1(F)$ transition[33]. The higher ε_{max} values observed further support a tetrahedral structure for these complexes[34].

The $[CuL_2Cl_2]$ complex shows broad bands in the region 24400–20000 cm^{-1} which may be due to the $^2B_{1g} \longrightarrow {}^2E_g$ transition. $[CuL_2Br_2]$, on the other hand, exhibits two bands around 15000 cm^{-1} and 24000 cm^{-1} and these may be due to $^2B_{1g} \longrightarrow {}^2E_g$ and $^2B_{1g} \longrightarrow {}^2B_{2g}$ transitions, respectively. The transitions observed in this region are characteristic of square planar copper(II) complexes[25]. Further, all the complexes exhibit strong bands in the range 46300–29000 cm^{-1} which may be assigned to intraligand transitions.

EPR spectra

The polycrystalline EPR spectra of the copper(II) complexes have been recorded at room temperature (Figure 4 & Figure 5). The 'g' values were calculated using Kneubuhl's procedure[35]. Two 'g' values were observed for both the chloro ($g_{\parallel}$ = 2.08; $g_{\perp}$ = 2.01) and the bromo complexes ($g_{\parallel}$ = 2.09; $g_{\perp}$ = 2.02). The higher value for $g_{\parallel}$ suggests a square planar geometry for the complexes[36]. Further, the values are less than 2.3, which indicates covalent character of the metal-ligand bond[37].

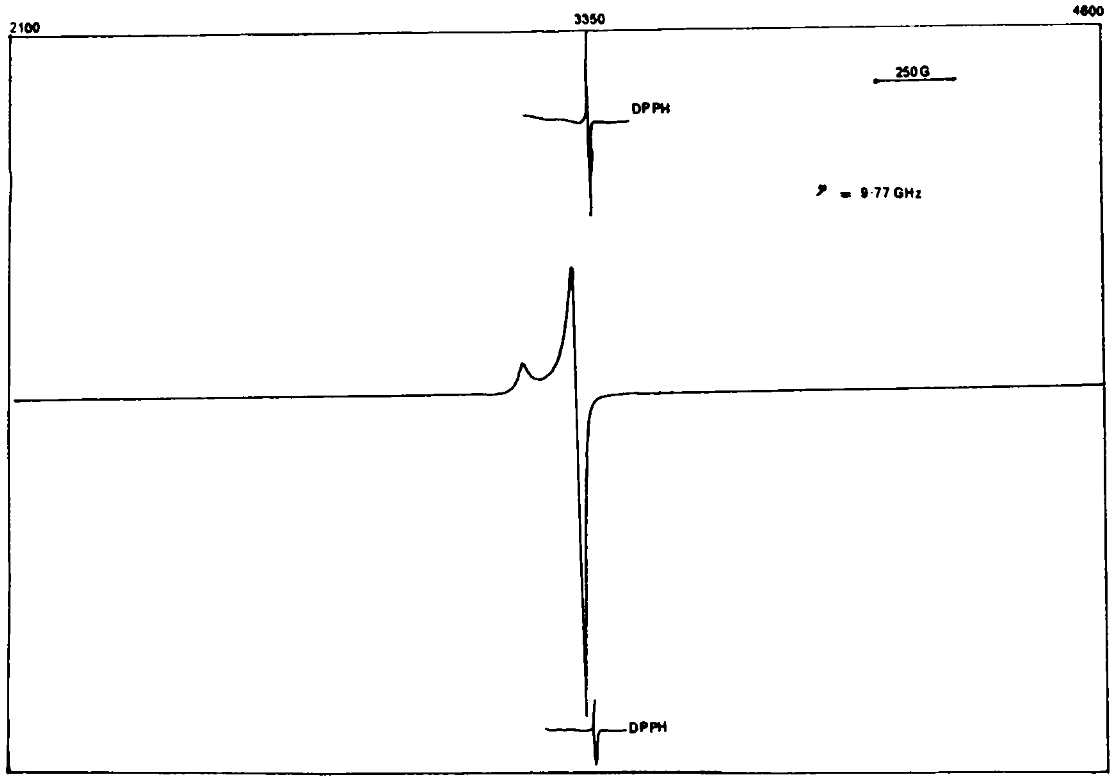


Figure 4. EPR spectrum of $[CuL_2Cl_2]$

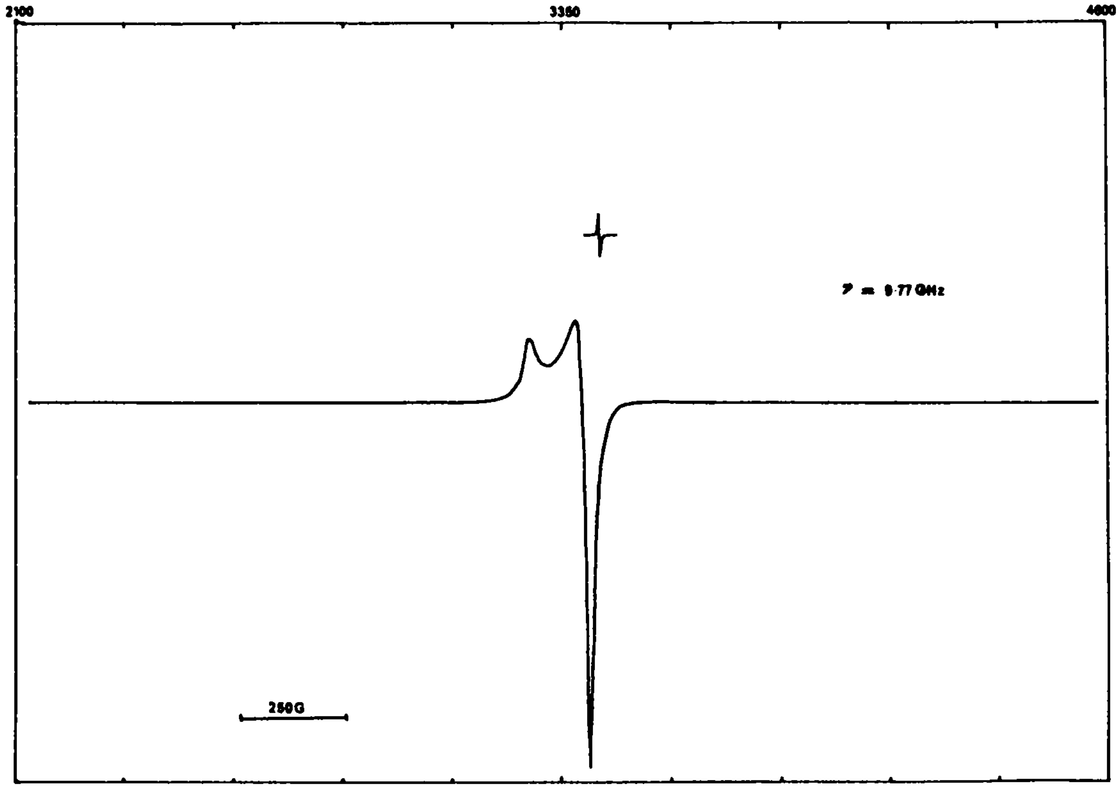


Figure 5. EPR spectrum of $[CuL_2Br_2]$

Cyclic voltammogram of the [CuL_2Cl_2] complex

The cyclic voltammogram of the [CuL_2Cl_2] complex is shown in Figure 6. The cyclic voltammetry of this complex features the reduction of copper(II) to copper(I) at a cathodic peak potential of −0.1540 V. Reoxidation of copper(I) occurs upon scan reversal at 0.0500 V. The separation between the anodic peak potential (Epa) and cathodic peak potential (Epc), ΔEp = 204 mV, indicates an irreversible, one electron redox process. The formal potential $E_{1/2}$ taken as the average of Epa and Epc is 0.0520 V.

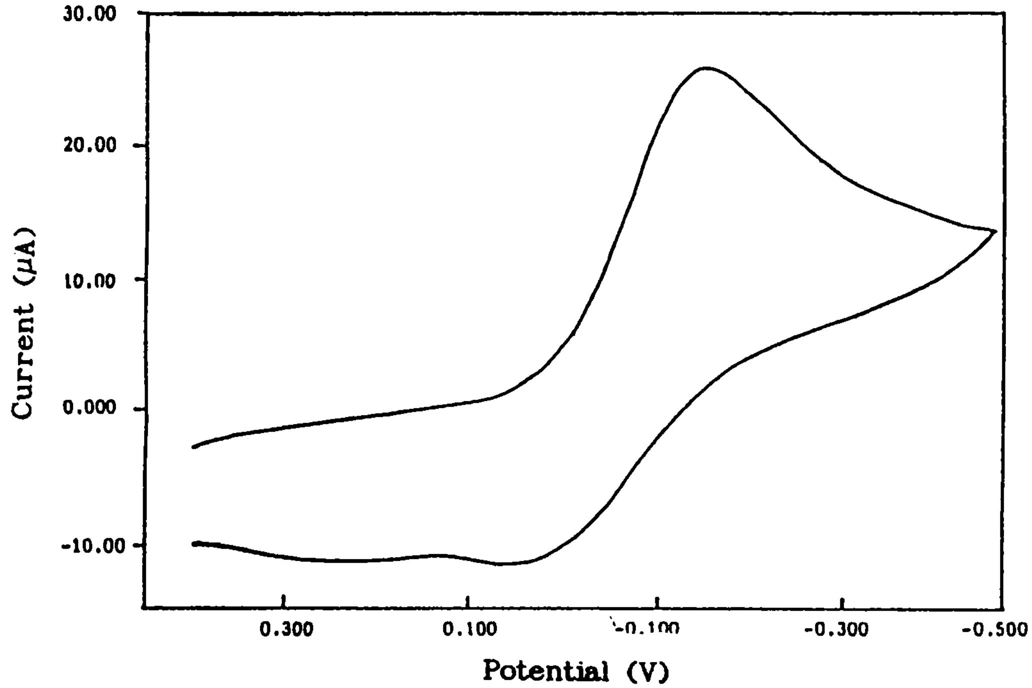
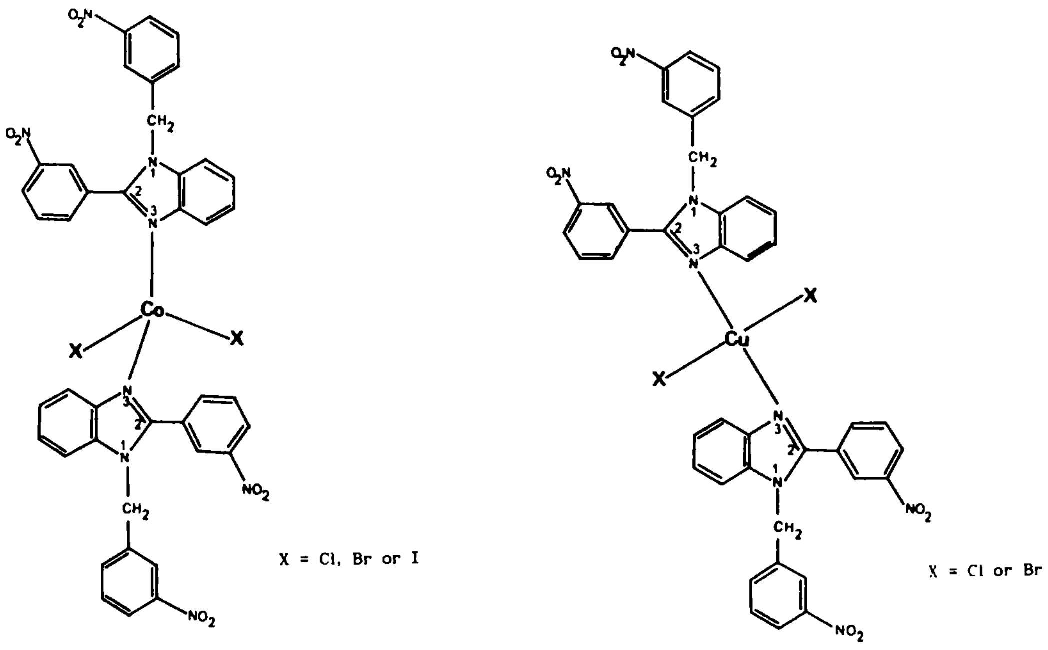


Figure 6. Cyclic voltammogram of the [CuL_2Cl_2] complex

Based on the elemental analyses and various physico-chemical studies, the structures shown in Figure 7 are tentatively proposed for the complexes.



X = Cl, Br or I

X = Cl or Br

Figure 7. Proposed structure of the complexes

REFERENCES

1. R. C. Boruah and E. B. Skibo, *J. Med. Chem.*, 37, 1625 (1994).

2. S. Yamada, T. Goto, E. Shimanuki and S. Narita, *Chem. Pharm. Bull.*, 42, 718 (1994).

3. M. Pedini, G. De Meo, A. Ricci, C. Tassi and L. Bastianini, *Farmaco*, 49, 303 (1994).

4. A. Cuadro, J. B. Perez, M. M. Pastor, J. A. Builla, M. M. M. Grueiro and A. R. M. Fernandez, *Farmaco*, 47, 477 (1992).

5. F. A. Badawey and Y. M. Gohar, *Farmaco*, 47, 489 (1992).

6. T. Gungor, A. Fouquet, J. M. Teulon, D. Provost, M. Cazes and A. Cloarec, *J. Med. Chem.*, 35, 4455 (1992).

7. A. Da Settimo, G. Primofiore, F. Da Settimo and A. M. Marini, *Farmaco*, 47, 1293 (1992).

8. S. Ram, D. S. Wise, L. L. Wotring, J. W. McCall and L. B. Townsend, *J. Med. Chem.*, 35, 539 (1992).

9. E. I. Elnima, M. U. Zubair and A. A. A. Badr, *Antimicrob. Agents Chemother.*, 19, 29 (1981).

10. E. Lacey and T. R. Watson, *Biochem. Pharmacol.*, 34, 1073 (1985).

11. S. P. Gosh, *J. Indian Chem. Soc.*, 28, 710 (1951).

12. S. P. Gosh and H. M. Gosh, *J. Indian Chem. Soc.*, 33, 894 (1956).

13. M. Goodgame and F. A. Cotton, *J. Am. Chem. Soc.*, 84, 1543 (1962).

14. D. M. L. Goodgame and M. Goodgame, *Inorg. Chem.*, 4, 139 (1965).

15. J. Reedijik, *J. Inorg. Nucl. Chem.*, 35, 239 (1973).

16. K. Nakamoto, "*Infrared and Raman Spectra of Inorganic and Coordination Compounds*", 3rd Edn., Wiley, New York, pp. 314, 1978.

17. J. R. Dyer, "*Applications of Absorption Spectroscopy of Organic Compounds*", Prentice Hall, New Jersey, pp. 33, 1965.

18. B. J. Hathaway, *J. Chem. Soc., Dalton Trans.*, 1196 (1972).

19. V. S. Misra, P. Shah and V. K. Saxena, *J. Indian Chem. Soc.*, LIX, 1074 (1982).

20. G. Vasilev and K. Davarski, *Dokl. Bolg. Acad. Nauk.*, 35, 1717 (1982); Chem. Abstr., 99: 17956h (1983).

21. N. V. S. Rao and C. V. Ratnam, *Proc. Indian Acad. Sci.*, 43A, 174 (1956).

22. J. B. Yadav, "*Advanced Practical Physical Chemistry*", Goel Publishing House, Meerut, 8th Edn., pp. 405, 1988.

23. N. N. Greenwood and A. Earnshaw, "*Chemistry of the Elements*", Pergamon Press, pp. 1315 & 1386, 1989.

24. B. R. Puri and L. R. Sharma, "*Principles of Inorganic Chemistry*", Vishal Publications, pp. 1035, 1980.

25. N. V. Murthy, P. Lingaiah and V. M. Reddy, *J. Indian Chem. Soc.*, LX, 524 (1983).

26. K. S. Bose and C. C. Patel, *J. Inorg. Chem.*, 32, 1141 (1970).

27. K. S. Bose and C. C. Patel, *J. Inorg. Chem.*, 33, 755 (1971).

28. P. T. Joseph, C. Pavithran and K. G. K. Warrier, *Trans. Met. Chem.*, 3, 286 (1978).

29. L. D. Prabhakar, K. M. M. S. Prakash and M. C. Chowdary, *Inorg. Chim. Acta*, 13, 233 (1987).

30. J. Francel, *Am. Chem. Soc.*, 74, 1265 (1952).

31. Lothrop, Handrick and Hainer, *Am. Chem. Soc.*, 73, 3581 (1951).

32. Silverstein, Bassler and Morrill, "*Spectrometric Identification of Organic Compounds*", John Wiley & Sons, 4th Edn., pp. 130, 1981.

33. K. K. M. Yusuff and R. Sreekala, *Thermochim. Acta*, 159, 357 (1990).

34. A. B. P.Lever, "*Inorganic Electronic Spectroscopy*", Elsevier, New York, pp. 496, 1984.

35. F. K. Kneubuhl, *J. Chem. Phys.*, 33, 1074 (1960).

36. B. Prabhakar, P. Lingaiah and K. L. Reddy, *Polyhedron*, 9, 805 (1990).

37. D. Kivelson and R. Neiman, *J. Chem. Phys.*, 35, 149 (1961).

CHAPTER IV

STUDIES ON POLYMER SUPPORTED COBALT(II) AND COPPER(II) COMPLEXES

INTRODUCTION

A polymer-metal complex is composed of a synthetic polymer and metal ions. Considerable attention has been paid in the past decades to the synthesis of polymer-metal complexes because of their interesting features. The polymer-metal complexes, prepared by complexation of metal ions with functional groups in the polymer matrix, have superior properties that are difficult to achieve from corresponding simple metal complexes[1]. A wide variety of investigations have been carried out on polymeric metal complexes; these include studies of semiconductivity, thermostability, redox reactions, collection of metal ions, biomedical effects, and so on[2-4]. These polymer-bound complexes are currently being investigated for applications in molecular electronics, chemical sensors and catalysis[5]. Further, in many catalytic reactions involving polymer-bound metal complexes, the activity of the catalyst not only depends on the metal complex, but also on the polymer backbone[6]. It has been reported that a pendant type polymer metal complexes are obtained by reacting a polymer ligand, which is made to coordinate to a vacant site of a previously prepared, stable, low-molecular weight metal complex. Further, it is understood from the literature survey that preparing these pendant type complexes, square planar structural arrangement is easier than that from the tetrahedral complexes, which is considered as a necessary pre-requisite for functioning as oxygen carriers, and also as oxidation catalysts. Cobalt(II) tetrahedral complexes do not generally have this capability. We have attempted to synthesize five coordinate complexes from both tetrahedral complexes of cobalt(II) and square planar complexes of copper(II) derived from 1-nitrobenzyl-2-nitrophenylbenzimidazole (NBPBI) in view of the possibility that such a change in stereochemistry might confer on them the ability to function as oxygen carriers. Based on this, the tetrahedral complexes, $[CoL_2X_2]$ (L = NBPBI; X = Cl, Br or I) or planar complexes, $[CuL_2X_2]$ (X = Cl or Br) was made to react with a new Schiff base obtained by the condensation of aminomethyl polystyrene and quinoxaline-2-carboxaldehyde, so as to obtain five coordinated complexes of cobalt(II) or copper(II). The results of our studies on the polymer supported complexes are presented in this chapter.

EXPERIMENTAL

The procedures for the preparation of aminomethyl polystyrene and quinoxaline-2-carboxaldehyde are already described in Chapter II. The techniques employed for the characterization of the polymer supported complexes are also presented in the same chapter.

Synthesis of the polymer supported Schiff base

A solution of quinoxaline-2-carboxaldehyde (0.5 g in 5 mL DMF) was added to the aminomethyl polystyrene (5 g), and the reaction mixture was refluxed for about 5 h. Brown coloured product thus

obtained was filtered, washed several times with DMF and acetone, and then dried *in vacuo* over anhydrous $CaCl_2$.
{Yield: 80 %}

Synthesis of the polymer supported complexes

The synthetic procedures for the simple complexes of $[Co(NBPBI)_2X_2]$ and $[Cu(NBPBI)_2X_2]$ are given in Chapter III.

Polymer supported complexes of cobalt(II) and copper(II) were synthesized by treating the polymer supported Schiff base with the simple complexes of cobalt(II) and copper(II) derived from NBPBI.

Polymer supported Schiff base (0.5 g) was swollen in acetone (10 mL) for about 1 h, and the solvent was decanted off. A solution of the simple complex of cobalt(II), {$[CoL_2X_2]$, L = NBPBI; X = Cl, Br or I} or copper(II), {$[CuL_2X_2]$ (X = Cl or Br)} (25 mg dissolved in 4 mL acetone) was introduced into the vessel containing the polymer supported Schiff base. The reaction mixture was shaken well for about 1 h and the product obtained was filtered, washed several times with acetone, and then dried *in vacuo* over anhydrous $CaCl_2$.
{Yield: 70 %}

RESULTS AND DISCUSSION

All the polymer supported complexes are light coloured, and are stable in air. They are insoluble in most of the common organic solvents.

Chloromethyl polystyrene (2 % crosslinked with divinylbenzene) beads were used as the starting material for the synthesis of the polymer-bound Schiff base. The chlorine content in this compound was compared with the percentage of chlorine calculated for all possible repeating units, which indicated that only alternative rings were chloromethylated. Thus, the repeating unit could be represented as sketched in Figure 1.

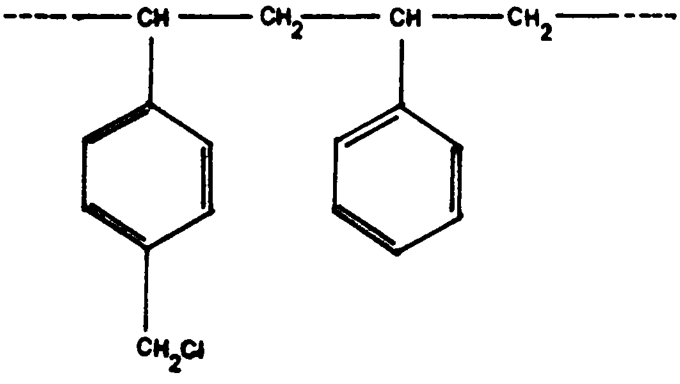
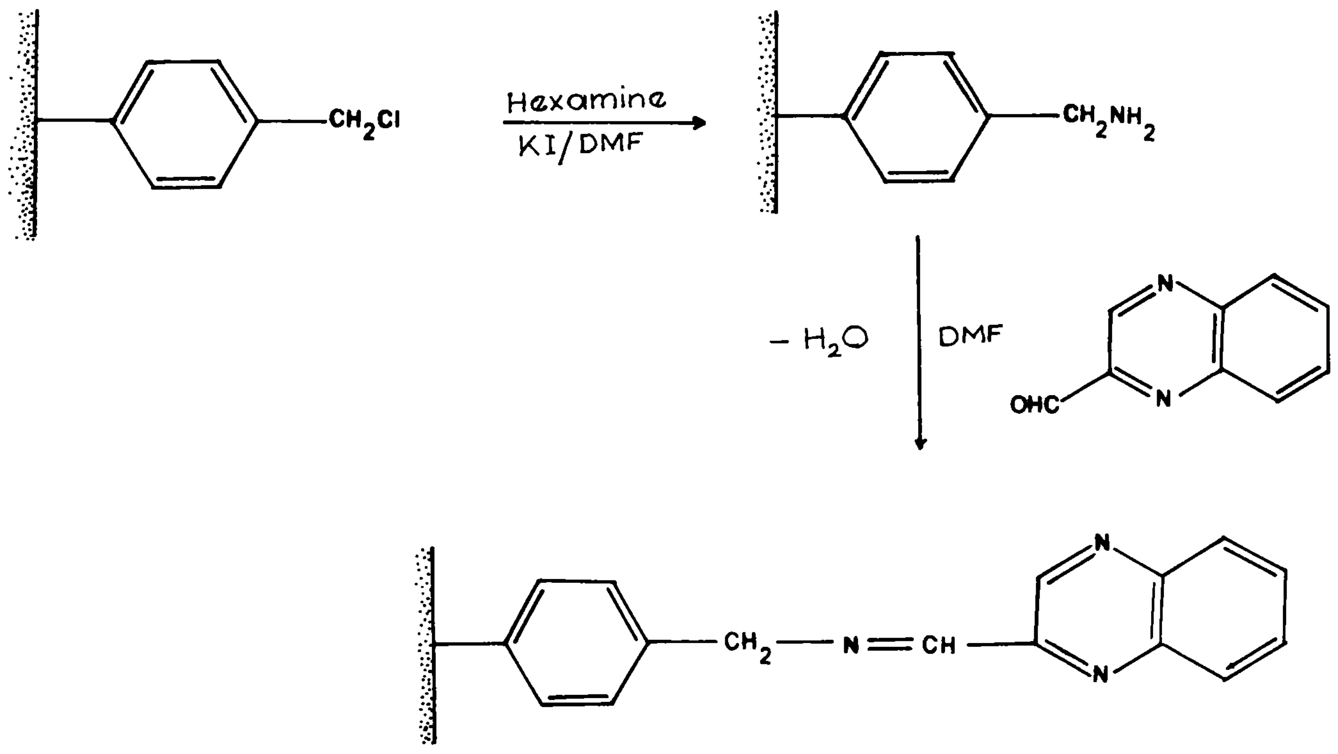


Figure 1. Chloromethyl polystyrene

The beads on treating with DMF yield polymer-bound amine, which is evidenced by a positive test with Ninhydrin reagent. The



Scheme I. Polymer-bound Schiff base

polymer-bound amine was then condensed with quinoxaline-2-carboxaldehyde to get polymer-bound Schiff base, as shown in Scheme I.

The polymer-bound ligand was allowed to interact with acetone solutions of the tetrahedral complexes, $[\mathrm{CoL_2X_2}]$ (L = NBPBI; X = Cl, Br or I) or planar complexes, $[\mathrm{CuL_2X_2}]$ (X = Cl or Br). In the resulting polymer supported complexes, the analytical data (Table I) indicates that only one Schiff base unit is coordinated to the metal ion. However, as pointed out by other workers, the analytical data for the polymer samples can be taken as a qualitative rather than a quantitative guide[2,7].

Table I

Analytical data for the polymer supported compounds

Compound	Found (Calc.) %				
	C	H	N	Co/Cu	Cl/Br/I
L	79.17 (80.54)	6.62 (6.63)	3.94 (4.42)	—	8.23 (8.39)
$[\mathrm{CoL(NBPBI)_2Cl_2}]$	68.83 (69.95)	5.69 (5.22)	7.20 (7.83)	2.10 (2.74)	8.89 (8.26)
$[\mathrm{CoL(NBPBI)_2Br_2}]$	68.52 (67.17)	5.70 (5.01)	7.44 (7.52)	2.80 (2.63)	11.03 (11.91)
$[\mathrm{CoL(NBPBI)_2I_2}]$	64.19 (64.45)	5.24 (4.81)	7.20 (7.21)	2.92 (2.53)	14.86 (15.47)
$[\mathrm{CuL(NBPBI)_2Cl_2}]$	69.35 (69.80)	5.13 (5.21)	7.77 (7.81)	3.20 (2.95)	8.15 (8.24)
$[\mathrm{CuL(NBPBI)_2Br_2}]$	67.58 (67.03)	5.55 (5.00)	6.94 (7.50)	3.10 (2.84)	11.55 (11.89)

L = Polymer-bound Schiff base

Magnetic susceptibility measurements

All the polymer supported complexes show positive magnetic susceptibility values indicating their paramagnetic nature.

Infrared spectra

A strong band is observed at 1610 cm^{-1} in the spectrum of the free ligand which may be attributed to the $\nu(C=N)$ stretching vibration[8]. This band appear at the same position in the spectra of the complexes which reveals nonparticipation of the azomethine nitrogen in coordination. A band of medium intensity observed at 1580 cm^{-1} in the spectrum of the polymer ligand, which may be assigned to the $\nu(C=N)$ stretching vibration of the quinoxaline ring nitrogen. In the spectra of all the complexes, this band is seen to shift towards lower frequency (1570 cm^{-1}), indicating the chelation of the quinoxaline ring nitrogen to the metal. Thus, the polymer supported ligand herein acts as a monodentate ligand coordinating through a quinoxaline ring nitrogen.

Electronic spectra

The electronic absorption spectral data do not provide any conclusive evidence for assigning the structure of these complexes.

All the polymer supported complexes show intraligand transitions in the range, 35900–25000 cm^{-1}.

EPR spectra

Powder EPR spectra of the polymer supported complexes of copper(II) recorded at room temperature are presented here.

The EPR spectrum of the polymer supported chloro complex (Figure 2) shows two 'g' values ($g_{\parallel}$ = 2.13, $g_{\perp}$ = 2.03; $A_{\parallel}$ = 75 G). The bromo complex (Figure 3) also exhibits two 'g' values ($g_{\parallel}$ = 2.19, $g_{\perp}$ = 2.06; $A_{\parallel}$ = 81 G). These values are characteristic for a five coordinated structure of copper(II) complex[9].

It is understood that there are three possibilities for a five coordinated structure. They are square pyramid, trigonal bipyramid and intermediate geometry between these two extremes. Further, it has been reported that for a square pyramid, $g_{\parallel}$ is in the range, 2.25–2.40 and $A_{\parallel}$ is 120–150 G range. In the present cases, the $g_{\parallel}$ values are not in the range reported for a square pyramid structure suggesting that the structure of a polymer supported complex may have either a intermediate geometry or a trigonal bipyramid[9].

EPR spectrum of the polymer supported chloro complex of cobalt(II), has also been recorded at both room and liquid nitrogen temperatures. This complex exhibits only a single 'g' value of 2.01 at

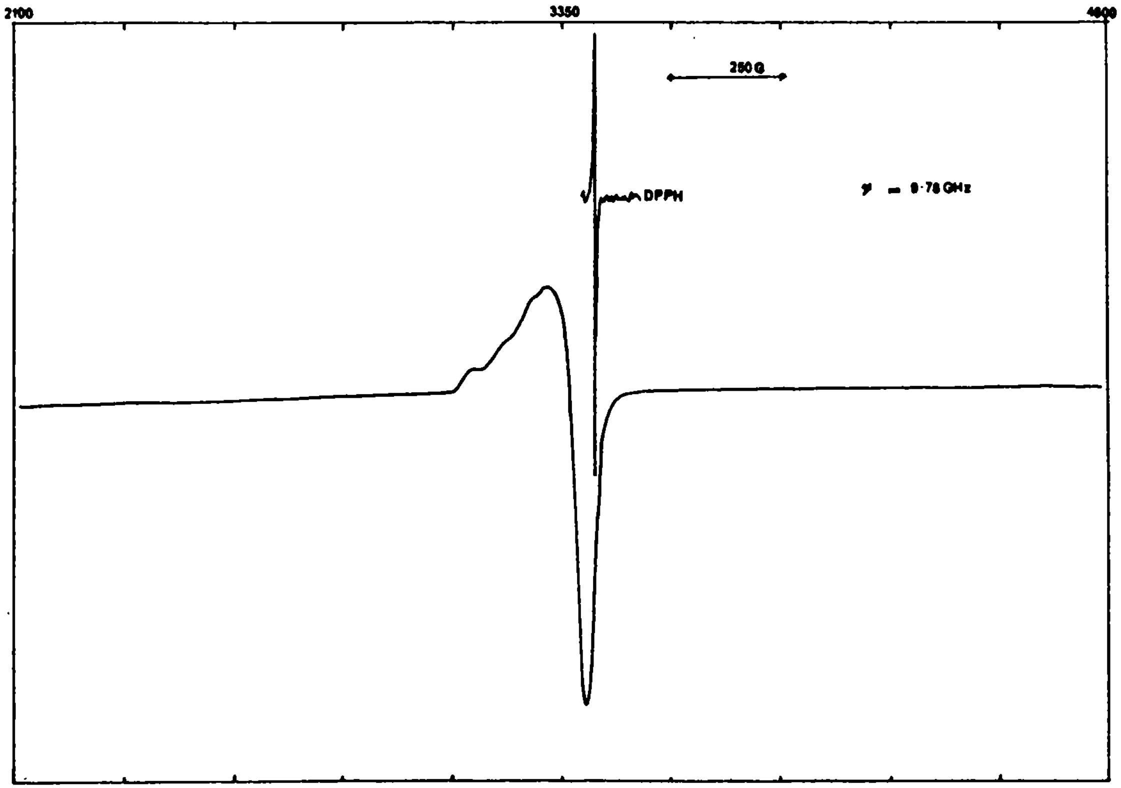


Figure 2. EPR spectrum of the polymer-bound copper(II) chloro complex

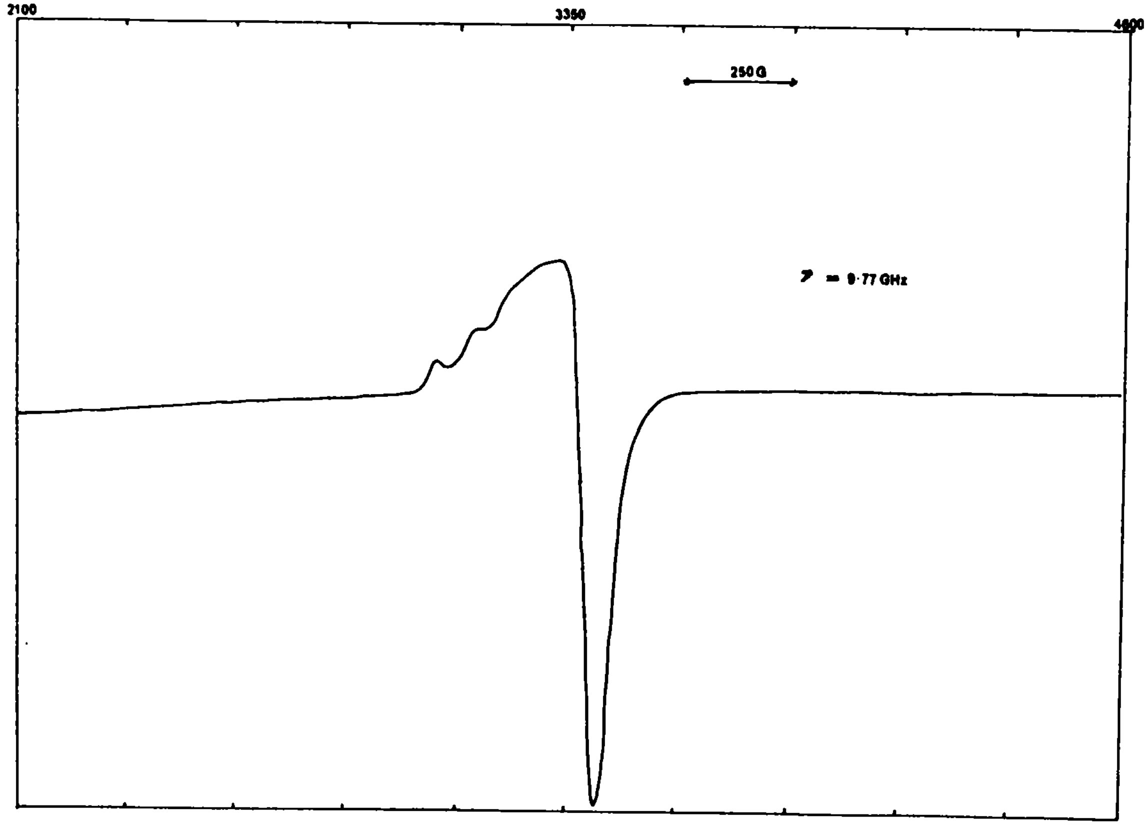


Figure 3. EPR spectrum of the polymer-bound copper(II) bromo complex

room temperature. However, the complex shows some hyperfine splittings at liquid nitrogen temperature, and the observed 'g' values are $g_{\parallel} = 1.88$; $g_{\perp} = 2.00$ and $A_{\parallel} = 80$ G . These values indicate the low-spin nature of the cobalt(II) complex. Further, it has been reported[9] that for the square pyramid complexes of cobalt(II) $g_{\perp} > g_{\parallel}$ and for the trigonal bipyramid complex $g_{\parallel} > g_{\perp}$. The $g_{\perp}$ value is found to be greater than the $g_{\parallel}$ value in the present case suggesting the square pyramid structure for the cobalt complex.

REFERENCES

1. P. Kannan and T. Kaliyappan, *J. Appl. Polym. Sci.*, 60, 947 (1996).

2. E. Tsuchida and Nishide, "*Advances in Polymer Science*", Springler-Verlag, Berlin, Vol. 24, 1977.

3. J. B. Sheridan, P. G. Elipe and I. Manners, *Macromol. Rapid Commun.*, 17, 319 (1996).

4. B. Mathew and V. N. R. Pillai, *Proc. Indian Acad. Sci.*, 108, 1 (1996).

5. L. M. Robinson and D. F. Sheriver, *J. Coord. Chem.*, 37, 119 (1996).

6. E. W. Neuse, "*Enclopedia of Polymer Sciences and Technology*", Interscience, New York, Vol. 8, 1968.

7. D. Wohrle, *Advances in Polymer Science,* Springler-Verlag, Berlin, Vol. 50, 1983.

8. K. K. Mohammed Yusuff and R. Sreekala, *J. Polym. Sci.: Part A: Polym. Chem.*, 30, 2595 (1992).

9. "*Transition Metal Chemistry*" (G. A. Melson and B. N. Figgis (Eds.)), Marcel Dekker, Inc., New York, Vol. 8, 1982.

CHAPTER V

COMPLEXES OF IRON(III), COBALT(II), NICKEL(II) AND COPPER(II) WITH 2-PHENYL-1,2,3-TRIAZOLE-4-CARBOXALIDENE-2-AMINOPHENOL

INTRODUCTION

Triazoles are known to have interesting applications in medicine and agriculture[1-4]. Further, complexes containing ligands derived from triazoles[5-8] are known to have spin-crossover properties. The Schiff base, PTCAP (Figure 1) formed by condensing 2-phenyl-1,2,3-triazole-4-carboxaldehyde with 2-aminophenol is interesting from the structural point of view due to the presence of three nitrogens in the triazole ring, an azomethine nitrogen, and a phenolic oxygen, all of which have the ability to coordinate. We have undertaken this study to ascertain whether the PTCAP ligand would enforce an unusual stereochemistry on certain transition metal ions such as iron(III), cobalt(II), nickel(II) and copper(II), and whether its complexes would display anomalous magnetic behaviour. The results of our studies on these complexes are discussed in this chapter.

EXPERIMENTAL

Synthetic procedure of the 2-phenyl-1,2,3-triazole-4-carboxaldehyde and the analytical methods employed for the characterization of the complexes derived from this aldehyde are presented in Chapter II. Further, the instrumental details regarding the measurement of cyclic voltammograms of the copper(II) and iron(III) complexes (scan rate = 50 mV s^{-1}) obtained at 25.0 ± 0.2 °C are also given in the same Chapter.

A three-electrode system consisting of a platinum sphere electrode, a platinum plate and a reference electrode Ag(s)/$AgNO_3$ was used. Tetrahexylammoniumperchlorate (THAP) (0.1 M) in DMF was used as the supporting electrolyte.

Synthesis of the ligand

2-Phenyl-1,2,3-triazole-4-carboxaldehyde (1.73 g, 0.01 mol) was dissolved in ethanol (25 mL), and was added to a solution of 2-aminophenol (1.09 g, 0.01 mol) in ethanol (25 mL). The mixture was boiled under reflux for 1 h on a water bath. The precipitated ligand was removed by filtration, washed with cold ethanol followed by ether, and dried *in vacuo* over anhydrous $CaCl_2$.
{Yield: 90 %; Melting point: 157 °C}

Synthesis of the complexes

All the complexes were synthesized by the following general procedure.

A solution containing the metal salt (0.005 mol) *{*$Fe(NO_3)_3.9H_2O$ (2.02 g), $Co(NO_3)_2.6H_2O$ (1.45 g), $Ni(NO_3)_2.6H_2O$ (1.45 g) or $Cu(NO_3)_2.3H_2O$ (1.20 g)*}* in ethanol (5 mL) was added to a solution containing PTCAP (2.64 g, 0.01 mol) in ethanol (50 mL). The mixture

was boiled under reflux on a water bath for 2 h and the complexes separated were filtered, washed with cold ethanol, ether and acetone, and dried *in vacuo* over anhydrous $CaCl_2$.
{Yield: 70–80 %; Melting points of the iron(III), cobalt(II) and copper(II) complexes are above 250 ^{o}C; for the nickel(II) complex, the melting point is 185 ^{o}C}

RESULTS AND DISCUSSION

The Schiff base ligand, PTCAP was synthesized by the condensation of 2-phenyl-1,2,3-triazole-4-carboxaldehyde and 2-aminophenol in 1:1 molar ratio. Analytical data suggest that the ligand has the empirical formula $C_{15}H_{12}N_4O$.

^{1}H NMR spectrum (Figure 2) in DMSO-d_6 exhibits the triazole proton as a singlet at δ 8.9 ppm, and the arylidine proton also as a singlet at δ 8.7 ppm. Distinct set of peaks observed between δ 8.1 and 6.8 ppm are characteristic of aromatic protons. A broad singlet observed between δ 9.0 and 9.5 ppm is due to the phenolic proton. Proton decoupled ^{13}C NMR spectrum (Figure 3) of this compound is also in agreement with the assigned structure. All these peaks were observed between 116.70 and 151.99 ppm region. The band observed at 1628 cm^{-1} in the infrared spectrum of this ligand indicates the formation of ν(C=N) of the azomethine group. Thus, both the IR and NMR data are in favour of the structure shown in Figure 1.

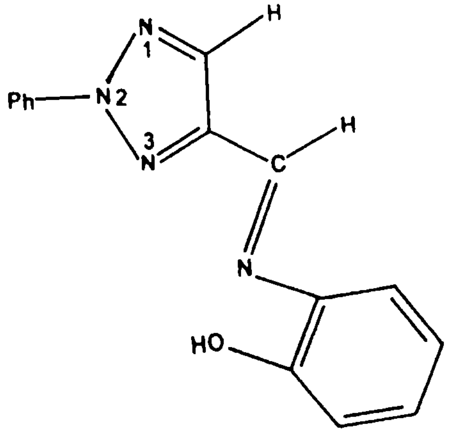


Figure 1. Structure of the PTCAP

All the complexes are coloured, non-hygroscopic, crystalline substances, and are stable in air. They are soluble in DMF and DMSO, slightly soluble in ethanol and nitrobenzene, and are insoluble in acetonitrile, chloroform, dichloromethane, benzene, acetone, dioxane, ether and toluene. The analytical data show that the complexes have the general formula, $[ML_2]$ (M = cobalt(II), nickel(II) or copper(II); L = PTCAP) or $[Fe(OH)L_2]$ and the data are given in Table I. The molar conductances of the complexes (Table II) reveal that they are non-electrolytes in DMF.

Infrared spectra

The IR spectrum of the PTCAP ligand (Table III) exhibits a sharp band at 1628 cm^{-1} indicating the presence of the azomethine $[\upsilon(C=N)]$

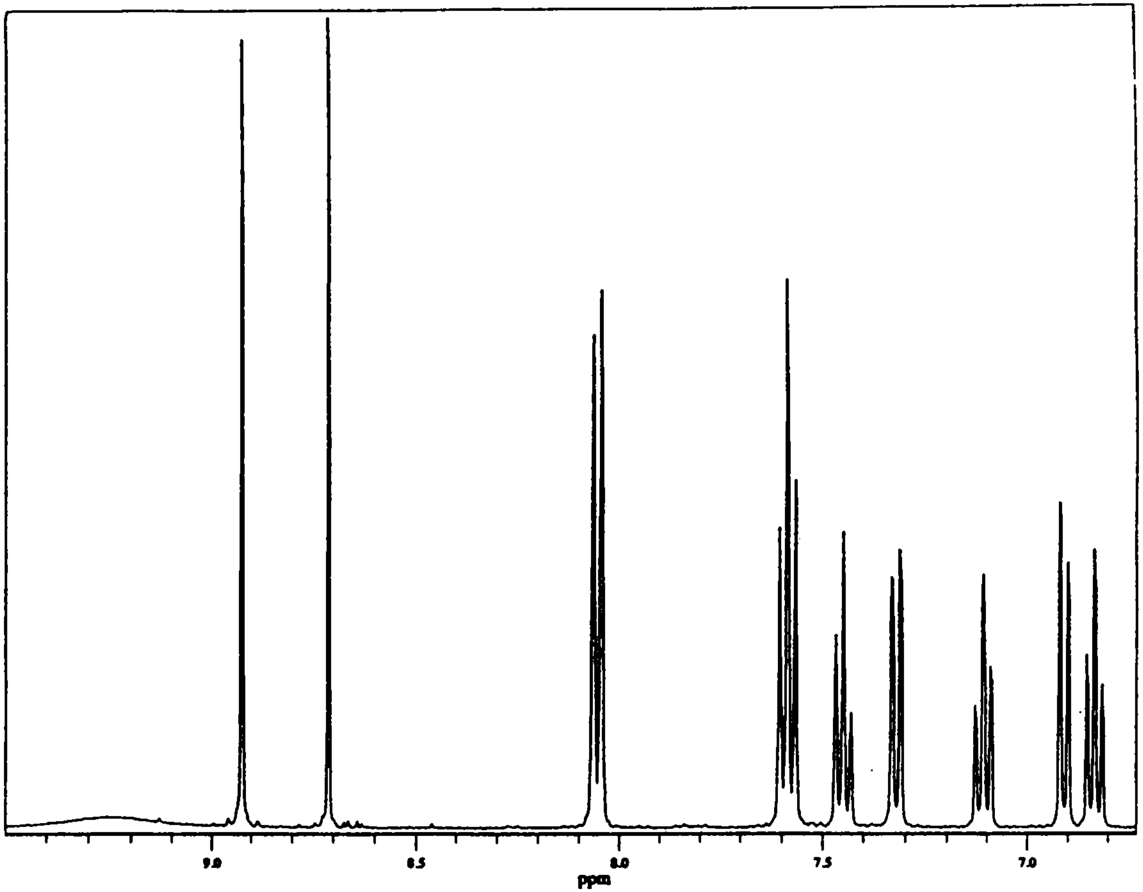


Figure 2. ^{1}H NMR spectrum of PTCAP

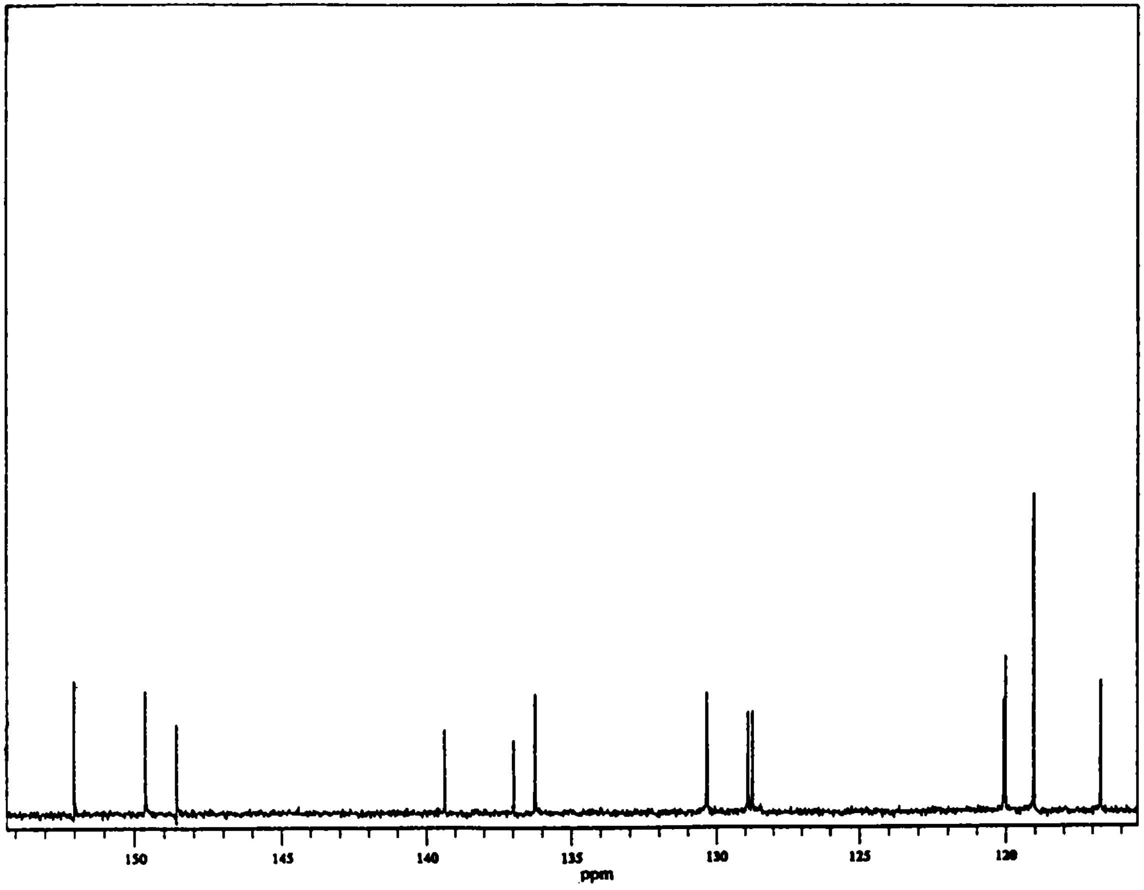


Figure 3. ^{13}C NMR spectrum of PTCAP

Table I

Analytical data and colour of the ligand and its complexes

Compound	Colour	Found (Calc.) %			
		C	H	N	M
L, Ligand	Yellow	68.0 (68.2)	4.5 (4.5)	21.1 (21.2)	—
[FeL$_2$(OH)]	Dark brown	60.2 (60.1)	4.0 (3.8)	18.8 (18.7)	9.2 (9.3)
[CoL$_2$]	Dark brown	61.6 (61.6)	3.7 (3.8)	19.3 (19.15)	9.7 (9.8)
[NiL$_2$]	Maroon	61.5 (61.6)	3.7 (3.8)	19.1 (19.15)	10.0 (10.0)
[CuL$_2$]	Blackish green	61.0 (61.1)	3.7 (3.7)	18.9 (19.0)	10.7 (10.8)

L = 2-Phenyl-1,2,3-triazole-4-carboxalidene-2-aminophenol (PTCAP)

Table II

Molar conductance and magnetic moment data for the complexes

Complex	Molar conductance ($ohm^{-1} cm^2 mol^{-1}$)	Magnetic moment (B.M.)
[FeL$_2$(OH)]	11.23	4.64
[CoL$_2$]	11.60	4.85
[NiL$_2$]	18.90	2.88
[CuL$_2$]	30.40	2.10

L = PTCAP

group. This band shifts to a lower frequency in all the complexes, which suggests the participation of the azomethine nitrogen in bonding to the metal[9,10].

The ligand also shows two more υ(C=N) bands: one at 1597 cm^{-1} and the other at 1585 cm^{-1}, characteristic of the triazole [υ(C=N)] ring[11]. The 1597 cm^{-1} band remains unchanged on complexation, however, the other band at 1585 cm^{-1} is shifted to a lower frequency, indicating that only one of the triazole ring nitrogens is coordinated to the central metal ion[8].

Table III

Some relevant IR spectral (cm^{-1}) data

I	II	III	IV	V	Tentative assignments
1628	1618	1618	1618	1618	ν(C=N) (azomethine)
1597	1597	1597	1597	1597	ν(C=N) (triazole)
1585	1575 1585	1571	1571	1570	ν(C=N) (triazole)
1250	1270	1265	1265	1270	ν(C-O) (phenolic group)
——	3500–3400	——	——	——	ν(OH) stretching
——	1120	——	——	——	ν(M-OH) bending

I = PTCAP; II = Iron(III) complex; III = Cobalt(II) complex;
IV = Nickel(II) complex and V = Copper(II) complex

Furthermore, the ligand exhibits a sharp band at 1250 cm^{-1}, due to the phenolic group [υ(C-O)]. This band shifts to 1270 cm^{-1} for the iron(III) and copper(II) complexes, and to 1265 cm^{-1} for the cobalt(II) and nickel(II) complexes, suggesting coordination of phenolic oxygen[12,13]. Thus, the ligand acts as tridentate ligand, coordinating through the triazole ring nitrogen, azomethine nitrogen, and phenolic oxygen in the cobalt(II), nickel(II) and copper(II) complexes. For the iron(III) complex, one of the two ligands acts as a bidentate (N,O), and the other as a tridentate (N,N,O) species. Moreover, the iron(III) complex exhibits a broad band at 3500-3400 cm^{-1}, which may be due to the presence of either a hydroxyl group[14] or of a water molecule. However, the band at 1600 cm^{-1}, characteristic of the HOH bending, was not observed in this complex; and an additional band due to the M-OH bending was observed at 1120 cm^{-1}, confirming the hydroxyl group bonding[15].

Magnetic measurements

The magnetic moments obtained for all the complexes are given in Table II.

The magnetic moment of the iron(III) complex was found to be 4.64 B.M. at room temperature, which lies between the expected spin-only value of 5.92 B.M. for a high-spin and 2.3 B.M. for a low-spin complex. This anomalous value may be due to the presence of a mixture of high-spin and low-spin octahedral complexes, or to an antiferromagnetically coupled binuclear complex. However, the IR spectral data suggest the absence of any bridged OH group[16]. Therefore, this anomalous behaviour may be due to the existence of a spin-crossover equilibrium.

The magnetic moment, 4.85 B.M., for the cobalt(II) complex indicates an octahedral structure[17]. The μ_{eff} values of 2.88 B.M. for the nickel(II) complex[17] and 2.10 B.M. for the copper(II) complex[17] suggest octahedral structures for these complexes also.

Mössbauer spectrum

At room temperature, the Mössbauer spectrum complex (Figure 4) shows two isomer shifts (0.0125; 0.5531 mm s^{-1}) and two quadrupole splittings (0.69; 2.26 mm s^{-1}) for the iron(III) complex. These values are typical of a mixture of high-spin and low-spin octahedral iron(III) complex[18]. Furthermore, their composition may be given as 4 % and 96 % respectively from the area of the peaks corresponding to low-spin and high-spin complexes.

EPR spectra

The EPR spectrum of the copper(II) complex (Figure 5) shows two 'g' values (2.191; 2.056), which may be attributed to a partially distorted octahedral structure. As the lowest 'g' value is also

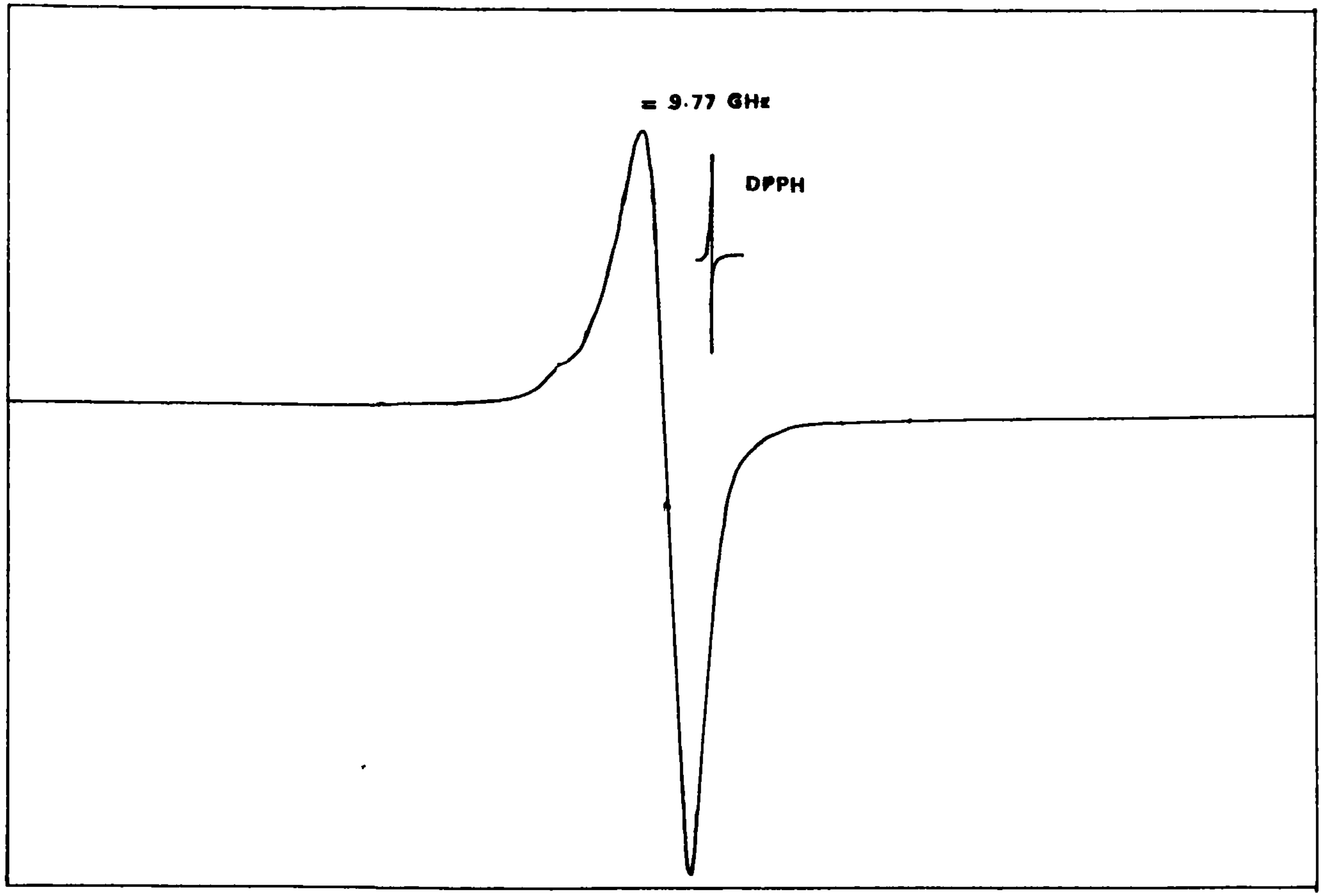


Figure 5. EPR spectrum of $[CuL_2]$

greater than 2.04, an elongated rhombic octahedral structure is proposed for the complex[19].

Electronic spectra

The electronic absorption spectral data of all the complexes recorded in DMF are given in Table IV.

The electronic spectrum of the iron(III) complex shows a broad absorption band at 22730 cm^{-1} and also some weak absorptions at 14000 cm^{-1} corresponding to a combination of the $^6A_{1g} \longrightarrow {}^4A_{1g}, {}^4E_g$ and $^6A_{1g} \longrightarrow {}^4T_{1g}$ forbidden transitions respectively in the octahedral symmetry. Occurrence of such forbidden transitions have been reported in the case of octahedral iron(III) complexes[20,21].

The cobalt(II) complex exhibits an absorption band with medium intensity at 22220 cm^{-1}, which can be assigned to the $^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P)$ transition and also a weak absorption observed at 10140 cm^{-1} due to the $^4T_{1g}(F) \longrightarrow {}^4T_{2g}$ transition[22].

The nickel(II) complex shows three absorptions at 10000 cm^{-1}, 20750 cm^{-1} and 24100 cm^{-1}, which can be attributed to the $^3A_{2g} \longrightarrow {}^3T_{2g}(F)$, $^3A_{2g} \longrightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \longrightarrow {}^3T_{1g}(P)$ transitions[23] in octahedral complexes.

The copper(II) complex shows a d-d transition at 14220 cm^{-1}. A medium band is also observed at 24150 cm^{-1}, which may be due to charge transfer transition. Further, all the complexes exhibit intraligand transitions around 36000 cm^{-1}.

Table IV

Electronic spectral (cm^{-1}) data for the complexes

Complex	Absorption maxima	ε_{max} $(l\ cm^{-1}\ mol^{-1})$	Tentative assignments
$[FeL_2(OH)]$	36360	2087	Intraligand transition
	22730	25	$^6A_{1g} \longrightarrow {}^4A_{1g}, {}^4E_g$
	14660	12	$^6A_{1g} \longrightarrow {}^4T_{1g}$
	14020	13	
$[CoL_2]$	36100	2104	Intraligand transition
	22220	30	$^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P)$
	17300	13	
	10140	4	$^4T_{1g}(F) \longrightarrow {}^4T_{2g}$
$[NiL_2]$	36230	1940	Intraligand transition
	24100	20	$^3A_{2g} \longrightarrow {}^3T_{1g}(P)$
	20750	27	$^3A_{2g} \longrightarrow {}^3T_{1g}(F)$
	17850	14	
	10680	4	$^3A_{2g} \longrightarrow {}^3T_{2g}(F)$
	10080	10	
	9750	5	
$[CuL_2]$	36230	1990	Intraligand transition
	24150	866	Charge transfer transition
	14220	9	$^2E_g \longrightarrow {}^2T_{2g}$

L = PTCAP

The electronic spectra of the complexes were recorded in both DMF and in solid state. The bands in both cases are almost at identical positions, which reveals that the coordinating solvent DMF does not influence the structure of the complexes.

Cyclic voltammetric studies

The CV of the copper(II) complex (Figure 6a) features the reduction of copper(II) to copper(I) at a cathodic peak potential of - 0.1980 V versus S.C.E. (Table V). Oxidation of the copper(I) species occurs at

Table V
Electrochemical characterization by cyclic voltammetry of the $Cu^{II}(PTCAP)_2$ in DMF

Scan rate (mVs^{-1})	E_{pc} (V)	i_{pc} (mA)	E_{pa} (V)	i_{pa} (mA)
10	−0.2160	2.830	0.0680	−4.46
20	−0.2360	5.460	0.0340	−6.080
50	−0.1980	12.440	0.0280	−10.90
100	−0.2220	16.430	0.0340	−14.81
200	−0.2200	30.400	0.0420	−24.10
500	−0.2380	52.900	0.1000	−39.10
1000	−0.2500	78.900	0.1420	−55.70

E_{pc} = Cathodic peak potential; i_{pc} = Cathodic peak current;

E_{pa} = Anodic peak potential and i_{pa} = Anodic peak current

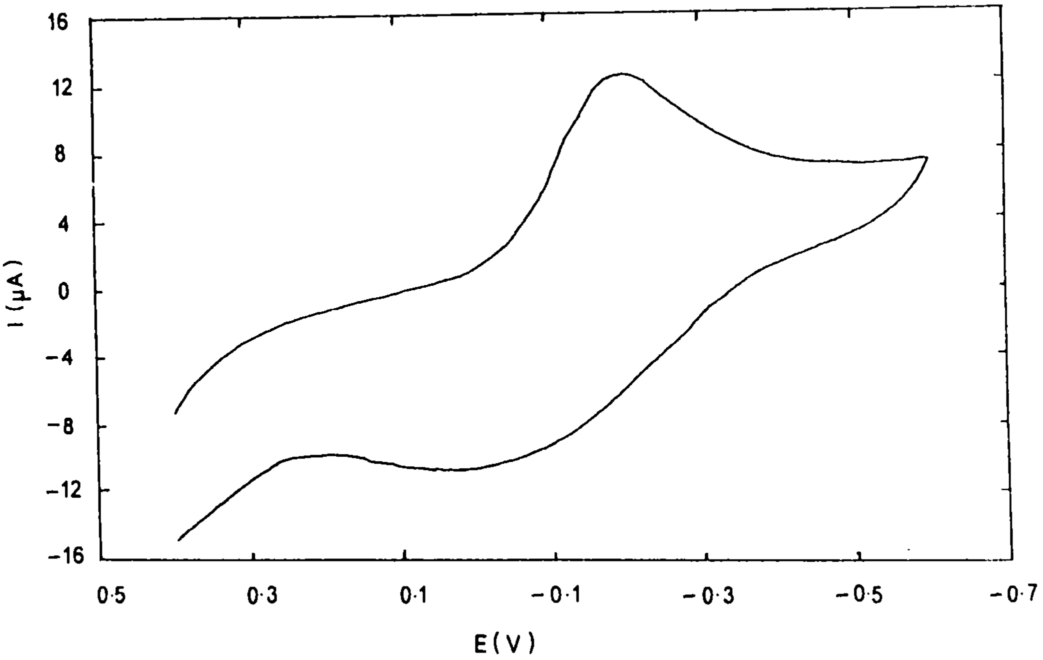


Figure 6a. Cyclic voltammogram of the [CuL_2] complex at 50 mV s^{-1}

an anodic peak potential of + 0.0280 V. The separation between the anodic and cathodic peak potentials, ΔE_p = 226 mV, indicates an irreversible, one electron redox process. The average peak potential for this complex is found to be, $E_{1/2}$ = − 0.0850 V. The cyclic voltammetric curves at different scan rates were also recorded and the overlay spectrum is shown in Figure 6b.

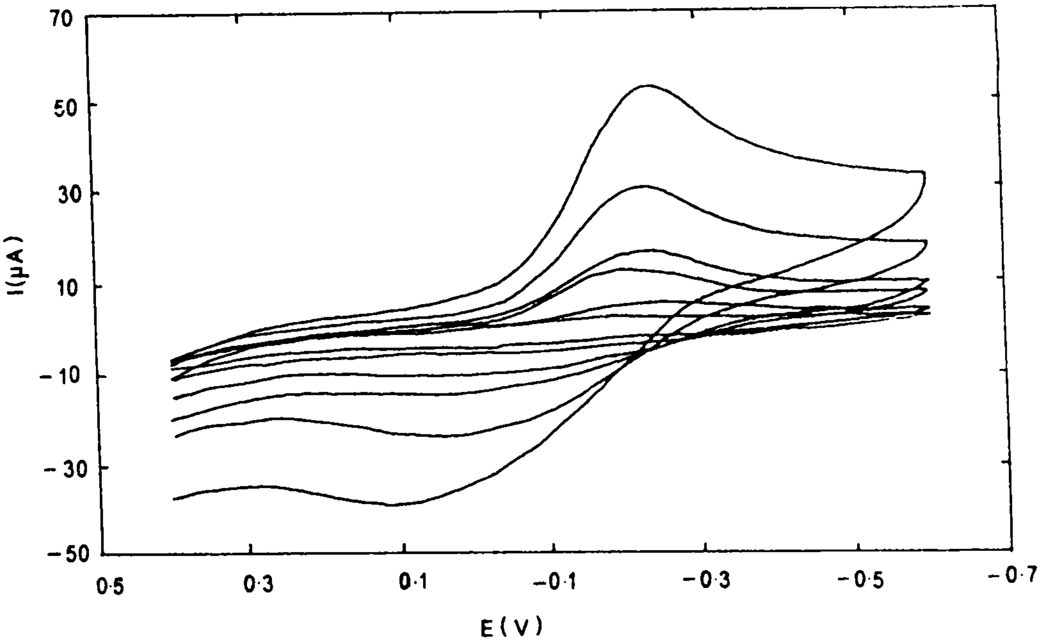


Figure 6b. Cyclic voltammograms of the [CuL_2] complex at different scan rates

The CV of the iron(III) complex (Figure 7) shows only a cathodic peak at a peak potential of − 0.2380 V indicating the reduction of iron(III) to iron(II) species and further no anodic peaks are observed even for different scan rates, up to 1000 mV s^{-1}. This excludes the possibility of oxidation reactions in this complex.

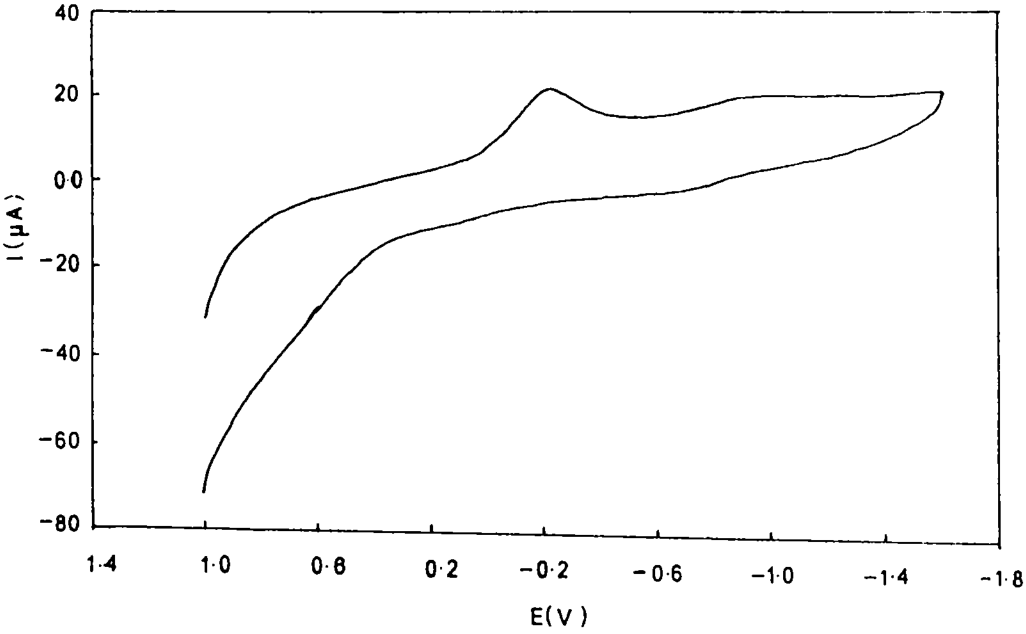
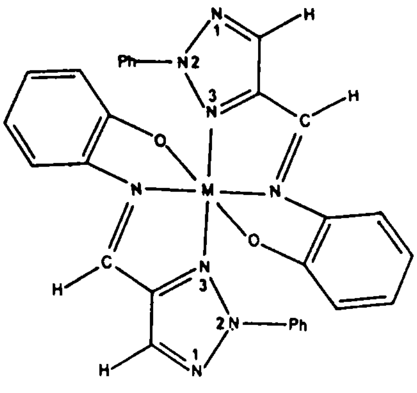


Figure 7. Cyclic voltammogram of the [$FeL_2(OH)$] complex at 50 mV s^{-1}

Based on the above investigations, an octahedral structure (Figure 8) has been proposed for all the complexes.



M = Co^{II}, Ni^{II} or Cu^{II}

Figure 8a. Proposed structure of the complexes

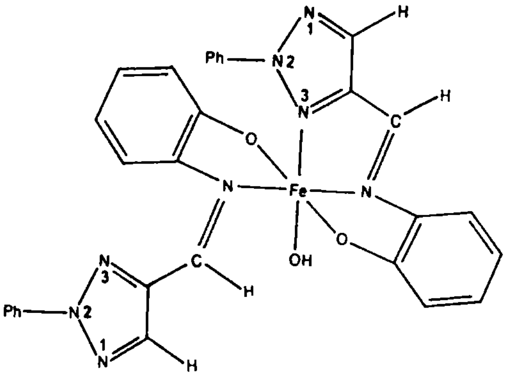


Figure 8b. Proposed structure of the iron complex

REFERENCES

1. M. D. Mullican, M. W. Wilson, D. T. Connor, C. R. Kostlan, D. T. Schrier and R. D. Dyer, *J. Med. Chem.*, 36, 1090 (1993).

2. A. Tasaka, K. Teranishi, Y. Matsushita, N. Tamura, R. Hayashi K. Okonogi and K. Itoh, *Chem. Pharm. Bull.*, 1, 85 (1994).

3. L. Savini, P. Massarelli, P. Corti, L. Chiasserini, C. Pellerano and G. Bruni, *Farmaco.*, 49, 363 (1994).

4. K. Smith, M. E. W. Hammond, D. M. James, I. J. Ellison and M. G. Hutchings, *Chem. Lett.*, 347 (1990).

5. M. Thomann, O. Khan, J. Guilhem and F. Varret, *Inorg. Chem.*, 33, 6029 (1994).

6. J. P. Martin, J. Zarembowitch, A. Bousseksou, A. Dworkin, J. G. Haaasnoot and F. Varret, *Inorg. Chem.*, 33, 6325 (1994).

7. P. Stupik, W. M. Reiff, R. Hage, J. Jacobs, J. G. Haasnoot and J. Reedijik, *Hyperfine-Interactions*, 40, 343 (1988).

8. K. K. M. Yusuff and C. Krishnakumar, *Synth. React. Inorg. Met.-Org. Chem.*, 23, 695 (1993).

9. G. R. Burns, *Inorg. Chem.*, 7, 277 (1968).

10. K. K. M. Yusuff and R. Sreekala, *Synth. React. Inorg. Met.-Org. Chem.*, 21, 553 (1991).

11. E. N. Alexandrou and N. A. Rodios, *J. Heterocyclic Chem.*, 27, 231 (1990).

12. K. K. M. Yusuff and R. Sreekala, *Thermochim. Acta*, 179, 313 (1991).

13. M. M. Aly and Z. H. Khalil, *Inorg. Chem.*, 42, 126 (1979).

14. J. R. Ferraro and W. R. Wacker, *Inorg. Chem.*, 4, 1382 (1965).

15. K. Nakamoto, "*Infrared and Raman Spectra of Inorganic and Coordination Compounds*", 4th Edn., Wiley Interscience, New York, pp. 230, 1986.

16. J. R. Ferraro, R. Driver, W. R. Walker and W. Wozniak, *Inorg. Chem.*, 6, 1586 (1967).

17. N. Saravanan, B. N. Sivasankar, S. Govindarajan and K. K. M. Yusuff, *Synth. React. Inorg. Met.-Org. Chem.*, 24, 703 (1994).

18. S. A. Cotton, *Coordn. Chem. Rev.*, 8, 192 (1972).

19. B. J. Hathaway and D. E. Billing, *Coordn. Chem. Rev.*, 5, 171 (1970).

20. A. K. Rana and J. R. Saha, *Indian J. Chem.*, 20A, 929 (1982).

21. A. B. P. Lever, "*Inorganic Electronic Spectroscopy*", Elsevier, New York, pp. 452 (1984).

22. E. Larsen, G. N. Lamar, B. E. Wagner, J. E. Parks and R. H. Holm, *Inorg. Chem.*, 11, 2652 (1972).

23. D. Nicholls and R. Suindells, *J. Inorg. Nucl. Chem.*, 30, 2211 (1968).

CHAPTER VI

INDOLE-3-CARBOXALIDENE-3-AMINO-1,2,4-TRIAZOLE COMPLEXES OF IRON(III), COBALT(II), NICKEL(II) AND COPPER(II)

INTRODUCTION

Triazoles are known to have wide applications in medicine[1-5]. Reactions of 3-amino-1,2,4-triazole (amitrole) with various aldehydes like pyridine-2-carboxaldehyde, benzaldehyde, hydroxybenzaldehyde, salicylaldehyde, vanillin, diphenylfurancarboxaldehyde, bromoacetaldehyde, dichlorobenzaldehyde, nitromalondialdehyde, coumaldehyde and furan-2-carboxaldehyde have been reported[6-10]. However, only studies of few examples of complexes with 3-amino-1,2,4-triazole, and Schiff bases derived from this amine[11-15] have appeared in the literature. The Schiff base ligand, indole-3-carboxalidene-3-amino-1,2,4-triazole

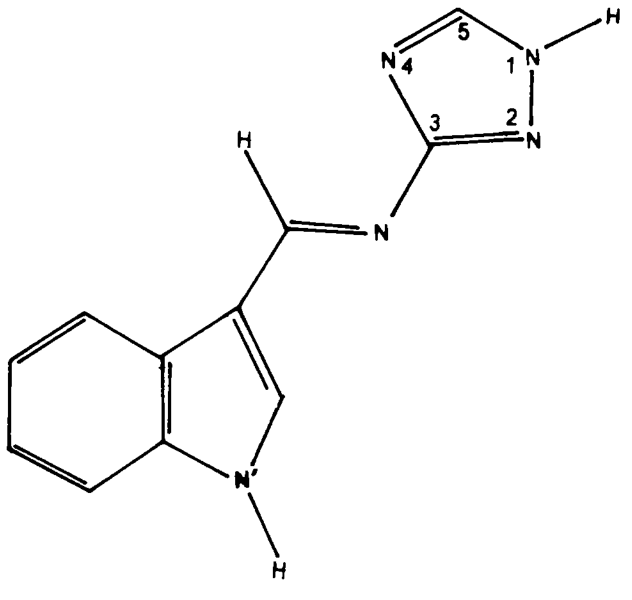


Figure 1. Structure of the ICAT

(ICAT) (Figure 1) formed by the condensation of indole-3-carboxaldehyde and 3-amino-1,2,4-triazole is interesting from the structural point of view due to the presence of a number of coordination sites: triazole ring nitrogens, azomethine nitrogen and indole ring nitrogen. However, there has been no report on the synthesis and characterization of complexes of ICAT. We have, therefore, taken up the synthesis and characterization of iron(III), cobalt(II), nickel(II) and copper(II) complexes with ICAT, the results of which are presented in this chapter.

EXPERIMENTAL

A procedure for the preparation of indole-3-carboxaldehyde and the characterization techniques are already described in Chapter II.

Synthesis of the ligand

Indole-3-carboxaldehyde (1.45 g, 0.01 mol) was dissolved in ethanol (10 mL), and was mixed with 3-amino-1,2,4-triazole (0.84 g, 0.01 mol) in 1:1 molar ratio. The resulting solution was boiled under reflux on a water bath for about 1 h. Yellow crystals formed at room temperature were collected, washed with little ethanol, and then dried *in vacuo* over anhydrous $CaCl_2$.

{Yield: 90 %, Melting point: 85 ^{o}C}

Synthesis of the complexes

The following general procedure was adopted for the synthesis of all the complexes.

The ligand, ICAT (2.11 g, 0.01 mol) was dissolved in ethanol (30 mL), and was mixed with a solution of the metal salt {(0.005 mol, 0.81 g of $FeCl_3$, 1.19 g of $CoCl_2.6H_2O$, 1.19 g of $NiCl_2.6H_2O$ or 0.85 g of $CuCl_2.2H_2O$)} in ethanol (20 mL). This solution was then boiled under reflux for about 2 h, and the resulting complex obtained was filtered, washed with ethanol, chloroform and ether. The complex was finally dried *in vacuo* over anhydrous $CaCl_2$.
{Yield: 80 %; Melting point for the iron(III), cobalt(II) and nickel(II) complexes are above 250 ^{o}C; for the copper(II) complex, the melting point is 208 ^{o}C}

RESULTS AND DISCUSSION

All the complexes are intensely coloured, non-hygroscopic, and are quite stable to aerial oxidation. They are soluble in DMSO and partially soluble in DMF, ethanol, methanol, acetonitrile, nitrobenzene, chloroform, dichloromethane and ether. The analytical data (Table I) reveal the empirical formula of the complexes to be $[M_2L_2Cl_2.3H_2O]$, for the cobalt(II), nickel(II) and copper(II) complexes, and $[Fe_2L_2(OH)_2Cl_2.4H_2O]$ for the iron(III) complex (L = ICAT). The molar conductance data for the complexes (Table II)

Table I

Elemental analyses and colour of the ligand and its complexes

Substance	Colour	Found (Calc.) %			
		M	N	Cl	H_2O^*
L, Ligand	Yellow	—	33.89 (33.17)	—	—
$[Fe_2L_2(OH)_2]Cl_2.4H_2O$	Brown	15.60 (15.72)	19.59 (19.70)	9.72 (9.97)	10.66 (10.13)
$[Co_2L_2Cl_2].3H_2O$	Maroon	17.61 (17.73)	21.33 (21.06)	10.65 (10.66)	8.09 (8.12)
$[Ni_2L_2Cl_2].3H_2O$	Grey	17.54 (17.67)	21.18 (21.07)	10.70 (10.67)	8.34 (8.13)
$[Cu_2L_2Cl_2].3H_2O$	Dark brown	18.62 (18.85)	20.98 (20.77)	10.26 (10.52)	8.24 (8.01)

L = Indole-3-carboxalidene-3-amino-1,2,4-triazole (ICAT)
* = Obtained from TG data

Table II

Molar conductance and magnetic moment data for the complexes

Complex	Molar conductance ($ohm^{-1}cm^2mol^{-1}$)	Magnetic moment (B.M.)
$[Fe_2L_2(OH)_2]Cl_2.4H_2O$	53.7	6.23
$[Co_2L_2Cl_2].3H_2O$	10.6	4.54
$[Ni_2L_2Cl_2].3H_2O$	2.7	3.44
$[Cu_2L_2Cl_2].3H_2O$	6.9	1.98

L = ICAT

show that they are non-electrolytes in DMSO, except for the iron(III) complex, which is found to be a 1:2 electrolyte[16]. A TG study (in the temperature range, 25–350 °C) was undertaken to know whether the water molecules are lattice or coordinated. About 10.66 % mass loss in the case of iron(III) complex, 8.09 % in the case of cobalt(II) complex, 8.34 % in the case of nickel(II) complex, and 8.24 % in the case of copper(II) complex have been observed in the temperature range, 30–80 °C, which corresponds to three molecules of water for cobalt(II), nickel(II) and copper(II) complexes, and four molecules of water for the iron(III) complex. This further confirms that all the water molecules are lattice held and are not coordinated. Thus, analytical data (Table I) along with the molar conductance data reveal the molecular formula of the complexes to be $[M_2L_2Cl_2].3H_2O$, for the cobalt(II), nickel(II) and copper(II) complexes, and $[Fe_2L_2(OH)_2]Cl_2.4H_2O$ for the iron(III) complex.

Infrared spectra

The medium bands observed in the spectrum of the ligand in the 3420–3200 cm^{-1} region have been assigned as ν(N-H) modes[17]. In the spectra of the complexes, these bands are found to be masked by the broad absorption band due to ν(OH) of lattice water[18].

The band observed at 1640 cm^{-1} in the spectrum of the ligand can be assigned to ν(C=N) of the azomethine group[19]. In the spectra of the complexes, there is no change in the position of azomethine band suggesting non-participation of this group with the metal ions.

Table III

Some important IR spectral (cm^{-1}) data

I	II	III	IV	V	Tentative assignments
1640	1640	1640	1640	1640	ν(C=N) (azomethine)
1590	1570	1580	1565	1580	ν(C=N) [triazole (N_1)]
1530	1530	1530	1530	1530	ν(C=N) [triazole (N_4)]
965	990	980	980	985	ν(N-N) stretching (N_1 and N_2 of the triazole)
—	1120	—	—	—	(M-OH) bending
—	495	—	—	—	ν(M-O) mode
—	445	450	450	455	ν(M-N) stretching
—	—	335	345	345	ν(M-Cl) mode

I = ICAT; II = Iron(III) complex; III = Cobalt(II) complex;

IV = Nickel(II) complex and V = Copper(II) complex.

The ligand exhibits two more bands due to the ν(C=N) of the triazole ring[20], which appear at 1590 (N_1) and 1530 cm^{-1} (N_4). The band observed at 1590 cm^{-1} is decreased to 1580 cm^{-1} in the case of the cobalt(II) and copper(II) complexes, 1570 cm^{-1} in the case of the iron(III) complex, and 1565 cm^{-1} in the case of the nickel(II) complex indicating the involvement of N_1 of a triazole ring[21]. However, the band at 1530 cm^{-1} does not change its position during complexation, which shows that the other nitrogen at N_4 in the triazole ring is not attached to the metal ion.

Further, the band observed at 965 cm^{-1} in the spectrum of the ligand, can be assigned to N-N stretching vibration[22]. The frequency of this band is shifted to higher frequency in the spectra of the complexes due to the chelation of nitrogen with the metal ion[23]. This indicates the involvement of both N_1 and N_2 of the triazole ring nitrogens with the metal ions.

A non-ligand band is observed at 335 cm^{-1} in the case of the cobalt(II) complex and at 345 cm^{-1} in the case of the nickel(II) and copper(II) complexes, which may be due to the M-Cl[24,25]. An additional band is also seen in the range, 445–455 cm^{-1} for the complexes due to the M-N stretching vibration[26,27]. Thus, the infrared spectral observations for the complexes indicate that the ICAT can act as a uninegative tridentate (N',N_1,N_2) ligand coordinating through N' of the indole ring nitrogen, and N_1, and N_2 of the triazole ring nitrogens. In the case of iron(III) complex, an additional band is seen at 495 cm^{-1}, which can be assigned to ν(M-O)[28,29]. Furthermore, a band at 1120 cm^{-1} is observed for this complex, which can be assigned to Fe–OH bending mode.

Thus, the IR data, along with the analytical and molar conductance data indicate dimeric structures for these complexes. These data further indicate a four coordinated structure for the complexes.

Magnetic measurements

The magnetic moments for all the complexes measured at room temperature are given in Table II. The observed values show that all these complexes are in the high-spin state.

The iron(III) complex shows magnetic moment of 6.23 B.M., which falls in the range reported for a high-spin state of iron(III)[30]. Magnetic moments of 4.54, 3.44 and 1.98 B.M. have been observed for the cobalt(II)[31], nickel(II)[32] and copper(II)[31] complexes respectively. These values indicate a tetrahedral geometry for the cobalt(II) and nickel(II) complexes, and a square planar structure for the copper(II) complex. Possibility of a tetrahedral structure cannot be excluded in the case of the iron(III) complex.

Electronic spectra

The electronic spectral data for all the complexes recorded in DMSO are given in Table IV.

The iron(III) complex shows only intraligand and charge transfer transitions. No d-d bands were observed for this complex, which may be due to the intense charge transfer transition bands masking the low intensity forbidden d-d bands[33,34].

The cobalt(II) complex exhibits a band at 16340 cm^{-1}, which may be due to the $^4A_2 \longrightarrow {}^4T_1(P)$ transition[32].

Table IV

Electronic spectral (cm^{-1}) data for the complexes

Complex	Absorption maxima	ε_{max} ($l\ cm^{-1} mol^{-1}$)	Tentative assignments
$[Fe_2L_2(OH)_2]Cl_2.4H_2O$	33330	2500	Intraligand transition
	31250	2346	Intraligand transition
	27320	2115	Charge transfer
$[Co_2L_2Cl_2].3H_2O$	32790	2490	Intraligand transition
	31250	2380	Intraligand transition
	26110	2190	Charge transfer
	24750	2076	Charge transfer
	16340	230	$^4A_2 \longrightarrow {^4T_1}(P)$
$[Ni_2L_2Cl_2].3H_2O$	31250	2320	Intraligand transition
	17760	77	$^3T_1(F) \longrightarrow {^3T_1}(P)$
$[Cu_2L_2Cl_2].3H_2O$	33560	2458	Intraligand transition
	27930	2010	Charge transfer
	21230	165	$^2B_{1g} \longrightarrow {^2E_g}$

L = ICAT

The nickel(II) complex shows a weak band at 17760 cm^{-1}, which can be assignable to the $^3T_1(F) \longrightarrow {^3T_1}(P)$ transition, characteristic for a tetrahedral geometry for this complex[35].

The copper(II) complex exhibits a medium band at 21230 cm^{-1} due to the $^2B_{1g} \longrightarrow {^2E_g}$ transition[32].

Apart from these observations, all the complexes show intraligand transitions in the 33500–31250 cm^{-1} region, and charge transfer bands in the 24750–27940 cm^{-1} region.

The solid state (Nujol mull) spectra were also recorded for these complexes. Both the nujol and DMSO spectra show absorption bands at identical positions indicating that the coordinating solvent DMSO has no effect in changing the structure of the complexes.

Mössbauer spectrum

The Mössbauer spectrum of the iron(III) complex recorded at room temperature is shown in Figure 2. The spectrum shows an isomer shift of 0.4128 mm s^{-1}, and an quadrupole splitting of 0.78 mm s^{-1} at this temperature. A low quadrupole splitting indicates the presence of a high-spin state iron in the complex. Further, the observed isomer shift value is closer to that observed for tetrahedral[36] $[FeCl_4]^-$ species (δ = 0.45 mm s^{-1}). Therefore, the results indicate a tetrahedral structure for the present iron(III) complex.

EPR spectra

The EPR spectrum of the copper(II) complex recorded at room temperature shows only broad signal, which might be due to the dimeric nature[37] of the complexes and the 'g' value corresponds to 2.14.

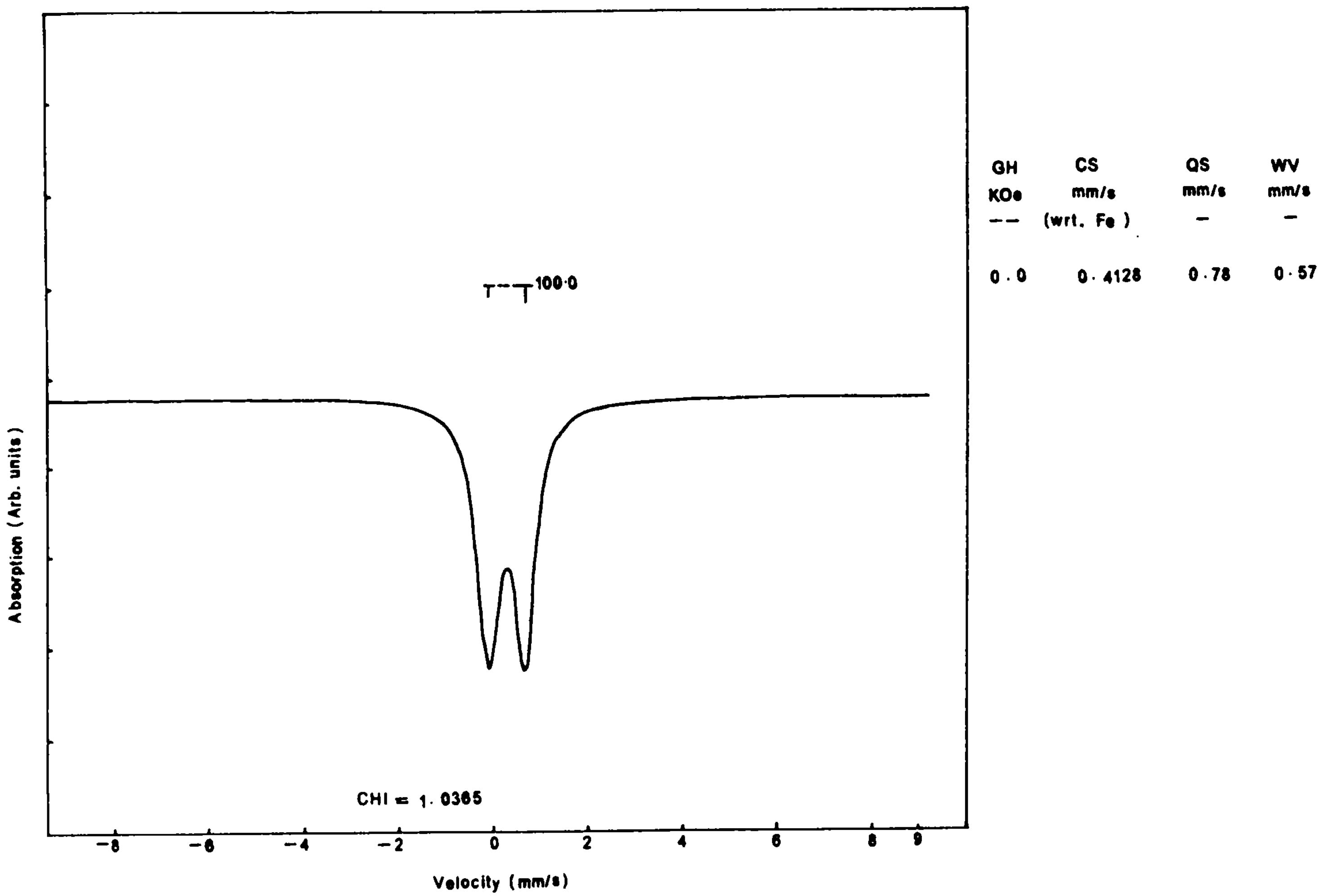


Figure 2. Mössbauer spectrum of $[Fe_2L_2(OH)_2]Cl_2.4H_2O$

Further, the low 'g' value (< 2.3) observed here exclude the possibility of a tetrahedarl structure for this complex.

Based on the above spectral and other analyses the structures shown in Figure 3 and Figure 4 have been proposed for the iron(III) and copper(II) complexes respectively. The structure shown in Figure 5 has been proposed for the cobalt(II) and nickel(II) complexes.

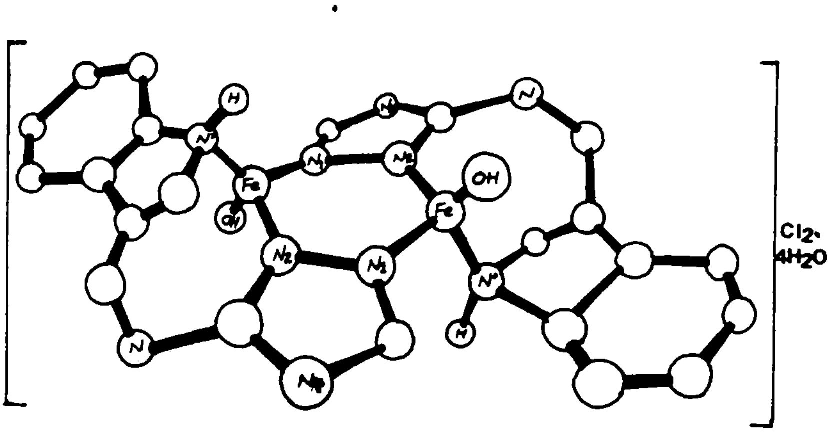


Figure 3. Proposed structure of the iron complex

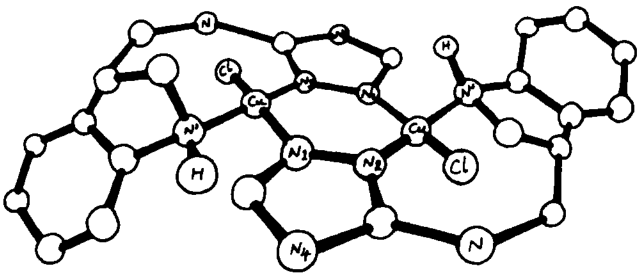
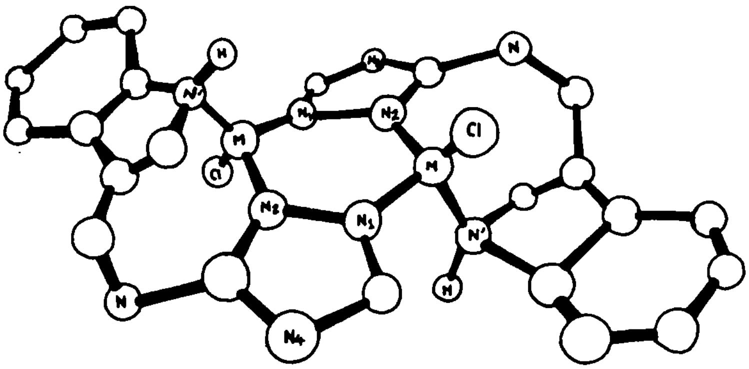


Figure 4. Proposed structure of the copper complex



$M = Co^{II}$ or Ni^{II}

Figure 5. Proposed structure of the cobalt and nickel complexes

REFERENCES

1. R. Simlot, R. A. Izydore, D. T. Wong and I. H. Hall, *J. Pharm. Sci.*, 83, 367 (1994).

2. D. Catarzi, I. Cecchi, V. Colotta, Filacchioni, C. Martini, L. Giusti, A. Lucacchini and G. Valle, *Farmaco*, 49, 89 (1994).

3. J. L. Mokrosz, M. H. Paluchowska, F. W. Chojnacka, M. Filip, S. M. Chieva, A. W. Deren and M. J. Mokrosz, *J. Med. Chem.*, 37, 2754 (1994).

4. W. T. Ashton, L. L. Chang, K. L. Flanagan, S. M. Hutchins, E. M. Naylor, P. K. Chakravarty, A. A. patchett, W. J. Greenlee, T. B. Chen and K. A. Faust, *J. Med. Chem.*, 37, 2808 (1994).

5. G. Biagi, I. Giorgi, O. Livi, V. Scartoni, A. Lucacchini, G. Senatore and P. L. Barili, *Farmaco*, 49, 357 (1994).

6. V. L. Rusinov, T. L. Pilicheva, O. N. Chupakhin, G. V. Kovalev, and E. P. Komina, *Khim.-Farm. Zh.*, 20, 947 (1986); Chem. Abstr. 105: 218619s (1986).

7. A. Deeb, B. E. Bayoumy and M. E. Mobayed, *J. Pharm. Sci.*, 27, 37 (1986); Chem. Abstr. No. 107, 175956w (1987).

8. Emilsson, Haakan, Selander and Hans, *Acta Pharm. Suec.*, 20, 419 (1983); Chem. Abstr. No. 101, 23400y (1984).

9. Yoshina, Shigetaka, Yamamoto and Katsumi, *Yakugaku Zasshi*, 95, 219 (1975); Chem. Abstr. No. 83, 43117z (1975).

10. A. A. Gabr, Asian J. Chem., 3, 212 (1991).

11. A. D. Garnovskii, A. M. Sladkov, O. A. Osipov, L. I. Kuznetsova, I. R. Gol'ding, V. G. Zaletov and Kh. M. Ismailov, *Zh. Obshch. Khim.*, 48 (6), 1398 (1978); Chem. Abstr., 89: 122192x (1978).

12. T. G. Leonova, L. G. Lavrenova, S. V. Larionov, V. N. Ikorskii, and Z. A. Grankina, *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk.*, 1, 82 (1984); Chem. Abstr., 100: 150068a (1984).

13. A. Lukasienicz, J. Michalik, J. Mikosz, L. Walis and I. Wozniak, *Mater. Lett.* 14, 127 (1992).

14. V. V. Ginzburg and A. N. Glebov, *Zh. Neorg. Khim.*, 38, 866 (1993); Chem. Abstr. No. 119, 240325d (1993).

15. M. Bala and A. I. P. Sinha, *Asian J. Chem.*, 1, 392 (1989).

16. J. Lewis and T. D. O'Donoghue, *J. Chem. Soc., Dalton Trans.*, 736 (1980).

17. L. J. Bellamy, "*The Infrared Spectra of Complex Molecules*", Chapman & Hall, London, 3rd Edn., Vol. 1, 1975.

18. K. K. Narang, M. K. Singh and V. P. Singh, *Synth. React. Inorg. Met.-Org. Chem.*, 1125 (1990).

19. K. K. M. Yusuff and R. Sreekala, *Synth. React. Inorg. Met.-Org. Chem.*, 21, 553 (1991).

20. E. Alexandrou, Nicholas and N. A. Rodios, *J. Heterocyclic Chem.*, 27, 231 (1990).

21. M. K. Said, Lallan Mishra, Anil, Richharia and R. S. Dubey, *Indian J. Chem.*, 35A, 214 (1996).

22. B. Singh, P. L. Mourya, B. V. Agrawal and A. K. Dey, *J. Indian Chem. Soc.*, 59, 29 (1982).

23. R. C. Sharma and J. Ambwani, *J. Indian Chem. Soc.*, 72, 507 (1995).

24. S. D. Dhumwad, K. B. Gudasi, T. R. Goudar, C. T Goudar and M. P. Chitrin, *Indian J. Chem.*, 34A, 38 (1995).

25. A. K. Banerjee, A. C. Varma and S. K. Roy, *J. Indian Chem. Soc.*, 72, 77 (1995).

26. R. C. Mishra, S. K. Mohapatra and D. Panda, *J. Indian Chem. Soc.*, 58, 80 (1983).

27. B. K. Mohapatra and B. Sahoo, *Indian J. Chem.*, 24, 653 (1985).

28. N. V. Thakkar and S. Z. Bootwala, *Indian J. Chem.*, 34A, 370 (1995).

29. C. Postmus and J. Farraro, *J. Chem. Phys.*, 48, 3605 (1968).

30. L Mishra and M. K. Said, *Indian J. Chem.*, 35A, 304 (1996).

31. N. Saravanan, K. K. M. Yusuff, P. V. Suresh and G. N. Prabhu, *Synth. React. Inorg. Met.-Org. Chem.*, (in press).

32. N. N. Greenwood and A. Earnshaw, "*Chemistry of the Elements*", Pergamon Press, Oxford, pp.1346, 1989.

33. R. L. Lintvedt and L. A. Kernitsky, *Inorg. Chem.*, 9, 491 (1970).

34. V. M. Leovic, L. J. Bielica, L. S. Jovanovic and S. Y. Chung, *Polyhedron*, 5, 983 (1986).

35. J. T. Donoghue and R. S. Drago, *Inorg. Chem.*, 1, 866 (1962).

36. S. A. Cotton, *Coord. Chem. Rev.*, 8, 203 (1972).

37. D. Kivelson and R. Neiman, *J. Chem. Phys.*, 35, 149 (1961).

CHAPTER VII

COBALT(II), NICKEL(II) AND COPPER(II) COMPLEXES OF 2-PHENYL-1,2,3-TRIAZOLE-4-CARBOXALIDENE-3-AMINO-1,2,4-TRIAZOLE

INTRODUCTION

Triazoles find applications in pharmaceutical and agrochemical industries, since they show fungicidal, herbicidal and plant growth regulatory properties[1]. Reaction of 3-amino-1,2,4-triazole (amitrole) with various aldehydes have been discussed in Chapter VI. The Schiff base, 2-phenyl-1,2,3-triazole-4-carboxalidene-3-amino-1,2,4-triazole (PTCAT) is interesting from the structural point of view since it has many N-donor centres, all of which have the ability to coordinate with metal ions. The complexes of this ligand has not hitherto reported. We have synthesised some new complexes of PTCAT with cobalt(II), nickel(II) and copper(II). However, our attempts to synthesise an iron(III) complex with PTCAT were not successful. In this chapter, the synthesis and characterization of complexes of cobalt(II), nickel(II) and copper(II) with PTCAT are presented.

EXPERIMENTAL

Procedure for the preparation of the 2-phenyl-1,2,3-triazole-4-carboxaldehyde and the instruments employed for the characterization of the complexes are given in Chapter II.

Synthesis of the ligand

An ethanolic solution (25 mL) of 2-phenyl-1,2,3-triazole-4-carboxaldehyde (1.73 g, 0.01 mol) was mixed with 3-amino-1,2,4-triazole (0.84 g, 0.01 mol) in 1:1 molar ratio. The resulting solution was refluxed on a water bath for about 1 h. An yellow coloured product thus obtained was filtered, washed with ethanol and acetone, and then dried *in vacuo* over anhydrous $CaCl_2$.
{Yield: 90 %; Melting point: 201 ^{o}C}

Synthesis of the complexes

The ligand, PTCAT (2.39 g, 0.01 mol) was melted and the ligand in the melted form was dissolved in glacial acetic acid (5 mL). The metal salt {(0.005 mol, 1.45 g of $Co(NO_3)_2.6H_2O$, 1.45 g of $Ni(NO_3)_2.6H_2O$ or 1.2 g of $Cu(NO_3)_2.3H_2O$)} was dissolved separately in acetic acid, and was mixed with the ligand solution. The resulting solution was refluxed on a water bath for about 2 h. The complex formed was filtered, washed with chloroform, and then dried *in vacuo* over anhydrous $CaCl_2$.
{Yield: 85 %; Melting points are above 250 ^{o}C}

RESULTS AND DISCUSSION

The Schiff base ligand, PTCAT (Figure 1) was obtained by condensing 2-phenyl-1,2,3-triazole-4-carboxaldehyde with 3-amino-1,2,4-triazole.

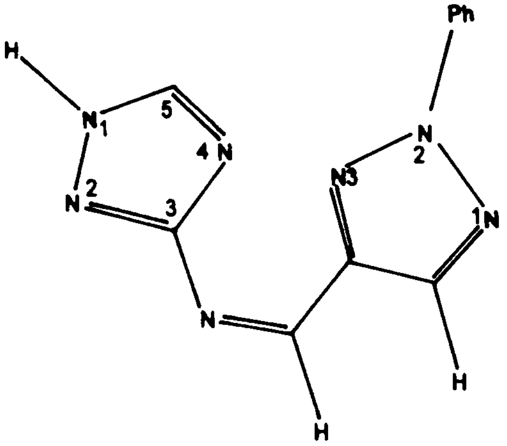


Figure 1. Structure of the PTCAT

The infrared spectrum of the ligand exhibits a band at 1655 cm^{-1} due to the formation of the ν(C=N) of the azomethine group. The CHN analyses suggest the empirical formula, $C_{11}H_9N_7$ for this ligand. The mass spectrum of the ligand (Figure 2) shows a parent ion peak at m/e 239 (100 %), which exactly corresponds to the molecular weight of this ligand. M+1 ion peak at m/e 240 (15 %) was also observed. ^{1}H NMR and ^{13}C NMR spectra for this substance could not be recorded due to its poor solubility in the common organic solvents.

The PTCAT ligand has very low solubility in most of the solvents; however, the solubility considerably increased on melting the ligand. Such melting procedures have already been used for complexation purposes. Furthermore, it would avoid the possibility of coordination of water molecules to the metal ions. The PTCAT ligand melts at 201 ^oC. TG of the ligand (Figure 3) reveals the ligand decomposes

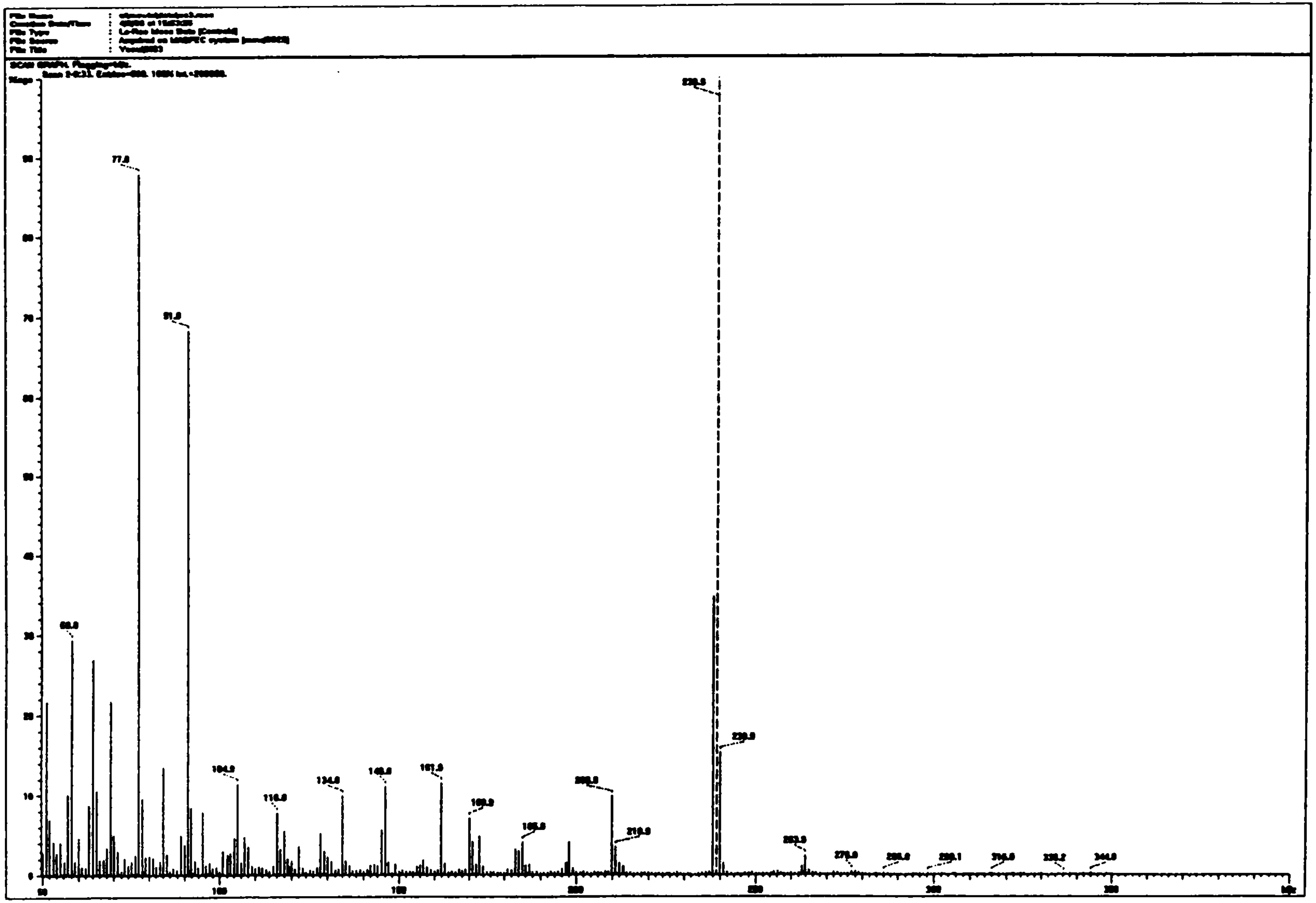


Figure 2. Mass spectrum of the PTCAT

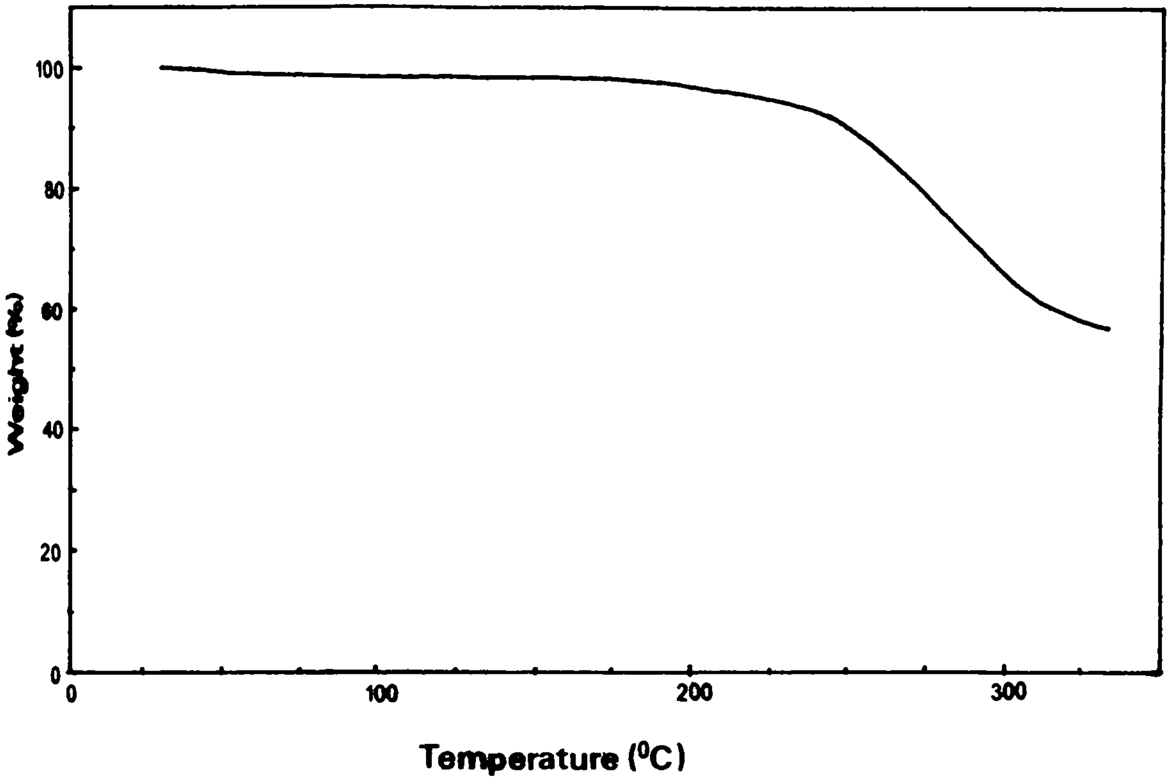


Figure 3. TG of the PTCAT

only at 230 ^{o}C. As the melting point is below the decomposition temperature, this ligand can be melted before dissolving in acetic acid.

All the complexes are coloured, non-hygroscopic and are stable to aerial oxidation. They are insoluble in common organic solvents except DMSO. The elemental analyses (Table I) and the molar conductance data (Table II) for the complexes suggest the general empirical formulae, $[ML(NO_3)]_2$ {where, M = cobalt(II) or copper(II) and L = PTCAT), and for the nickel(II) complex, it corresponds to $[Ni_2L_2(NO_3)_2(H_2O)]$.

Table I

Elemental analyses and colour of the complexes

Substance	Colour	Found (Calc.) %			
		C	H	N	M
L, Ligand	Pale yellow	54.95	3.75	41.36	—
		(55.23)	(3.76)	(41.00)	—
$[Co_2L_2(NO_3)_2]$	Brown	36.82	2.56	31.07	16.62
		(36.67)	(2.50)	(31.11)	(16.37)
$[Ni_2L_2(NO_3)(H_2O)].(NO_3)$	Flesh	35.62	2.80	30.72	16.20
		(35.80)	(2.71)	(30.37)	(15.92)
$[Cu_2L_2(NO_3)_2]$	Green	36.32	2.12	31.09	17.24
		(36.21)	(2.47)	(30.72)	(17.43)

L = 2-Phenyl-1,2,3-triazole-4-carboxalidene-3-amino-1,2,4-triazole (PTCAT)

Molar conductance measurements

Molar conductance values of the complexes in DMSO are given in

Table II. The data suggest that the cobalt(II) and copper(II) complexes are non-electrolytic in DMSO. The molar conductance of nickel(II) complex is found to be 68.7 ohm^{-1} cm^{2} mol^{-1}, which indicates that the complex is a 1:1 electrolyte[2]. Therefore, the molecular formula of the nickel complex can be represented as, $[Ni_2L_2(NO_3)(H_2O)](NO_3)$.

Magnetic susceptibility measurements

The room temperature magnetic moments for the complexes are given in Table II.

Table II

Molar conductance and magnetic moment data for the complexes

Complex	Molar conductance (ohm^{-1} cm^{2} mol^{-1})	Magnetic Moment (B.M.)
$[Co_2L_2(NO_3)_2]$	14.6	4.20
$[Ni_2L_2(NO_3)(H_2O)](NO_3)$	68.7	3.92
$[Cu_2L_2(NO_3)_2]$	16.2	1.81

L = PTCAT

The magnetic moment values of 4.20 and 3.92 B.M. for the cobalt(II) and nickel(II) complexes indicate a tetrahedral structure for these complexes[3,4]. The copper(II) complex shows 1.81 B.M., which indicates the absence of any metal-metal interactions and also exclude the possibility of this complex having a tetrahedral structure[5].

Infrared spectra

The infrared spectral data of the ligand and its complexes are given in Table III.

Table III

Some relevant IR spectral (cm^{-1}) data

I	II	III	IV	Tentative assignments
1655	1655	1655	1655	ν(C=N) (azomethine)
1597	1597	1597	1597	ν(C=N) (N1 of 1,2,3-triazole)
1560	1545	1550	1550	ν(C=N) (N3 of 1,2,3-triazole)
—	1490	1495	1490	NO_3 unidentate
—	—	1380	—	NO_3 ionic
—	—	822	—	
—	—	730	—	
960	970	990	970	ν(N-N) stretching (N1 and N2 of 1,2,4-triazole)
—	—	870	—	ν(OH) (coordinated water)
—	460	450	465	ν(M-N) mode

I = PTCAT; II = Cobalt(II) complex; III= Nickel(II) complex

and IV = Copper(II) complex

The ligand, PTCAT shows medium bands in the region, 3240-3140 cm^{-1} due to the ν(N-H) stretching vibration. The intensity of these bands are decreased in the spectra of the complexes indicating the bonding of this nitrogen to the metal ion[6]. Further, the band observed at 960 cm^{-1} in the spectrum of the ligand is due to the ν(N–N) stretching vibration[7]. This band is shifted to higher frequency in the spectra of the complexes suggesting the participation of N_1 and N_2 of the 1,2,4-triazole ring nitrogens during complexation.

The band observed at 1655 cm^{-1} is attributed to the ν(C=N) of the azomethine group[8]. This band does not shift to lower frequency in the spectra of the complexes indicating the non-participation of the azomethine nitrogen in coordination to the metal ion.

Further, the bands observed at 1597 cm^{-1} and 1560 cm^{-1} are characteristic for the triazole ring nitrogens[5]. The band at 1597 cm^{-1} does not change its position in the spectra of complexes indicating the nonparticipation of N_1 of the 1,2,3-triazole ring nitrogens. The other band at 1560 cm^{-1} is shifted to a lower frequency in the spectra of the complexes suggesting the participation of N_3 of the 1,2,3-triazole ring nitrogens. Thus, PTCAT acts as a uninegative tridentate ligand in these complexes coordinating through N_3 of the 1,2,3-triazole ring, and N_1 and N_2 of the 1,2,4-triazole ring.

All complexes exhibit band at 1495–1490 cm^{-1} which can be attributed to a unidentate nitrate group[9,10]. In the case of the nickel(II) complex, additional bands due to the noncoordinated nitrate group[11] appear at 1380, 822 and 730 cm^{-1}. These bands are not found in the spectra of other complexes which indicate the absence of any ionic nitrate species in the cobalt(II) and copper(II) complexes.

Furthermore, a broad absorption band is also observed in the spectrum of the nickel complex, which may be due to the of ν(O–H) stretching[8] of a water molecule in the region 3450–3150 cm^{-1}. The appearance of a band at 870 cm^{-1} also support the presence of a coordinated water in the nickel(II) complex[12]. Presence of coordinated water is further confirmed from a TG study of this complex. The first stage decomposition of the complex is above 200 °C, which suggests that the water is not lattice held. Moreover, the mass loss in the range, 220–260 °C corresponds to the loss of one molecule of water and one nitrate group.
(% Weight loss, Found: 11.02; Calc.: 10.85).

The band in the region, 450–465 cm^{-1} in the spectra of the complexes is assigned to the ν(M–N) mode[13].

Electronic spectra

The electronic absorption spectra of the complexes (DMSO) show only intraligand and charge transfer transitions. Further, the intraligand transitions are in the region, 27300–37100 cm^{-1} and the charge transfer transitions are in the region, 29100–24900 cm^{-1} were found for the complexes. No d–d bands were observed for these complexes, which may be due to the masking of these bands by the intense charge transfer transitions.

EPR spectra

The powder EPR spectrum of the copper(II) complex is found to be isotropic with a 'g' value, 2.12 and a square planar structure for the copper complex[14]. Further, the magnetic moment indicates the absence of any Cu-Cu interaction in this complex.

Based on the above studies, dimeric tetrahedral structures have been tentatively proposed for the cobalt(II) (Figure 4) and nickel(II) (Figure 5) complexes, and a square planar structure (Figure 6) has been proposed for the copper(II) complex.

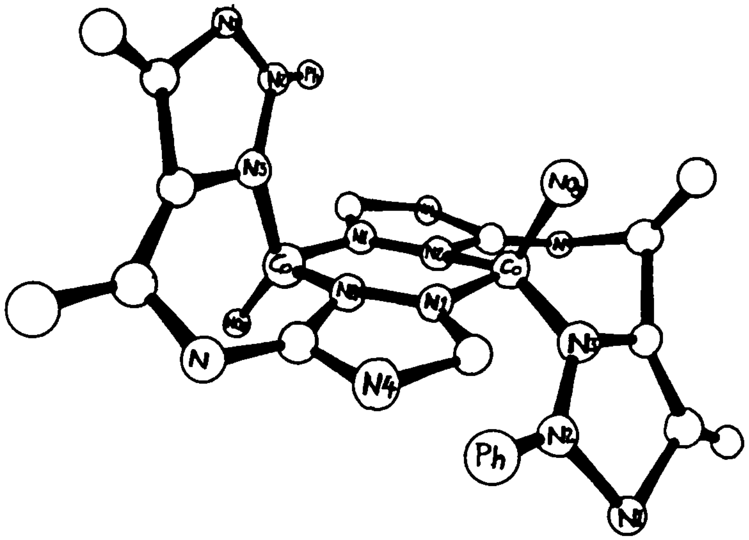


Figure 4. Proposed structure of cobalt(II) complex

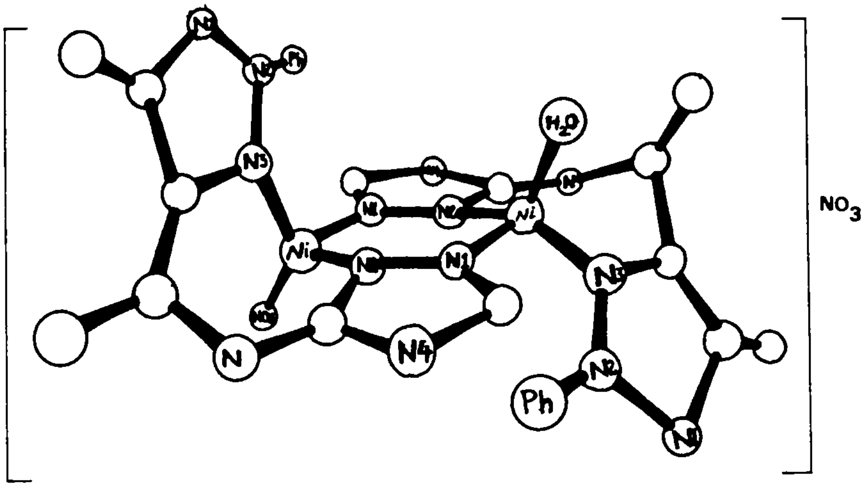


Figure 5. Proposed structure of nickel(II) complex

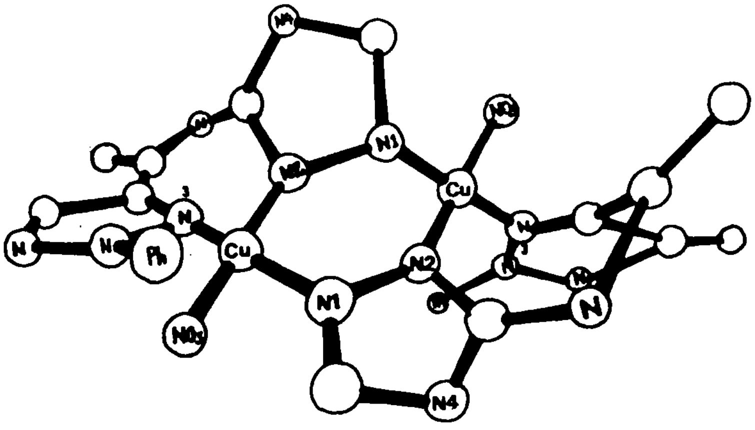


Figure 6. Proposed structure of copper(II) complex

REFERENCES

1. K. Smith, A. Small and M. G. Hutchings, *Chemistry Letters*, 347 (1990).

2. J. Lewis and T. D. O'Donoghue, *J. Chem. Soc. Dalton Trans.*, 736 (1980).

3. M. Goodgame and F. A. Cotton, *J. Am. Chem. Soc.*, 84, 1543 (1962).

4. F. A. Cotton and G. Wilkinson, "*Advanced Inorganic Chemistry*" (*A* Comprehensive Text), 3rd Edn., Wiley Eastern Limited, New Delhi, 896, 1972.

5. K. K. M. Yusuff and C. Krishnakumar, *Synth. React. Inorg. Met.-Org. Chem.*, 23, 695 (1993).

6. N. Kanoongo, R. V. Singh and J. P. Tandon, *Indian J. Chem.*, 29A, 560 (1990).

7. D. N. Sathyanarayana and D. Nicholls, *Spectrochim. Acta*, 34A, 263 (1978).

8. N. Nawar, M. A. Khattab, M. M. Bekheit and A. Kaddah, *Indian J. Chem.*, 35A, 308 (1996).

9. G. Paolucci, G. Mhrangoni, G. Bandoli and D. A. Clementi, *J. Chem. Soc., Dalton Trans.*, 459 (1980).

10. K. Dey, A. K. Sinha Roy, K. K. Bhasin and R. D. Verma, *Indian J. Chem.*, 26A, 230 (1987).

11. P. K. Rai and R. N. Prasad, *Synth. React. Inorg. Met.-Org. Chem.*, 24, 749 (1994).

12. K. Nakamoto, "*Infrared and Raman Spectra of Inorganic and Coordination Compounds*", Wiley, New York, pp. 228 & 441, 1978.

13. R. C. Mishra, S. K. Mohapatra and D. Panda, *J. Indian Chem. Soc.*, 58, 80 (1983).

14. E. F. Hasty, L. J. Wilson and D. N. Hendrickson, *Inorg. Chem.*, 17, 1835 (1978).

CHAPTER VIII

ANTIBACTERIAL AND CATALYTIC ACTIVITY STUDIES ON SOME COBALT(II) AND COPPER(II) COMPLEXES OF 1-NITROBENZYL-2-NITROPHENYLBENZIMIDAZOLE

Apart from our work on the synthesis and characterization of some new metal complexes, a study was also undertaken to know the catalytic activity, antimicrobial activity and thermal diffusivity of some of the complexes reported in this thesis. In this chapter, we describe the results of our studies on the antimicrobial and catalytic activity of the complexes of cobalt(II) and copper(II) derived from NBPBI.

This chapter comprises of two sections, Section A and Section B. Antibacterial activity studies of the simple complexes of cobalt(II) and copper(II) derived from 1-nitrobenzyl-2-nitrophenylbenzimidazole (NBPBI) are described in Section A of this chapter. Section B deals with the catalytic activity studies of both simple and polymer supported cobalt(II) and copper(II) complexes derived from NBPBI. The simple complexes of cobalt(II) and copper(II) have been screened for their catalytic activity in the oxidation of 3,5-ditertiarybutyl-catechol (Part I), and that of the polymer supported complexes in the decomposition of hydrogen peroxide (Part II).

The thermal diffusivity of the simple and polymer supported complexes of cobalt(II) and copper(II) derived from NBPBI have been carried out in collaboration with the International School of Photonics of our University, and the results of this work have very recently been reported elsewhere[1,2]. The studies show that the polymer supported complexes have higher values of thermal diffusivity than the corresponding simple complexes.

SECTION A

ANTIBACTERIAL ACTIVITY STUDIES

INTRODUCTION

Benzimidazole derivatives exhibit useful pharmacological activities and these increase over many folds when these compounds are complexed with metal ions. The antimicrobial activity and other medicinal applications of some transition metal complexes have been reported[3-27] in the recent literature. This observation prompted us to study the antibacterial activity of the ligand, NBPBI and its cobalt(II) and copper(II) complexes towards both Gram positive and Gram negative bacteria, the results of which are presented here.

EXPERIMENTAL

Materials and methods

Details regarding the synthesis and characterization of simple complexes of cobalt(II) and copper(II) derived from NBPBI are given in Chapter III.

The antibacterial activity of the complexes of cobalt(II) and copper(II) derived from NBPBI was determined by assessing the rate of growth of selected Gram negative (G-ve) and Gram positive (G+ve) bacteria in the presence of the prepared complexes in growth medium, as described below.

Source and maintenance of bacteria

Microbial strains used in the present study included G-ve *Escherichia coli* (CBT GS 109), *Vibrio costicola* (ACMR 267) and *Pseudomonas flourescence* (ACMR 171), and G+ve *Bacillus polymyxa* (CBTB 25) and *Streptoverticillium sp.* (CBT SA 133). They were obtained from the culture collection of the Department of Biotechnology, Cochin University of Science and Technology, Kochi, India. *E. coli*, *V. costicola* and *B. polymyxa* were maintained on nutrient agar (HiMedia, India) while *Streptoverticillium sp.* was maintained on Bennet's agar (HiMedia, India) slants.

Inoculum preparation

B. polymyxa, V. costicola and *P. flourescence were* grown in nutrient broth (HiMedia, India). *E. coli* was cultured in Luria broth (HiMedia, India) and *Streptoverticillium sp.* was grown in glucose-peptone-yeast extract-beef extract broth[28]. The following procedure was adopted for the preparation of inoculum.

(i) A loopful of 18-24 h old culture was transferred asceptically to 10 mL of the respective sterile media taken in test tubes, and incubated at room temperature (28 ± 2 °C) for 24 h on a rotary shaker at 150 rpm. In the case of *Streptoverticillium sp.* 4 day dd slant culture was used as inoculum and the inoculated medium was incubated for 48 h.

(ii) After incubation for the said period, the culture grown in the test tube was added to 100 mL of sterile medium respective of each test strain, and incubated further for 24 h (48 h for *Streptoverticillium sp.*) at room temperature (28 ± 2 °C) on a rotary shaker (150 rpm).

(iii) After the growth, the cells were harvested by centrifugation at 10,000 rpm for 15 minutes in a refrigerated high speed centrifuge (Kuboto, Japan), washed twice with sterile physiological saline (NaCl, 0.85 %) and resuspended in the same. This prepared cell suspension was adjusted to a cell concentration of 10^8 cells per mL.

Effect of the complexes of cobalt(II) and copper(II) derived from 1-nitrobenzyl-2-nitrophenylbenzimidazole on the bacterial growth.

Different dilutions of the complexes ($[CoL_2Cl_2]$, $[CoL_2Br_2]$, $[CoL_2I_2]$, $[CuL_2Cl_2]$ and $[CuL_2Br_2]$, where L = NBPBI) in the range 100 µg/mL to 500 µg/mL were prepared from a stock solution containing 1 mg/mL in DMF, added to 5 mL of the respective media taken in test tubes, sterilized by autoclaving at 121 °C for 15 minutes, cooled to room temperature and uniformly inoculated with the prepared inoculum at 1.5 % for *E. coli*, *B. polymyxa*, *V. costicola* and *P. flourescence*, and at 4 % for *Streptoverticillium sp.* The inoculated tubes were incubated on a rotary shaker at 150 rpm for 24 h / 48 h at room temperature. Growth was determined by measuring the turbidity at A_{600}

using a Shimadzu 160A UV-Visible spectrophotometer. Appropriate control tubes were also maintained for all the complexes at all the dilutions tested.

RESULTS AND DISCUSSION

The simple complexes of cobalt(II) and copper(II) derived from 1-nitrobenzyl-2-nitrophenylbenzimidazole (NBPBI) were tested for their antibacterial activity against both G+ve and G-ve bacteria. All complexes showed inhibition of growth of all the strains in a linear fashion, along with an increase in concentration from 100 μg/mL to 500 μg/mL (Table I). Maximal inhibition of growth was observed at 500 μg/mL concentration. The percentage of growth inhibition varied between 88-91 % for *E. coli*, 89-93 % for *B. polymyxa*, 93-96 % for *V. costicola*, 85-89 % for *P. flourescence* and 55-71 % for *Streptoverticillium sp.* for all complexes, $[CoL_2Cl_2]$, $[CoL_2Br_2]$, $[CoL_2I_2]$, $[CuL_2Cl_2]$ and $[CuL_2Br_2]$. Interestingly, $[CoL_2Cl_2]$ and $[CoL_2I_2]$, were observed to effect inhibition of growth around 50 % of *P. flourescence*. Among the strains, *V. costicola* was more sensitive to the complexes tested. Unlike other strains, *B. polymyxa* was sensitive to the complexes tested only when the concentration was 500 μg/mL. The 19-25 % inhibition observed with this strain at 300 μg/mL was very low compared to other strains, which showed inhibition around 50 %. An increase in the concentration from 300 μg/mL to 500 μg/mL did not show any significant effect on *Streptoverticillum sp.*, unlike in others.

Table I

Antibacterial activity of cobalt(II) and copper(II) complexes with NBPBI

		Percentage inhibition of growth				
Substance	Conc. µg/mL	*E. coli*	*B. polymyxa*	*V. costicola*	*P. fluorescence*	*Streptoverticillium* sp.
$[CoL_2Cl_2]$	100	7.00	8.00	0.20	24.00	5.00
	300	54.00	23.00	68.00	41.00	29.00
	500	88.00	89.00	93.00	43.00	65.00
$[CoL_2Br_2]$	100	8.00	13.00	0.80	16.00	48.00
	300	53.00	20.00	55.00	47.00	55.00
	500	91.00	93.00	95.00	89.00	66.00
$[CoL_2I_2]$	100	16.00	9.00	3.00	24.00	46.00
	300	51.00	25.00	56.00	45.00	48.00
	500	91.00	93.00	96.00	48.00	55.00
$[CuL_2Cl_2]$	100	1.00	5.00	+2.00	18.00	8.00
	300	48.00	19.00	55.00	42.00	47.00
	500	89.00	91.00	94.00	85.00	66.00
$[CuL_2Br_2]$	100	4.00	6.00	+0.70	31.00	8.00
	300	51.00	22.00	52.00	44.00	29.00
	500	88.00	90.00	93.00	91.00	71.00
L, Ligand (NBPBI)	100	+6.00	+3.00	+1.00	12.00	8.00
	300	+3.00	+5.00	+4.00	19.00	42.00
	500	1.00	+7.00	+6.00	22.00	43.00

DMF was used as a control and showed nil activity against the above microorganisms

The antibacterial activity of the ligand, NBPBI was also studied. The ligand did not show any significant effect on *E. coli, V. costicola* and *B. polymyxa*. However, *P. flourescence* and *Streptoverticillum sp.* had inhibited growth at 42-43 % and 19-22 %, respectively, at 500 µg/mL of the ligand.

SECTION B

CATALYTIC ACTIVITY STUDIES

PART I

CATALYTIC ACTIVITY OF THE SIMPLE COMPLEXES OF COBALT(II) AND COPPER(II) DERIVED FROM 1-NITROBENZYL-2-NITROPHENYLBENZIMIDAZOLE IN THE OXIDATION OF 3,5-DITERTIARYBUTYLCATECHOL

INTRODUCTION

Transition metal complexes have wide applications in the field of catalysis which mainly include the conversion of organic molecules to products of pharmacological interest, synthetic chemicals, and so on. Liquid phase oxidation of catechol and its derivatives to the corresponding benzoquinone using metal complex catalysts have been reported by several workers[29,30]. Further, a few Schiff base complexes of cobalt(II) have been used[31] for the oxidation of DTBC.

Catalytic activity of the complex, bis(acetate)-bis(imidazole)copper(II) and bis(valproato)bis(imidazole)copper(II) toward the aerial oxidation of DTBC to 3,5-ditertiary-butyl-*o*-benzoquinone have recently been reported[32], and a dinuclear copper(II) complex was also reported[33] to exhibit catalytic activity in this reaction.

Studies on the oxidation of DTBC by $FeCl_3$ in THF-pyridine solvent has recently been published, and the formation of the intermediate iron(II)-3,5-ditertiary-*o*-semiquinone (DTBSQ) species, which is responsible for the reaction with oxygen, has been detected by EPR and electronic spectroscopy[34]. Furthermore, some iron(III) complexes derived from benzimidazole ligands have been reported to catalyse this oxidation reaction[35]. This kind of studies would provide new information on the activation of oxygen by metal ions, a subject of interest to synthetic organic chemists. In view of these, we have made an attempt to study the catalytic activity of the simple NBPBI complexes of cobalt(II) and copper(II). Oxidation of DTBC (Figure 1) was chosen for this purpose, as the formation of the oxidation product, ditertiarybutylquinone, can be easily followed by noting the absorbance at 400 nm (Quinone exhibits a characteristic absorption peak at this wavelength). The results of our studies on the catalytic

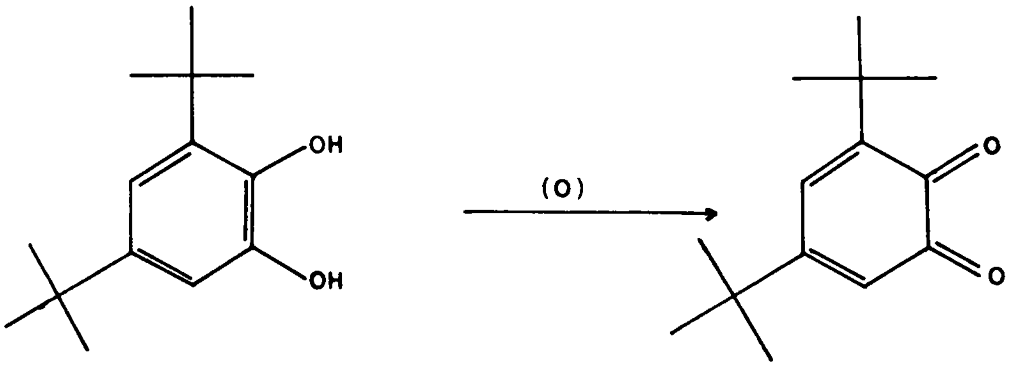


Figure 1. Oxidation of DTBC in the presence of catalyst

activity of simple complexes of cobalt(II) and copper(II) in the oxidation of DTBC are presented in this part.

EXPERIMENTAL

Materials

Details regarding the syntheses of the complexes are described in Chapter III. The stock solutions of the complexes (10^{-3} M) and that of DTBC (10^{-2} M) were prepared afresh before each experiment by dissolving solid samples in triethylamine–DMF mixture (1.5 %). The concentration of DTBC in the reaction mixtures was maintained at 1.0×10^{-3} M and that of the catalyst at 1.0×10^{-4} M. The weights of the catalysts per 100 mL of the reaction mixture are given in Table II. The presence of triethylamine in DMF was required to render the latter alkaline.

Catalytic experiments

All kinetic runs were carried out at a constant temperature of 30 ± 0.1 °C in 1.5 % triethylamine–DMF mixture. The reaction was initiated by transferring calculated amount of the complex solution into the reaction flask. The reaction is monitored by following the absorbance of the product, ditertiarybutylquinone, at 400 nm. A solution of the same amount of the catalyst in the same solvent was used as blank. The absorbance measurements were made by extracting about 3 mL of the reaction solutions at regular time intervals of 1 minute. A Shimadzu double beam spectrophotometer, model UV 160A with 1 cm quartz cells is used for absorption measurements. The concentration of the product formed was obtained from the absorbance data using a molar absorption coefficient of 2818 at 400 nm. The initial rates of the reaction were obtained by fitting the concentration versus time data into a polynomial of the form,

$$c = a_1 + a_2 t + a_3 t^2 + \ldots\ldots$$

and obtaining the slope of the curve at t = 0. A software called "Axum" (Trimetrix, 1989) was used for this purpose. All the kinetic results were found to be reproducible within an error of ± 5 %.

RESULTS AND DISCUSSION

The rate of oxidation of DTBC in the presence of the complexes are given in Table II. These catalytic experiments suggest that all these complexes can act as catalysts in the above reaction.

On the basis of the results obtained, it may be inferred that the chloro complex of cobalt(II) has greater activity than the corresponding bromo and iodo complexes. Thus, the rate of the reaction varies in the following order:

$$[CoL_2Cl_2] > [CoL_2Br_2] > [CoL_2L_2]$$

On the contrary, in the case of the copper(II) complexes, the bromo complex has better activity than the corresponding chloro complex. A comparison of the activities of the cobalt(II) and copper(II) complexes was also made and the studies indicate that the cobalt(II) complexes are better catalysts than their copper(II) analogues in the oxidation of DTBC.

Table II

The rate of oxidation of 3,5-ditertiarybutylcatechol in the presence of the simple complexes

Complex	Weight of the complex taken (mg/100 mL)	Initial rate x 10^7 ($M\ s^{-1}$)
$[CoL_2Cl_2]$	89	8.94
$[CoL_2Br_2]$	97	5.27
$[CoL_2I_2]$	106	4.57
$[CuL_2Cl_2]$	89	0.75
$[CuL_2Br_2]$	98	1.67

L = NBPBI

PART II

CATALYTIC ACTIVITY OF THE POLYMER SUPPORTED COMPLEXES IN THE DECOMPOSITION OF HYDROGEN PEROXIDE

INTRODUCTION

The decomposition of hydrogen peroxide is often employed as a standard reaction to determine the catalytic activity of a polymer metal complex[36]. Metals having stable oxidation states that differ by one {manganese(II), iron(III) and copper(II)} are very effective catalysts for the decomposition of hydrogen peroxide. Such metal ions function both as an oxidising and as reducing agent in the catalysed decomposition mechanism[37,38]. Furthermore, some Schiff base complexes of metal ions like manganese(III) and iron(III) have been reported to exhibit catalytic activity in the decomposition of hydrogen peroxide[39–44]. However, reports on the use of polymer supported metal complexes as catalysts towards decomposition of hydrogen peroxide are rather scanty[45,46]. We have studied the catalytic activity of the polymer supported complexes of cobalt(II) and copper(II) derived from NBPBI in the decomposition of hydrogen peroxide, and the results of our studies are presented in this part.

EXPERIMENTAL

Materials

The syntheses of the polymer supported complexes of cobalt(II) and copper(II) are already described in Chapter IV. Hydrogen peroxide (Merck, 30 %) was made 10 % with ion free water.

Catalytic experiments

The experimental set-up is as shown in Figure 2. The following procedure was adopted to study the decomposition of hydrogen peroxide.

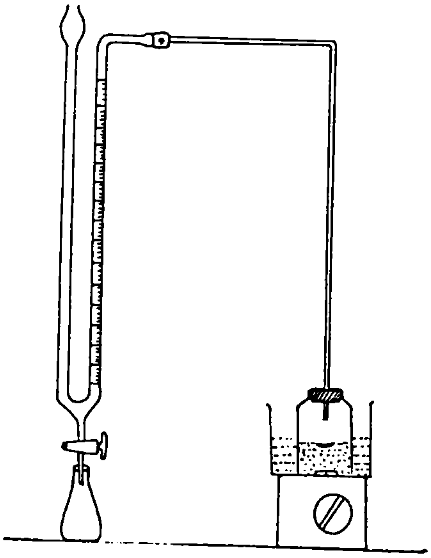


Figure 2. Experimental set-up for H_2O_2 decomposition study

The reaction vessel containing H_2O_2 solution (10 %, 20 mL) and magnetic paddle was kept at room temperature (28 ± 2 °C). The polymer supported complex (2-2.5 mg) was taken in a plastic float and was placed over the solution. The gas burette was filled with potassium permanganate solution for easy detection of the levels, and was attached to the reaction vessel. Then the vessel was tightly closed and the levels in the two arms of the gas burette were made equal, and the reading was noticed. A stop watch was started at the moment when the polymer supported complex was introduced into the H_2O_2 solution being stirred by a magnetic stirrer. As the reaction proceeds, oxygen gas is produced, and the level in the right arm is lowered. This was balanced by running away the solution through the tap. Readings were recorded at an interval of 2 minutes after making the levels in the two arms equal. Computations were done to find the initial rate of the reaction[47], as has been described in Section B.

RESULTS AND DISCUSSION

The rate of decomposition of hydrogen peroxide in the presence of the polymer supported complexes are as shown in Table III. The catalytic experiments suggest that all these complexes act as catalysts towards this decomposition reaction.

In the case of the polymer supported cobalt(II) complexes, the bromo complex has better activity than the corresponding iodo and chloro complexes. The rate of the reaction was found to vary in the following order:

$$\text{P-CoL}_2\text{Br}_2 > \text{P-CoL}_2\text{I}_2 > \text{P-CoL}_2\text{Cl}_2$$

But, in the case of the polymer suppported copper(II) complexes, the chloro complex exhibits greater activity than the corresponding bromo complex.

Table III

Rate of decomposition of hydrogen peroxide in presence of polymer supported complexes

Complex	Weight of the complex taken (mg)	Initial rate x 10 (mL s^{-1})
P-CoL_2Cl_2	2.1	1.16
P-CoL_2Br_2	2.3	1.85
P-CoL_2I_2	2.3	1.53
P-CuL_2 Cl_2	2.2	1.79
P-CuL_2 Br_2	2.5	1.39

P = Polymer supported Schiff base and L = NBPBI

REFERENCES

1. S. Sankara Raman, V. P. N. Nampoori, C. P. G. Vallabhan, N. Saravanan and K. K. M. Yusuff, *J. Mat. Sci. Lett.* (in press)

2. S. Sankara Raman, Anneita Philip, V. P. N. Nampoori, C. P. G. Vallabhan, N. Saravanan and K. K. M. Yusuff, *Modn. Phys. Lett. B.* (in press).

3. T. Sudershan, C. Tirupataiah, D. Radharamana and S. Srihari, *J. Indian Chem. Soc.*, 72, 307 (1995).

4. L. M. Mohanty, R. C. Mishra and B. K. Mohapatra, *J. Indian Chem. Soc.*, 72, 311 (1995).

5. G. Narain and J. K. Jain, *J. Indian Chem. Soc.*, 71, 101 (1994).

6. J. A. Obaleye, C. L. Orjiekwe and O. Famurewa, *Indian J. Chem.*, 34A, 310 (1995).

7. U. Hartmann and H. Vahrenkamp, *Inorganic Chim. Acta*, 239, 13 (1995).

8. J. C. Chang, K. L. Mikkelsen, I. M. Simet, J. Dundec, M. R. Steenblock and J. E. Jurgenson, *Synth. React. Inorg. Met.-Org. Chem.*, 25, 1653 (1995).

9. S. C. Wallis, L. R. Gahan, B. G. Charles, T. W. Hambley and P. A. Duckworth, *J. Inorg. Biochem.*, 62, 1 (1996).

10. S. L. Sumalan, J. Casanova, G. Alzuet, J. Borras, A. Castineiras and C. T. Supuran, *J. Inorg. Biochem.*, 62, 31 (1996).

11. J. S. Cases, T. M. S. Garcia, M. C. Maichle, M. C. A. Rodroguez, A. Sanchez, J. Sordo, V. A. Vazquez, S. Pinelli, P. Lunghi and R. Albertini, *J. Inorg. Biochem.*, 62, 41 (1996).

12. W. E. Antholine, B. Kalyanaraman and D. H. Petering, *Environ. Health Perspectives*, 64, 19 (1985).

13. E. W. Ainscough, A. M. Brodie, J. D. Rand ford and J. M. Waters, *J. Chem. Soc., Dalton Trans.*, 2125 (1991).

14. S. Shamsuddin and A. R. Khokhar, *J. Coord. Chem.*, 33, 83 (1994).

15. S. A. Baker, Z. H. Sidik, A. R. Khokhar, *J. Coord. Chem.*, 31, 109 (1994).

16. U. P. Singh, B. N. Singh, A. K. Ghose, R. K. Singh and K. Annapoora, *J. Inorg. Biochem.*, 44, 55 (1991).

17. A. R. Khokhar, Y. Deng, S. A. Baker, M. Yoshida and Z. H. Siddik, *J. Inorg. Biochem.*, 51, 677 (1993).

18. M. B. Ferrari, G. G. Fava, P. Tarasconi, R. Albertini, S. Pinelli and R. Starcich, *J. Inorg. Biochem.*, 53, 13 (1994).

19. F. Blasco, R. Ortiz, C. Perello, J. Borras, J. Amigo and T. Debaerdemaeker, *J. Inorg. Biochem.*, 53, 117 (1994).

20. P. Yang, H. F. Wang, F. Gao and B. S. Yang, *J. Inorg. Biochem.*, 62, 137 (1996).

21. Z. H. Chohan and A. Rauf, *Synth. React. Inorg. Met.-Org. Chem.*, 26, 591 (1996).

22. K. K. Narang, V. P. Singh, S. K. Singh and G. D. Mishra, *Synth. React. Inorg. Met.-Org. Chem.*, 26, 191 (1996).

23. F. Blasco, L. Perello, J. Borras and S. G. Garcia, *J. Inorg. BioChem.*, 61, 143 (1996).

24. P. J. Sadler, "*Advances in Inorganic Chemistry*", Academic Press, Inc., Vol. 36, pp. 1, 1991.

25. N. Fahmi, C. Saxena and R. V. Singh, *Bull. Chem. Soc., PPN,* 69, 963 (1996).

26 S. A. B. Shamsuddin, Z. H. Siddik and A. R. Khokhar, *Inorg. Chim. Acta*, 241, 101 (1996).

27. K. J. Barnham, M. I. Djuran, Piedad del Socorro Murdoch, J. D. Ranford and P. J. Sadler, *Inorg. Chem.*, 35, 1065 (1996).

28. F. W. Korn and H. J. kutzner, "*The Prokaryotes - A Handbook on the Biology of Bacteria: Ecophysiology, Isolation, Identification, Application*", Springler-Verlag, New York, 2nd Edn., Vol. 1, pp. 921, 1992.

29. O. Hayashi and K. J. Hashimoto, *J. Bio. Chem.*, 37, 371 (1970).

30. S. Tsuruya, S. Yanai and M. Masai, *Inorg. Chem.*, 25, 141 (1986).

31. B. Srivas and P. S. Zacharias, *Trans. Met. Chem.*, 16, 521 (1991).

32. A. Latif Abuhijleh, *Polyhedron*, 15, 285 (1996).

33. U. Casellato, D. Fregona, S. Sitran, S. Tamburini, P. A. Vigato and P. Zanello, *Inorg. Chim. Acta*, 95, 279 (1984).

34. T. Funabiki, I. Yoneda, M. Ishikawa, M. Vjiie, Y. Nagai and S. Yoshida, *J. Chem. Soc., Chem. Commun.*, 1453 (1994).

35. R. Viswanathan and M. Palaniandavar, *J. Chem. Soc., Dalton Trans.*, 1259 (1995).

36. E. Tsuchida and H. Nishide, *Adv. Polym. Sci.*, 24, 1 (1977).

37. G. W. Parshall and S. D. Ittel, "*Homogeneous Catalysis: The Application and Chemistry of Catalysis by Soluble Transition Metal Complexes*", Wiley, New York, 1992.

38. M. E. Rerek, I. Weil and M. Hill, *Coordination Chem. Rev.*, 105, 251 (1990).

39. I. A. Salam, S. A. Aner, *Trans. Met. Chem.*, 20, 494 (1995).

40. M. Y. El-Sheikh, F. M. Ashmawy, I. A. Salem, A. B. Zaki and U. Nikel, *Trans. Met. Chem.*, 16, 319 (1991).

41 H. Hermal and R. Havemann, *Biochim. Biophys. Acta*, 128, 283 (1966).

42. M. K. Nath and J. Cheema, *Indian J. Chem.*, 32A, 108 (1993).

43. H. S. Mason, "*The Biochemistry of Copper*", Academic Press, New York, 1966.

44. H. Sigel, *Angew. Chem. Internat. Ed.*, 8, 167 (1969).

45. T. Sasaki and E. Matsunaga, *Bull. Chem. Soc. Japan*, 41, 2440 (1968).

46. R. Sreekala and K. K. Mohammed Yusuff, *Indian J. Chem.*, 34A, 994 (1995).

47. N. Sridevi, "*Some Kinetic and Mechanistic Studies on the Oxidation of Selenium(IV)*", *Ph.D. Thesis*, Andhra University, Visakhapatnam, India, 1991.

SUMMARY

The thesis deals with the studies on some new 3d-transition metal complexes of ligands derived from benzimidazole and triazole. The thesis comprises of eight chapters.

CHAPTER I

A brief review on the metal complexes of triazole and benzimidazole based compounds is given in this chapter. The scope of the present investigation is also outlined in the introductory chapter.

CHAPTER II

Details regarding the general reagents used, preparation of the aldehydes and aminomethylpolystyrene, and various analytical and physico-chemical techniques employed for the characterization of the ligands and the metal complexes are presented in this chapter.

CHAPTER III

The ligand, 1-nitrobenzyl-2-nitrophenylbenzimidazole (NBPBI) was synthesized and studied by C, H and N analyses, and IR, ^{1}H NMR, ^{13}C NMR and mass spectral methods. The C, H and N analyses of the ligand, NBPBI corresponds to the empirical formula, $C_{20}H_{14}N_4O_4$. The IR spectrum of this compound exhibits an intense band at 1475 cm^{-1} which may be attributed to the ν(C=N) stretching vibration of the benzimidazole group. The NMR data of the ligand are also in accordance with the structure shown in Figure 1, Chapter III and the mass spectrum of this compound exhibits a molecular ion peak at m/e 374 which exactly corresponds to the molecular weight of the NBPBI.

Complexes of this ligand with cobalt(II) and copper(II) metal ions were synthesized. These complexes were characterized using various physico-chemical techniques like elemental analyses, conductance, magnetic susceptibility measurements, UV-visible, near-IR, IR, EPR, and cyclic voltammetry studies. The analytical data show that the cobalt(II) complexes have the general formula, $[CoL_2X_2]$, (where, L = NBPBI and X = Cl, Br or I) and the copper complexes $[CuL_2X_2]$, (where, L = NBPBI and X = Cl or Br). The molar conductance values of the complexes indicate that all complexes are non-electrolytes in acetone. All the cobalt(II) complexes exhibit magnetic moment values in the region, 4.1-4.6 B.M. suggesting a tetrahedral geometry for these complexes. In the case of the copper(II) complexes, these values are found to be around 2.0 B.M., which indicates a square planar geometry for these complexes. The infrared spectra of the complexes indicate that the NBPBI ligand can act as a unidentate ligand coordinating through N-3 of the benzimidazole moiety. These studies suggest a tetrahedral structure for the cobalt(II) complexes and a square planar geometry for the copper(II) complexes. Cyclic votammetric studies of the $[CuL_2Cl_2]$ complex indicate that the redox reaction is irreversible and the reaction involves one electron transfer. The `g' values obtained from the EPR spectra of the copper(II) complexes suggest square planar geometry for these complexes. However, attempts to synthesize the iron(III) and nickel(II) complexes were not successful with this ligand.

CHAPTER IV

The complexes resulting from the interaction of a new polymer-bound Schiff base ligand (derived from crosslinked polystyrene bound amine and quinoxaline-2-carboxaldehyde) with tetrahedral complexes, $[CoL_2X_2]$, (where, L = NBPBI and X = Cl, Br or I), and also with square planar complexes, $[CuL_2X_2]$, (where, L = NBPBI and X = Cl or Br) have been characterized. The analytical data of the complexes show that only one Schiff base ligand unit is coordinated to metal. Infrared spectra of the complexes suggest that the bonding of the polymer ligand to metal is through the N-3 atom of the benzimidazole moiety. The EPR spectral observations indicate that all the polymer supported complexes have five coordinated structure. A trigonal bipyramid structure and a square pyramidal structure have been assigned for the copper(II) and cobalt(II) complexes respectively.

CHAPTER V

The Schiff base ligand, 2-phenyl-1,2,3-triazole-4-carboxalidene-2-aminophenol (PTCAP) has been synthesized. The ligand was characterized with elemental analyses, infrared, ^1H NMR and ^{13}C NMR spectral techniques. The analytical data suggest that the ligand has the formula, $C_{15}H_{12}N_4O$. The infrared spectrum for this ligand shows a band at 1628 cm^{-1}, which indicates the formation of $\nu(C=N)$ of the azomethine group.

Iron(III), cobalt(II), nickel(II) and copper(II) complexes of PTCAP were synthesized and characterized by elemental analyses, molar conductance and magnetic susceptibility measurements, and by UV-visible, IR and EPR spectral observations. The general formula for the cobalt(II), nickel(II) and copper(II) complexes is ML_2 (where, L = PTCAP), and for the iron(III) complex, the formula is $[FeL_2(OH)]$. The molar conductance values of the complexes reveal that they are non-electrolytes in DMF. The magnetic moment values and the electronic spectral data indicate an octahedral structure for the complexes. The IR spectra suggest that the ligand acts as a tridentate (NNO donor) ligand towards cobalt(II), nickel(II) and copper(II), and in the iron(III) complex, one of the ligand molecules acts as bidentate NO donor and the other as a tridentate NNO donor. The Mössbauer spectrum of the iron(III) complex suggests the presence of a spin equlibrium at room temperature. Cyclic voltammograms are also recorded for the copper(II) and iron(III) complexes.

CHAPTER VI

Iron(III), cobalt(II), nickel(II) and copper(II) complexes of the Schiff base, indole-3-carboxalidene-3-amino-1,2,4-triazole (ICAT) have been synthesized and characterized. The analytical, molar conductance and TG data for the complexes suggest the general formula, $[M_2L_2Cl_2].3H_2O$ for the cobalt(II), nickel(II) and copper(II) complexes (L = ICAT), and $[Fe_2L_2(OH)_2]Cl_2.4H_2O$ for the iron(III) complex. The electronic spectra and the magnetic moment data are in well agreement with a tetrahedral structure for the cobalt(II), nickel(II) and iron(III) complexes, and a square planar structure for the copper(II) complex. The infrared spectra of the complexes indicate that the ligand ICAT acts in a uninegative tridentate manner by coordinating through N_1 and N_2 of the 1,2,4-triazole ring nitrogens and N' of the indole ring nitrogen. The Mössbauer spectrum of the iron(III) complex indicates a tetrahedral geometry for this complex and further it indicates the absence of a spin equilibrium at room temperature.

CHAPTER VII

The Schiff base ligand, 2-phenyl-1,2,3-triazole-4-carboxalidene-3-amino-1,2,4-triazole (PTCAT) was formed by the condensation between 2-phenyl-1,2,3-triazole-4-carboxaldehyde and 3-amino-1,2,4-triazole in 1:1 ratio. The ligand was characterized by analytical data, and infrared and mass spectra. The analytical data suggest the empirical formula, $C_{11}H_9N_7$ for this compound. The band observed at 1655 cm^{-1} in the IR spectrum of the ligand indicates the presence of a Schiff base group. The mass spectrum exhibits a parent ion peak at m/e 239 (100 %), which is in good agreement with the molecular weight of this ligand.

Complexation behaviour of the PTCAT ligand towards iron(III), cobalt(II), nickel(II) and cobalt(II) has been studied. Attempts to synthesize iron(III) complex with this ligand were not successful. The analytical and molar conductance data indicate the general formula, $[M_2L_2(NO_3)_2]$ for the cobalt(II) or copper(II) complexes, and $[Ni_2L_2(NO_3)(H_2O)](NO_3)$ for the nickel complex. Magentic moment values indicate a tetrahedral structure for the cobalt(II) and nickel(II) complexes and a square planar structure for the copper(II) complex. The infrared spectra of the complexes suggest that the PTCAT ligand can acts as a uninegative tridentate ligand coordinating through N3 of the 1,2,3-triazole ring, and N1 and N2 of the 1,2,4-triazole ring.

CHAPTER VIII

The studies on the applications of some of the synthesized complexes are presented in this chapter. This chapter consists of two sections, Section A and Section B. The section A deals with the antibacterial studies of the simple complexes of cobalt(II) and copper(II) derived from NBPBI towards *E. coli*, *B. polymyxa*, *V. costicola*, and *P. flourescence* and *Streptoverticillium sp.* All complexes showed inhibition of growth of all these strains in a linear fashion, along with an increase in concentration from 100 μg/mL to 500 μg/mL. Maximal inhibition of growth was observed at 500 μg/mL concentration. The percentage of growth inhibition varied between 88-91 % for *E. coli*, 83-93 % for *B. polymyxa*, 93-96 % for *V. costicola*, 85-89 % for *P. flourescence* and 55-71 % for *Streptoverticillium sp.* for all complexes.

Section B of this chapter deals with the catalytic activity of both simple and polymer supported NBPBI complexes of cobalt(II) and copper(II). Section B is further classified into Part I and Part II. The simple complexes were screened for their catalytic activity in the oxidation of 3,5-di-tertiarybutylcatechol (DTBC) is discussed in Part I. The obtained results indicate that the chloro complex of cobalt(II) has greater activity than the corresponding bromo and iodo complex. In the case of the copper(II) complexes, the bromo complex has better activity than the corresponding chloro complex. Further, it has been observed that the cobalt(II) complexes have shown better activity than their copper(II) analogues in the oxidation of DTBC.

The catalytic activity of the polymer supported complexes in the decomposition of hydrogen peroxide is given in part II. In the case of the polymer supported cobalt(II) complexes, the bromo complex has greater activity than the corresponding iodo and chloro complexes. But, in the case of polymer supported copper(II) complexes, the chloro complex has better activity than the corresponding bromo complex.