

CHAPTER I

INTRODUCTION

Chemistry of metal complexes is now attaining importance in diverse fields like catalysis, medicine, microanalysis, separation of ions, preconcentration techniques and electrolysis. It is therefore necessary to study in great details new metal complexes with a view to study synthesis, characterisation, reactions and structure, bonding and stereochemistry. With the advent of new analytical techniques, we are in a position to throw light on various structural features of molecules. New ligands with favourable bonding and coordinating sites are being investigated. Amongst them those featuring structures parallel to biologically significant molecules are quite interesting. Thiiazoles with nitrogen and sulphur atoms in the heterocycle and the attached NH_2 groups offering exocyclic coordinating nitrogen sites in aminothiazoles and diamothiazoles form interesting complexes with metal ions. The present thesis deals with metal complexes of a diamine, 2,4 diamino-5-chloro thiazole and its schiff base.

1.1 A Brief Historical Account

1.1.1 Thiazole Complexes

Erlenmeyer and Schmid synthesised (1) the first coordinated compound $\alpha\text{-CoCl}_2 \cdot 2\text{TH}$ which shows β isomer in chloroform which on

standing at room temperature revert back to α -form. The complexes have 1:2 and 1:4 stoichiometry.

Eilbeck et al. (2) studied the thiazole complexes $\text{Ni}(\text{thiazole})_4 \text{Cl}_2$, $\text{Co}(\text{thiazole})_2 \text{Cl}_2$ and $\text{Cu}(\text{thiazole})_2 \text{Cl}_2$ and are shown to have essentially octahedral structure.

Goodgame (3) et al. studied the complexes of 2 methyl benzothiazole and suggest that ligand is N-bonded.

Duff et al. (4) prepared the complexes of benzo-thiazole (BT) with Co(II), Ni(II), Cu(II) and Zn(II) halides, thiocyanates and perchlorates. The complexes $\text{Zn}(\text{BT})_2 \text{X}_2$ (X = Cl, Br), $\text{Co}(\text{BT})_2 \text{X}_2$ (X = Cl, Br, I, NCS) and $\text{Ni}(\text{BT})_2 \text{I}_2$ possess tetrahedral geometry whereas $\text{Ni}(\text{BT})_4 \text{Br}_2$, $\text{Ni}(\text{BT})_2 \text{X}_2$ (X = Cl, Br), $\text{Ni}(\text{BT})_2 \text{Br}_2$ have octahedral or distorted octahedral geometry. The Cu(II) complexes $\text{Cu}(\text{BT})_2 \text{X}_2$ (X = Cl, Br) and $\text{Cu}(\text{BT})_2 \text{X}_2$ are dimeric. The benzo-thiazole coordinates through the nitrogen heteroatom in these complexes.

The octahedral thiazole complexes of the type $\text{M}(\text{TH})_6 \text{X}_2$, $\text{M}(\text{TH})_4 \text{X}_2$, $\text{M}(\text{TH})_2 \text{X}_2$ and $\text{M}(\text{TH}) \text{X}_2$ with Co(II), Ni(II), Cu(II), Zn(II) and Pd(II) have been reported by Hughes and Ruff (5).

Ford et al. (6) studied Cu(II) and Co(II) complexes of Benzothiazole (PT). The reflectance spectra of these complexes is similar to that of the complexes with analogous N-donor ligands. This suggests that coordination takes place through the ring nitrogen and not through the S atom. Thiazole is also found to coordinate through nitrogen atom (6).

Lenarcik et al. (7) studied the stability constants^s of Co(II), Ni(II) and Zn(II) complexes of thiazole. The acid dissociation constant and absorption spectra suggested that all complexes are pseudooctahedral.

The complexes of 4 and 2-4 dialkyl substituted thiazoles with Cu(II), Ni(II), Co(II), Zn(II) and Pt(II) containing various anions have synthesized by Weaver et al. (8). The complexes are generally of the form MX_2L_2 (X = Cl, Br, I or NO_3). The Zn and Co complexes are tetrahedral, the 4-methyl copper and nickel complexes are octahedral while dialkyl complexes of Cu, Ni and Pt are square planar.

Hughes and Ruff (9) reported the study of the complexes of 2-acetamidothiazole (acam) and 2-acetamidobenzothiazole (acamb) with Ni(II) and Cu(II). A number of different types of ligand behaviour have been observed on the basis of their IR spectra.

A series of Co(II), Cu(II) and Zn(II) complexes of the 2-2'-~~o~~-phenylene bis-benzothiazole are reported by John Charles et al. (10). The 1:1 complexes of Co and Zn have four coordinated pseudotetrahedral structure, while for Cu distorted square geometries are suggested. Six coordinated 1:1 derivatives are also obtained for cobalt and copper. The 1:2 derivative of copper may be square planar.

Co(II) and Ni(II) complexes of benzothiazole were studied by Goodgame and his co-workers (11). The complexes have general

formula ML_2X_2 and ML_4X_2 ($X = Cl, Br, I, NCS$ or ClO_4). $Co(II)$ complexes and $Ni_2L_2I_2$ have tetrahedral structure and for remaining complexes have octahedral structure.

1.1.2 Aminothiazole Complexes

Campbell et al. (12) studied $Co(II)$ and $Ni(II)$ halide complexes of 2-aminobenzothiazole (ATB). The complexes are of the type $M(ATB)X_2$ where $X = Cl, Br$ or I . $Ni(II)$ complexes ($X = Cl$ or Br) have pseudo-tetrahedral structure similar to the structure of complexes of benzimidazole 2-methylbenzimidazole or 2-methylbenzothiazole complexes (13, 14). The cobalt(II) complexes show pseudo-tetrahedral structure and possess magnetic moment of 4.4 B.M. The complexes of the type $[(C_2H_5)_4N][M(ATB)X_3]$ where $M = Co(II)$ or $Ni(II)$ and $X = Cl$ or Br have been studied. The $Ni(II)$ complexes possess tetrahedral structure with magnetic moment 3.3 - 3.7 B.M. Square planar structure is suggested for the complex with $X = I$. $Co(II)$ complexes ($X = Cl, Br$) have been shown to have pseudo-tetrahedral structure on the basis of electronic spectra and magnetic properties. Reflectance spectra of all the complexes suggest that the coordination takes place through the ring nitrogen rather than sulphur.

Manhas et al. (15) reported $Co(II)$, $Ni(II)$ and $Cd(II)$ complexes with 2-aminothiazole. The magnetic study of $Ni(II)$ and $Cu(II)$ complexes suggested approximately octahedral and pseudo-octahedral stereochemistry respectively (16). The magnetic moments of $Cu(II)$ complexes are in the range 1.65 to 1.61 B.M. while that of $Ni(II)$ complexes are in the range 3.05 - 3.09 B.M.

Manhas (17) reported the Co(II), Ni(II) and Cu(II) complexes with 4-methyl-2-aminothiazole and 4-phenyl 2-aminothiazole. The distorted tetrahedral and distorted octahedral structures have been suggested for Co(II) and Ni(II) complexes respectively while Cu(II) complexes have been assigned either square planar or an octahedral structure. In all complexes coordination takes place through ring nitrogen atom. It is predicted that the substitution at 4 position in 2-aminothiazole changes the stoichiometry.

Molecular addition complexes of the type ML_2X_2 [$M = Co(II)$, $X = Cl, Br, I$ and $L = 2\text{-aminothiazole}$ and $2\text{-acetylaminothiazole}$] are studied by Singh and Srivastava (18). The IR and electronic spectra of the complexes suggest the coordination through exocyclic nitrogen in 2-aminothiazole and through carboxyl oxygen in 2-acetylaminothiazole. The complexes were found to possess tetrahedral structure. The ligand field parameters show more co-valency in 2-aminothiazole complexes than 2-acetylaminothiazole. Complexes suggest a weak ligand field for both the ligands.

Nickel complexes of the types NiL_4X_2 ($X = Cl, Br, I$), $NiL_4(ClO_4)_2$ and $[L_2][NiL_4(ClO_4)_2]$ with 2-aminothiazole were studied to determine actual site of coordination by Singh and Srivastava (19).

Magnetic data, electronic spectra and ligand field parameters suggested that all complexes possess octahedral structures and the probable site of bonding is nitrogen and not sulphur (20).

When the IR spectra of complexes were compared with IR spectra of the ligand, a negative shift in $\nu(\text{N-H})$ and a positive shift in $\delta(\text{NH}_2)$ were observed. These shifts indicate coordination through nitrogen of the amino group (21-23). The spectra of complexes were recorded in acetone solution which is similar to the solution spectra of typical nickel(II) tetrahedral complexes. This suggests that the complexes require tetrahedral structure in solution. Hughes and Ruff (24) have noted a similar change in nickel complex.

Co(II), Cu(II), Cd(II), Hg(II) complexes of 2-amino, 2-amino-4-chloro, 2-amino-4-methylbenzothiazoles were studied by Malik et al. (25). The IR studies of the complexes show the coordination through the ring nitrogen of the thiazole group. Distorted tetrahedral and octahedral structures are proposed for Co(II) and Cu(II) complexes respectively. The magnetic moment of cobalt complexes lie in the range 3.91 to 4.35 B.M. and copper complexes in the range 1.53 - 1.83 B.M.

Fe(III) complexes of 2-aminobenzothiazole (ABT) of the type $\text{Fe}(\text{ABT})\text{OH} \cdot \text{X}_2$ (X = Cl, Br), $\text{Fe}(\text{ABT})_3 \cdot \text{X}_3$ (X = Cl, Br), $\text{Fe}(\text{ABT})(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$, $\text{Fe}_2(\text{ABT})_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ have been studied by Campbell et al. (26).

Hg(II) complexes of 2-amino-6-methyl benzothiazole and 2-amino-6-chlorobenzothiazole were studied by Mishra et al. (27). These complexes have molecular formula HgL_2X_2 (X = Cl, Br, I, NO_3 , SCN, OAC) and possess tetrahedral structures.

Complexes of the type MX_4L_2 (X = Cl, Br, I) of 2-aminothiazole, acetylaminothiazole with Sn(IV) and Ti(IV) have been studied by Singh et al. (28). IR studies of these complexes indicate exocyclic nitrogen of 2-aminothiazole and carbonyl oxygen of acetylaminothiazole as the donor sites. Far-infrared spectra suggest that 2-acetylaminothiazole complexes are trans and 2-aminothiazole complexes are cis octahedral.

Berdon (29) studied the thallium(III) complexes of the type TlX_3L_2 (X = Cl, Br) with the heterocyclic ligands. L = Benzothiazole, 2-aminobenzothiazole.

Antimony(III) and Bismuth(III) complexes of 2-methylbenzothiazole has been synthesized and studied by Giusti et al. (30). The ligand is N-bonded when monodentate and S,N-bonded as a bridging ligand.

Nickel(II) complexes of bidentate substituted benzothiazoles have studied by Thompson et al. (31). The 1,2 bis-(2-benzothiazolyl) benzene which has an o-phenylene bridge, forms square planar derivative with NiX_2 (X = I, ClO_4), octahedral derivative with NiX_2 (X = NCS, NO_3) and five co-ordinated derivative with NiX_2 (X = Cl, Br). 1-2 bis (2-benzothiazolyl) ethane which has an ethylene bridge forms tetrahedral derivative with NiX_2 (X = Cl, Br, I) and an octahedral complex with $Ni(NO_3)_2$.

Dimeric copper(II) acetate complexes of thiazoles of the type $Cu(OAC)_2L$ (L = Thiazole, benzothiazole, 2 methyl benzothiazole, 2-4 dimethyl thiazole, 2,4,5 trimethyl(thiazole) were prepared by Tokii et al. (32). All show antiferromagnetism.

Singh et al. (33) prepared the thiocyanato and cyanato complexes of Zn(II), Cd(II), Hg(II), Fe(II), Pd(II), Co(II), Ni(II) and Cu(II) with 2-aminothiazole, 2(N-acetyl) aminothiazole and characterised from molar conductance, magnetic moment, IR and electronic spectra.

Giustic et al. (34) studied the copper(I) and Silver(I) complexes of 2-aminobenzothiazole. The ligand is co-ordinated through the ring N atom. The Cr(III) complexes of 2-aminobenzothiazole (35) were prepared and characterised by IR and UV spectroscopy. In all complexes ligand co-ordinated through amine N atom.

Sonar et al. (36) studied the Co(II) and Cu(II) complexes with substituted 2-amino and 2-acetyl aminothiazoles. The spectral results suggest coordination through the amino nitrogen and carbonyl oxygen in the Co(II) and N bonding for all Cu(II) complexes.

Chaurasia et al. (37, 38) reported the transition metal complexes of 6-methyl 2-amino benzothiazole and 2-methylbenzimidazole of the type MLX_2 , ML_2X_2 , ML_4X_2 (M = Cu, Ni, Co, Fe, Zn, Cd, and Hg, X = I, CNS and OAC).

Sinha et al. (39) reported metal complexes of 6-ethoxy-2-aminobenzothiazole of the type ML_2X_2 (M = Pd, Pt, X = Cl, Br). Ligand co-ordinated through the ring nitrogen in all complexes.

Metal complexes of 2-amino-5 nitrothiazole with Co(II), Ni(II), Cu(II), Cd(II), Cu(I) and Ag(I) reported by Dichalsjian et al. (40). The ligand is coordinated through ring N.

The complexes of 2,4-diaminobenzothiazole are reported for the first time in this work.

1.2 Schiff's Base derived from Heterocyclic amines and their Metal Complexes

Schiff's bases derived from heterocyclic amines are biologically active. The complexes of the Schiff bases derived from heterocyclic amines also possess biological activity.

Dash and Mahapatra have synthesised Co(II), Ni(II), Cu(II) and Zn(II) complexes of Schiff bases derived from 4-aryl-2-aminothiazole and salicylaldehyde. Square planar and tetrahedral structures are proposed for Co(II) and Zn(II) complexes respectively, whereas octahedral structure is proposed for both Ni(II) and Cu(II) complexes on the basis of electronic spectra and magnetic susceptibility measurement (41).

Co(II), Co(III), Ni(II), Cu(II) and Pd(II) complexes of Schiff bases obtained from salicylaldehyde derivatives and 2-amino ethyl pyridine studied by Yamada et al. (42). Electronic spectra of Co(II) and Ni(II) complexes in solid state agree with the six coordinated octahedral structure. In Co(II) and Ni(II) complexes the ligand X-Sal-2EPy [where Epy = ethyl pyridine] acts as a tetradentate ligand while in Co(II) complexes it function as bidentate ligand.

Mishra et al. (43) studied Ni(II) complexes of Schiff bases derived from salicylaldehyde and 2- and 3-amino pyridine. The complexes $Ni[Sal L']_2 \cdot H_2O$ [where $Sal L'$ = Schiff's base derived from salicylaldehyde and 2-amino pyridine] and $Ni(Sal'')_2$ (where Sal'' = Schiff base derived from salicylaldehyde and 3-amino pyridine) are supposed to have polymeric octahedral structure.

Cu(II), Pd(II) and Pt(II) complexes of tridentate Schiff bases derived from 2-(2-amino ethyl) pyridine and salicylaldehyde, o-hydroxy acetophenone, o-hydroxypropiophenone or o-hydroxy butyrophenone ^{were} studied by Rastogi et al. (44). Structure of above complexes are square-planar. IR studies show that the metal atom is co-ordinated through the nitrogen atom of imine group and heterocyclic ring and oxygen atom of the phenolic group.

Ramaswamy et al. (45) studied Pd(II) and Zn(II) complexes of Schiff bases derived from methyl substituted 2-aminopyridine and salicylaldehyde. The proposed structure for Pd(II) and Zn(II) complexes are square planar and tetrahedral respectively.

Co(II), Ni(II), Cu(II), Th(IV) and U(VI) complexes of some heterocyclic Schiff bases derived from 2-amino pyridine and salicylaldehyde [L], p-hydroxybenzaldehyde [L'] and vanilline [L''] have been prepared by Mohmoud et al. (46). It is concluded that the molecules and not the ions of L are coordinated to the metal ions as bidentate ligand. The two bonding sites are the central azomethine nitrogen and aldehydic-OH group on the other hand, the neutral molecules of L' and L'' are coordinated to the metal ions as monodentate ligands where the nitrogen pyridine ring is the bonding site.

Verkhovodova et al. (47) reported Cu(II) complexes of Schiff bases derived from salicylaldehyde and 2-aminopyridine. Sen Gupta et al. (48) carried out the potentiometric study of the proton-ligand stability constants of 2-hydroxy-1-naphthalene-2-iminopyridine and its 1:1 complexes with Pr(III), Nd(III), Sm(III) and Cd(III).

Ni(II) complexes of Schiff bases derived from salicylaldehyde with 2- and 3-amino pyridine and 3-, 4-, 5- and 6-methyl derivatives of 2-amino pyridine studied by Csaszaz et al. (49). Characterised by chemical analysis, IR electronic and NMR spectra and magnetic moments. The ligand [HL] acts as bidentate to give octahedral structure.

$\text{NiL}_2(\text{H}_2\text{O})_2$ complexes except in case of the ligand derived from 6-methyl-2-amino-pyridine which is tridentate and give octahedral $[\text{NiL}_2]$ structure.

Chjo Ki Hyang (50) studied the complexes of Mo(VI), Mo(V), Mo(IV), Mo(III) with Schiff base ligands salicylidene amino-pyridine [HL'] and salicylidene amino-o-thiobenzene [H_2L]. Their physical, chemical properties were studied by visible, IR spectra and elemental analysis and DTA. Ligand acts as tridentate and form six coordinate complexes. $[\text{MoO}_2(\text{H}_2\text{O})\text{L}]$, $[\text{MoO}_2(\text{H}_2\text{O})\text{L}']$, $[\text{MoO}(\text{H}_2\text{O})(\text{SCN})\text{L}']$, $[\text{MoO}(\text{H}_2\text{O})_2\text{L}']$ which octahedral, whereas $[\text{Mo}(\text{H}_2\text{O})_2\text{L}]_2\text{O}$, $[\text{MoO}(\text{H}_2\text{O})\text{L}]_2\text{O}$, $[\text{Mo}(\text{SCN})(\text{H}_2\text{O})\text{L}]_2\text{O}$ and $[\text{Mo}(\text{H}_2\text{O})_2\text{L}]_2$ are binuclear octahedral with Mo-O-Mo [Mo-O-bridge bond].

Co(II), Ni(II) and Zn(II) complexes of Schiff base reported by Cho, Ki Hyung et al. (51). The complexes with ligand [H_2L = salicylidene amino-o-thiobenzene]. The complexes of Ni(II) and Zn(II) are six-coordinated i.e. $\text{NiL}(\text{H}_2\text{O})_3$ and $\text{ZnL}(\text{H}_2\text{O})_3$ and copper(II) complex are N-coordinated.

Oxovanadium (IV) complexes of Schiff base derived from salicylaldehyde derivatives, o-hydroxyphenones and 2-2'-aminoethyl

pyridine were studied by Rastogi et al. (52). The complexes have subnormal magnetic moment which may be due to the presence of exchange coupled antiferromagnetism. The electronic and IR spectral data suggest that binuclear o-bridged tetragonally distorted octahedral structure in which the elongation is along the z axis [Oh \rightarrow D_{4h}] owing to the presence of ligands of unequal donor strength. Electronic spectra show A, F, P levels and Ds and Dt ligand field parameter.

Rastogi et al. (53) studied the complexes of Ni(II), Co(II) and Cr(III) of tridentate Schiff base derived-2-(2'-aminoethyl) pyridine and salicylaldehyde substituted salicylaldehyde [X-sal, X = 5-Cl, 5-NO₂, 5,6-here) (X = salaep), o-hydroxyacetophenone (Hapaep), o-hydroxy propiophenone [Happaep], o-hydroxybutyrophenone [Hbpaep] on conductance measurement, magnetic and electronic and IR spectral data shows all complexes have octahedral geometry.

Kuma et al. (54) studied Co(II), Ni(II) complexes with Schiff base obtained from salicylaldehyde derivatives and N-(2-aminoethyl) piperazine Bis(Schiff base). The ligand acts as tetradentate. All complexes have octahedral structure.

Ranganathan et al. (55) reported Cu(II), Ni(II) and Co(II) complexes of Schiff base derived from 2-amino-5-methyl pyridine and salicylaldehyde. Square planar structure for Cu(II) complexes and Co(II) and Ni(II) were tetrahedral^{ly} coordinated.

Mahamound M.R. et al. (56) reported Co(II), Ni(II) and Cu(II) complexes with heterocyclic Schiff base i.e. 2-(salicylidene

amino)-4-phenylthiazole [L^1] 2-(p-hydroxybenzylidene-amino)-4-phenylthiazole [L^2] and 2-(hydroxy-m-methoxybenzylidene amino-4-phenylthiazole) [L^3] were prepared and characterised on the basis of IR and electronic spectral data. The Schiff bases L^2 and L^3 are weaker ligand compound to the corresponding derivatives of 2-arylidene amino) pyridines. This is ascribed to the low basicity of the nitrogen in the thiazole ring relative to the nitrogen in the pyridine ring.

Co(II) complexes of Schiff base ^{the} derived from 2-naphthaldehyde with 2-aminothiazole ^{were} studied by Verma et al. (57). The complexes are nonelectrolytic with high spin octahedral geometry.

Mahapatra et al. (58) studied Cu(II), Ni(II) and Zn(II), Cd(II) and Hg(II) complexes of Schiff bases. The complexes with ligand EL_2 [3-amino-1-phenylpyridine-5-one] with salicylaldehyde. The complexes are either octahedral or distorted octahedral.

Co(II), Ni(II) and Cu(II) complexes of Schiff base reported by Saha et al. (59). The N-benzylidene-S(3)-methylpyrazole-3(5)-carbohydrazone Schiff base were characterised by using technique [BMPCH], magnetic and electronic spectral data indicates that $M(BMPCH)_2X_2 \cdot nH_2O$ ($X = Cl, Br, I, NO_3, BF_4, ClO_4, SCN, O_5$ son; $M = Co, Ni, Cu$; $n = 0, 2, 4$) are grossly octahedral except the halocomplexes of Co(II) which are mixture of octahedral and tetrahedral. The ligand exhibits neutral tridentate (NON) behaviour ~~xxxxx~~ coordinating through the tertiary nitrogen of the pyrazole ring.

Cu(II), Ni(II) and Zn(II) complexes of tridentate Schiff bases derived from 4-Aryl-2-aminothiazole and its substituted derivative with substituted o-hydroxyaldehyde were studied by More P.G. et al. (60). The tridentate ligands form ML_2 type of complexes (where M = Ni, Cu or Zn). All complexes are octahedral in geometry. The Zn(II) complexes of ZnL_2 type excludes the formation of polymeric species.

In the earlier work from our laboratory Schiff bases derived from substituted 2-aminobenzothiazoles and substituted vic-hydroxy aromatic aldehyde were used as ligand (61), ligand field theory and interelectronic repulsion parameters for several complexes were reported. Mass spectral analysis and complete fragmentation scheme have been reported. In addition to that sixtyfour new complexes from sixteen new ligands are reported (62) ^{using} ~~and~~ conventional structural approach a detailed spectrochemical study and ligand field parameter as well as x-ray absorption and x-ray photo electron spectral studies of complexes.

Co(II) complexes of tridentate Schiff bases derived from 4-(R-substituted)-2-aminothiazole (R=H, CH_3 , CMe, Cl) with β -hydroxy-2-naphthaldehyde or 5-(R'-substituted) salicylaldehyde (R'= CH_3 , Cl) were studied by More P.G. et al. (63) structure of above complexes are octahedral and complexes are non-conducting.

The complexes of the Schiff base formed by the condensation of 2,4-diamino 5-chloro thiazole and vic-hydroxy aldehyde salicylaldehyde are reported in this thesis.

References

1. H. Erlenmeyer and E.H. Schmid
Helv. Chim. Acta 24, 869 (1941).
2. W.J. Eilbeck, F. Holmes and A.E. Underhill,
J. Chem. Soc. A. 757 (1967).
3. M. Goodgame and M.J. Weeks,
J. Chem. Soc. (A) 1156 (1966).
4. E.C. J. Duff, M.N. Hughes and K.J. Ruff,
J. Chem. Soc. (A) 2354 (1968).
5. M.N. Hughes and K.T. Ruff,
J. Chem. Soc. (A) 18, 3015 (1971).
6. R.A. Ford, G. Halkyard and A.E. Underhill,
Inorg. Nucl. Chem. Lett. 4, 507 (1968).
7. B. Lenarcik, J. Kulling and B. Pazzs,
Rozniki. Chem. 48, 2111 (1974).
8. J. A. Weaver, P. Hambright, P. T. Talbert,
Kang and Thorpe,
J. Inorg. Chem. 9, 268 (1970).
9. M.N. Hughes and K.J. Ruff,
10. J.C.I. Rendell and L.K. Thompson,
Can. J. Chem. 57, 1 (1979).
11. N.N.G. Charge, M. Goodgame and M.J. Weeks,
J. Chem. Soc. A. 2499 (1968).
12. M.J.M. Campbell, D.W. Card, R. Grzeskowiak and M. Goldstine,
Inorg. Nucl. Chem. Lett. 5, 39 (1969).

13. D.M.L. Goodgame, G. Goodgame and M.J. Weeks,
J. Chem. Soc. A. 1076 (1967).
14. M. Goodgame and M.J. Weeks,
J. Chem. Soc. A. 1156 (1966).
15. B.S. Manhas and U.K. Phatia,
Ind. J. Chem. 10, 947 (1972).
16. Figgis, B.N. and Lewis
J. Progr. Inorg. Chem. 6, 37 (1964).
17. B.S. Manhas, V.K. Phatia and O.P. Chitkara,
Ind. J. Chem. 14A, 206 (1976).
18. P.P. Singh and A.K. Srivastava,
Aust. J. Chem. 27, 509 (1974).
19. P.P. Singh and A.K. Srivastava,
J. Inorg. Nucl. Chem. 36, 928 (1974).
20. D.F. Orster and D.M.L. Goodgame,
Inorg. Chem. 4, 823 (1965).
21. P.P. Singh and R. Rivest,
Can. J. Chem. 46, 2361 (1968).
22. S.C. Jain and R. Rivest,
Can. J. Chem. 29, 2793 (1967).
23. S.K. Madan and C. Goldstein,
J. Inorg. Nucl. Chem. 28, 1251 (1966).
24. A.F.P. Lever
Coord. Chem. Rev. 3, 119 (1968).
25. W.A. Malik, K.D. Sharma, R.D. Sharma and J.S. Upadhyaya,
Ind. J. Chem. 15A, 152 (1977).

26. M.J.M. Campbell, R. Grzeskowiak and S.S. Juneja,
J. Inorg. Nucl. Chem. 40, 1247 (1978).
27. R.P. Mishra, P.B. Mahapatra and S. Gum,
J. Ind. Chem. Soc. 56, 832 (1979).
28. P.P. Singh and U.P. Shukla,
Aust. J. Chem. 27, 1827 (1974).
29. Berdon,
Chim. Ing. Chim. 26, 21 (1980).
30. Giustic, A., Peyronel, G.,
J. Inorg. Nucl. Chem. 43, 2675 (1981).
31. Thompson, R., John C. T.,
Can. J. Chem. 60, 514 (1982).
32. Tokii, T., Muto, Y.,
Bull. Chem. Soc. Jpn. 56, 1549 (1983).
33. P.P. Singh, U.P. Shukla, J.N. Seth,
Ind. J. Chem. 14A, 684 (1976).
34. Giusti, A., Peyronel, G.,
Giliberti E.,
Spectro Chim. Acta. Part A. 38A(II) 1185 (1982).
35. Giusti A., Peyronel G., Giliberti E.,
Spectro Chim. Acta. Part A, 40(A) 275 (1984).
36. Sonar, M.H., Murty,
J. Inorg. Nucl. Chem. 42, 793 (1980).
37. Chaurasia, M.R. Shukla, P.,
J. Ind. Chem. Soc. 60(ii), 1011 (1983).
38. Chaurasia, M.R., Shukla P., Singh, N.K.
Def. Sci. J. 32, 75 (1982).

39. Sinha, A.I., Tiwari, S.P.
Chim. Sci. 55(8), 386 (1986).
40. Dichalsjian, S., Farago, M., E.
Inorg. Chim. Acta, 108(4), 249 (1985).
41. B. Dash and S.K. Mahapatra,
J. Inorg. Nucl. Chem. 37, 271 (1975).
42. K. Yamanouchi and S. Yamada,
Inorg. Chim. Acta, 12, 109 (1975).
43. M.K. Mishra, R.C. Das and S.K. Mohanty,
Ind. J. Chem. 14A, 679 (1976).
44. D.K. Rastogi and P.C. Pachauri,
Ind. J. Chem. 15A, 47 (1977).
45. H. Ranganathan, D. Ramaswamy and M. Santappa,
Ind. J. Chem. 18A, 189 (1979).
46. M.R. Mohmoud and M.T. Elhaty,
J. Inorg. Nucl. Chem. 42, 349 (1980).
47. D.S. Verkhovodovo and M.I. Kynazhanskii,
Zn. Neorg. Khim. 12, 1549 (1967).
48. G.S. Sengupta and C.R. Bera,
J. Ind. Chem. Soc. 57, 558 (1980)..
49. Csaszaz, T. Balog, J.
Acta Chim. Acad. Sci. Hung. 87 , 321 (1975).
50. Cho, Ki Hyung
Dachan Hwahak Hwoejee 18 : 66 (1974).
51. Cho Ki Hyung
Dachan Hwahak. Hwoejee 18 : , 189 (1974).

52. Rastogi, D.K., Pancham, P.C.,
J. Inorg. Nucl. Chem. 39(1), 151 (1977).
53. Rastogi, D.K., Pancham, P.C.
Ind. J. Chem. 15(A), 748 (1977).
54. Kuma, H., Yamada, S.,
Bull. Chem. Soc. Japan 49(9), 2635 (1976).
55. Ranganathan, H.
Curr. Sci. 47(10), 330 (1978).
56. Mahmound, M.R., Al-Hamid, R.
Ind. J. Chem. 19(A) 345 (1980).
57. Verma, H.S., Pal, A., Saxena, R.G., Katiyar, A.K.
J. Chem. Soc. 60(11), 85 (1983).
58. Mahapatra, B.B., Panda, D., Patel, B.K.,
Ind. J. Chem. 23A, 2129 (1984).
59. Saha, N., Sinha S.,
Ind. J. Chem., 24A, 203 (1985).
60. Bhaskare, C.K., More, P.G.
Ind. J. Chem. 25A, 166 (1986).
61. P.G. More,
Ph.D. Thesis (1980) Shivaji University, Kolhapur.
62. P.P. Hankare,
Ph.D. Thesis (1983), Shivaji University, Kolhapur.
63. Bhaskare, C.K., and More, P.G.
J. Ind. Chem. Soc. 63(3), 270 (1986).