Bull. Chem. Soc. Ethiop. **2001**, 15(1), 29-37.
Printed in Ethiopia

ISSN 1011-3294

STUDIES OF TRANSITION METAL COMPLEXES OF HERBICIDAL COMPOUNDS. I: TRANSITION METAL COMPLEXES OF 2-METHYLTHIO-4-AZIDO-6-ISOPROPYLAMINO-*S*-TRIAZINE (AZIPROTRYN)

Worku Dinku[1], Negussie Megersa[1], V.J.T. Raju[1,2], Theodros Solomon[1], Jan Åke Jönsson[3] and Negussie Retta[1*]

[1]Department of Chemistry, Addis Ababa University, P.O. Box 1176, Addis Ababa, Ethiopia
[2]Department of Chemistry, Osmania University, Hyderabad 500 007, India
[3]Department of Analytical Chemistry, Lund University, Box 124, S-221 00 Lund, Sweden

(Received December 25, 2000; revised March 1, 2001)

ABSTRACT. Divalent cobalt, nickel, copper and zinc complexes of herbicidally active 2-methylthio-4-azido-6-isopropylamino-s-triazine (aziprotryn, AZP) were synthesized and characterized on the basis of conductance, IR, NMR and electronic spectral studies. The metal:ligand:chloride ratio was 1:2:2 in Co(II), Ni(II) and Cu(II) complexes while it was 1:1:2 in the Zn(II) complex. The Zn(II) complex is a 1:1 electrolyte while the others are 1:2 electrolytes. AZP behaves as a neutral bidentate NN donor, with terminal azido nitrogen and N-5 ring nitrogen acting as metal binding sites. A tetrahedral geometry for Co(II), Ni(II) and Zn(II) complexes and square planar geometry for the Cu(II) complex are proposed.

KEY WORDS: Transition metal complexes, Derivatization, *s*-Triazine herbicides, Degradation, Herbicide detoxification, Neutral bidentate NN donor, Azomethine ring

INTRODUCTION

Metal complexes of biologically active organic compounds have promising applications in view of enhanced liposolubilities and reorganized electron density distributions. Modified antimicrobial, insecticidal, insect growth regulating, herbicidal and plant growth regulating activities of metal complexes derived from active organic ligands have been documented in the literature [1-4]. Enhancing and diminishing effects on the derivatives of the ligands have been explained on the basis of the coordinating centers and structures of the metal complexes.

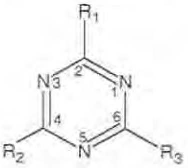
Symmetrical triazines (1,3,5-triazines or *s*-triazines) (Table 1) with -Cl, $-OCH_3$, $-SCH_3$, $-NR_2$ (R = H or alkyl) substituents as atrazine, simazine, prometone, prometryn, aziprotryn, etc., have gained worldwide recognition for their established and outstanding herbicidal properties [5]. Due to the electronegativity difference between nitrogen and carbon, the π-electrons in the ring of *s*-triazines are located in the vicinity of nitrogen centers. A polar mesomeric form II (Figure 1) that bears additional unshared pair of electrons on each nitrogen is likely to result in potential metal binding characteristics [6].

Residual herbicides in agricultural products are causing symptoms of illness in animal and human consumers. Fast degradation of residual herbicides is a challenging problem in advanced as well as developing countries. Derivatization into less harmful compounds is one of the approaches to detoxify the remnant herbicides after crop development [7-10]. Existing reports also indicate metal ion assisted degradation of some triazine based herbicides [11] as another promising path. The heteroatoms that are understood to be responsible for the herbicidal activity could easily be targeted by metal ions through complex formation. It is, thus, reasonable to

---

*Corresponding author. E-mail: chemistry.aau@telecom.net.et expect suppression of herbicide activity when active centers are bound to metal ions. Dependin on the intensity of metal-ligand interaction, the stability of the triazine ring could be affected.

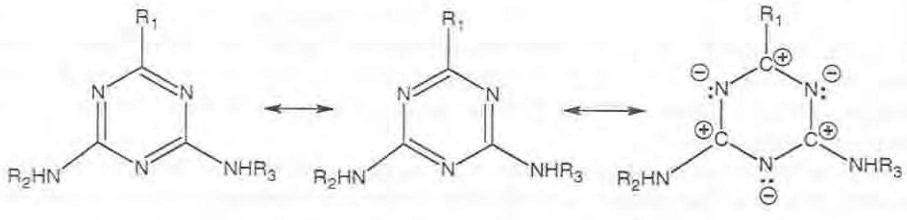
Table 1. Structure and some physical constants of selected *s*-triazine compounds [5, 6].



Common name	Substituents			Solubility*	m.p. (°C)	pK$_a$ value
	R₁	*R₂*	*R₃*			
Simazine	Cl	NHC_2H_5	NHC_2H_5	5	225 – 227	1.65
Atrazine		NHC_2H_5	$NHCH(CH_3)_2$	33	175 –177	1.68
Propazine		$NHCH(CH_3)_2$	$NHCH(CH_3)_2$	8.6	212 – 214	1.85
Atratone	OCH_3	NHC_2H_5	$NHCH(CH_3)_2$	1650	-	4.2
Prometone		$NHCH(CH_3)_2$	$NHCH(CH_3)_2$	750	91 – 92	4.2
Ametryn	SCH_3	NHC_2H_5	$NHCH(CH_3)_2$	185	84 – 86	4.1
Desmetryn		$NHCH_3$	$NHCH(CH_3)_2$	580	84 – 86	4.0
Aziprotryn		N_3	$NHCH(CH_3)_2$	50	95	1.4
Terbutryn		NHC_2H_5	$NHC(CH_3)_3$	58	104 – 105	4.3
Dipropetryn	SC_2H_5	$NHCH(CH_3)_2$	$NHCH(CH_3)_2$	16	104 – 106	4.3

*Solubility in water (ppm) (20-25 °C).

A literature survey reveals a growing interest in the synthesis, structural studies anc applications of transition and non-transition metal complexes of various substituted *s*-triazine [12-14]. However, the growth of the literature on the production and use of *s*-triazines has nc parallel development with respect to their coordination chemistry. In particular, metal ior promoted herbicide detoxification or degradation studies need a more systematic approach. Ir view of this, investigation of the coordination chemistry of some selected N-heterocycli herbicides like *s*-triazines has been initiated and the results of a study of complex formation o aziprotryn (AZP) (2-methylthio-4-azido-isopropylamino-*s*-triazine) with Co(II), Ni(II), Cu(II and Zn(II) are reported in this paper.



(I)

(II)

Figure 1. Resonance structure of *s*-triazines; R_1 represents -Cl, -OCH_3 or -SCH_3 and R_2 and R represent straight or branched chain alkyl groups.

EXPERIMENTAL

All of the chemicals used were of Analar grade. The solvents used in this study such as methanol, ethanol, petroleum ether, chloroform, *iso*-propanol, *n*-butanol and 1,4-dioxane were purified by known procedures [15]. During the synthesis of complexes a 5% (v/v) methanol concentrated ammonia solution was used to adjust the pH. A pure sample of aziprotryn was obtained from Promochem (Wesel, Germany). Analar grade metal chlorides of Co(II), Ni(II), Cu(II) and Zn(II) were procured from Aldrich chemicals.

Vibrational (IR) spectra were recorded on a Pye Unicam SP 2000 spectrophotometer in the 200-40,000 cm^{-1} range, with a KBr disc as reference material. Electronic spectra of the complex solution in methanol were measured in the range 200-900 nm at room temperature with a Beckman DU-65 spectrophotometer. Conductance measurements of the complexes were made in freshly prepared methanol solution (10^{-3} M), using a Philip Harris conductivity meter. Melting points of ligands and complexes were determined on a Bock-Monoscop apparatus and are uncorrected. The purity of the ligand and complexes was tested by thin layer chromatography (TLC). ^{1}H-NMR spectra were recorded in D_2O using a Varian Unity 300 spectrometer operating at 299.779 MHz.

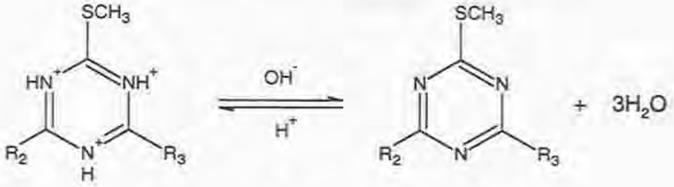
The metal complexes were analyzed for metal and chlorine. Cobalt(II) and zinc(II) were estimated complexometrically using EDTA. Nickel(II) and copper(II) were estimated gravimetrically using dimethylglyoxime as $Ni(DMG)_2$ and Cu(benzoin-α-oxime), respectively. Chloride contents were analyzed as AgCl [16].

Synthesis of metal complexes. Metal complexes of AZP were synthesized from non-aqueous media. The complexes were observed to form in methanol, ethanol, *iso*-propanol and *n*-butanol. The following general method was employed for the synthesis of metal complexes of AZP. To the methanol solution (10 mL) of divalent metal chloride (0.22 mmol), a methanol solution (10 mL) of AZP (0.44 mmol) was added in small portions to obtain a clear solution. The pH of the reaction mixture was adjusted to 6 by adding 5% (v/v) methanol concentrated ammonia solution. The reaction mixture was then refluxed for 6 h on a steam bath and was finally concentrated. The coloured product obtained was filtered while hot and washed successively with small amounts of methanol and petroleum ether. Purity of the complexes was tested by TLC using different solvent mixtures. The yields of the compounds are given in Table 2.

RESULTS AND DISCUSSION

The solubility of AZP in methanol and also aqueous system increased markedly in the presence of metal ions. The separation of complexes was increasingly facile with decreasing polarity of the solvent. The pH of the reaction medium affected complex formation; a pH range 5.0-6.0 gave best yields. This is probably because of the pH dependent equilibrium in Figure 2. The equilibrium is likely to shift to the right at high pH (about 6), thus making the lone pair on any ring nitrogen available for metal binding interaction. Hence, the preferred structure in complex formation is (II).

All metal complexes except that of zinc are coloured and are stable to air and moisture. They decompose at high temperature (110-160 °C). They are soluble in common organic solvents like methanol, ethanol, chloroform and acetonitrile.



(I) (II)

Figure 2. pH dependent equilibrium in aziprotryn; R_2 and R_3 represent N_3 and $NHCH(CH_3)_2$, respectively.

Elemental analysis. Table 2 presents the analytical data of the complexes. The complexes have been analyzed for metal and chloride percentages. Based on the percentage of metal and chloride the following formulations have been assigned: $Co(C_7H_{11}N_7S)_2Cl_2$, $Ni(C_7H_{11}N_7S)_2Cl_2$, $Cu(C_7H_{11}N_7S)_2Cl_2$ and $[Zn(C_7H_{11}N_7S)(H_2O)Cl]Cl$. The data show that the M:L:Cl ratio is 1:2:2 in the Co(II), Ni(II) and Cu(II) complexes while it is 1:1:2 in the Zn(II) complex. The presence of two chlorides per metal ion indicates the neutral form of the ligand in the complexes.

Table 2. Analytical data of the complexes of aziprotryn.

Complex	Colour	m.p./dec. temp. (°C)	Yield (%)	Found (calculated), % Chlorine	Metal	Λ_m ($\Omega^{-1}cm^2mol^{-1}$)
$[Co(AZP)_2]Cl_2$	Blue	150 – 160	50	12.23 (12.1)	10.16 (10.20)	152
$[Ni(AZP)_2]Cl_2$	Light green	110 –120	55	12.14 (12.20)	10.10 (10.13)	143
$[Cu(AZP)_2]Cl_2$	Green	130 – 140	55	12.13 (12.03)	10.85 (10.83)	133
$[Zn(AZP)(H_2O)Cl]Cl$	White	120 – 130	50	12.46 (12.51)	11.46 (11.39)	74

Conductance studies. The molar conductance data presented in Table 2 show that the Co(II), Ni(II) and Cu(II) complexes are 1:2 electrolyte while the Zn(II) complex is a 1:1 electrolyte. From conductance studies it is concluded that the two chloride ions of the Co(II), Ni(II) and Cu(II) complexes are present as free ions in solution, which means the metal ion is bound to two AZP molecules in its coordination sphere. The data for the Zn(II) complex, however, suggest a 1:1 electrolyte behaviour, with one chloro ligand on the Zn center.

IR spectra. Comparison of the IR spectra of AZP and its metal complexes reveals the bidentate nature of the ligand. The data in Table 3 suggested that AZP binds to the metal ions through a nitrogen of the N_3 group and an azomethine/ring nitrogen. Thus, it may be deduced that AZP is behaving as a neutral NN donor. The following discussion presents the details.

The IR spectrum of free AZP has characteristic bands corresponding to $\nu_{a(NNN)}$, $\nu_{s(NNN)}$, $\nu_{(C=N)}$ and $\nu_{(C-S)}$ vibrations together with several other bands assignable to C_3N_3 ring vibrations as also documented in the literature [17]. The strong, sharp band at 3290 cm^{-1} is due to $\nu_{(NH)}$, while the intense band at 2110 cm^{-1} is assignable to $\nu_{a(NNN)}$ [18]. Another multiplet observed in the 1610-1595 cm^{-1} range is characteristic of the three ring azomethane units of the *s*-triazine moiety. The bands of relatively less intensity at 1580 cm^{-1} may be due to $\delta_{(N-H)}$. Bands observed around 1400, 800, 730 and 550 cm^{-1} are due to C_3N_3 ring vibrations [17]. Bands due to $\nu_{s(NNN)}$ and $\delta_{(NNN)}$ are located at 1375 cm^{-1}and 670 cm^{-1}, respectively [18].

The characteristic features observed in the spectra of the metal complexes are: (i) a higher frequency shift in $\nu_{a(NNN)}$ bands and a lower frequency shift in $\nu_{s(NNN)}$ and $\delta_{(NNN)}$, (ii) splitting of the $\nu_{(C=N)}$ band, and (iii) the appearance of non-ligand bands.

The participation of the N_3 group in coordination is evidenced by an upward shift of $\nu_{a(NNN)}$ and a downward shift of $\nu_{s(NNN)}$ and $\delta_{(NNN)}$, exhibited in the spectra of the Co(II), Ni(II), Cu(II) and Zn(II) complexes. The $\nu_{a(NNN)}$ in these complexes appears in the range 2130-2200 cm^{-1} compared with that of free aziprotryn (2110-2160 cm^{-1}). The intensity of $\nu_{a(NNN)}$ decreases in the order free AZP > Co(AZP) > Ni(AZP) > Zn(AZP) > Cu(AZP). This decreasing intensity order of the $\nu_{a(NNN)}$ band may be attributed to increasing metal ligand interactions. The $\nu_{s(NNN)}$ shows a decreased frequencies in all the complexes. In addition, the low intensity band of AZP at 670 cm^{-1} is at lower frequency in the complexes (Table 3). This feature supports coordination through the azido group [18].

Table 3. Characteristics infrared frequencies (cm^{-1}) of the complexes of aziprotryn.

Compound	$\nu_{(N-H)}$	$\nu_{a(NNN)}$	$\nu_{(C=N)}$	$\nu_{s(NNN)}$	$\delta_{(NNN)}$	New bands
Ligand	3290	2160	1610 - 1595	1375	670	-
Co(II) complex	3100 – 3600	2180	1600 - 1630	1360	625	450, 560
Ni(II) complex	3160 – 3500	2170	1615 - 1625	1370	660	430, 480, 490
Cu(II) complex	3320 – 3480	2170	1620 - 1650	1360	620	475
Zn(II) complex	3320 – 3580	2190	1610 - 1640	1370	650	900 - 910, 605, 490

The Azido (N_3) group of AZP is represented as a resonance hybrid of the forms shown in Figure 3. Based on the availability of a non-bonding electron pair and the chelate size with ring nitrogen as another binding center, it is reasonable to conclude that the terminal nitrogen is the only possible binding center. While ionic azide is symmetrical and linear, the covalent azides are not expected to be so symmetric [19]. Further, when the terminal nitrogen is involved in bonding, the symmetry and the linearity of NNN are much reduced.

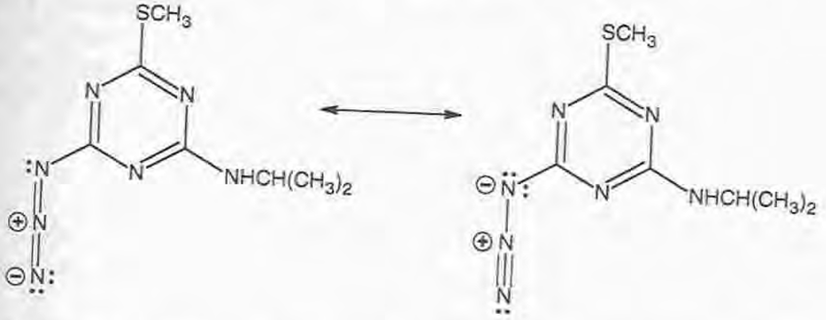


Figure 3. Resonance structure of aziprotryn, indicating the non-bonding electron pairs on nitrogen of the azido group.

The other interesting feature in the spectra of these complexes is the splitting of the multiple band assignable to $\nu_{(C=N)}$. In free aziprotryn, the three azomethine (ring) functions do not have identical environments due to the presence of S-CH_3, N_3 and $NHCH(CH_3)_2$ groups. This could be the reason for the appearance of a triplet like structure corresponding to $\nu_{(C=N)}$ in the free aziprotryn spectrum.

The expected bands for $\nu_{(N=N)}$ and $\delta_{(NH)}$ are present in the same region. In the spectra of the complexes, the $\nu_{(C=N)}$ shows a distinct division into at least three well separated components in the 1600-1650 cm^{-1} range. This provides evidence to suggest that one of the azomethine nitrogens is involved in coordination.

The spectra of the complexes show evidence for M-N vibrations that appear as bands of low intensity in the range 430-560 cm^{-1} [20]. For the Zn(II) complex, the presence of coordinated water is indicated by non-ligand bands at 800-910 cm^{-1}, which are characteristics of rocking and wagging modes [21].

NMR spectra. The inferences drawn on the basis of IR spectral data support bonding of AZP to metal ions through azide nitrogen and one of the adjacent ring nitrogens (positions -3 or -5 in Table 1). Attempts have been made to obtain some complementary information from NMR spectra. The Zn^{2+} and Cu^{2+} complexes have sufficient solubilities in D_2O to obtain useful NMR spectra (Table 4). Comparison of the spectra shows that the thiomethyl protons ($-SCH_3$) which appear as a singlet seem to be in similar environments in both complexes, while the signals due to isopropyl groups, i.e., -CH and $-CH_3$ protons appearing as a septet and as a doublet with integral strengths 1:6, respectively, are different in the Cu^{2+} to the Zn^{2+} complexes. Resonance due to the methyl proton moves upfield while that due to -CH moves downfield in the spectrum of the Zn^{2+} complex compared with that in the Cu^{2+} complex. These differences seem to be consequences of steric factors caused by the presence of different metal ions in the vicinity of the secondary amine function at position -6. In view of this, chelation of the azide nitrogen and N-5 nitrogen seem to be more preferable than azide and the N-3 nitrogen (Table 1).

Table 4. NMR spectra of complex in D_2O (δ values in ppm).

Complex	-CH	$-SCH_3$	$-CH_3$
Cu^{2+} complex	3.76 - 3.86 (septet)	2.56 (singlet)	2.67 (doublet)
Zn^{2+} complex	4.1 - 4.2 (broad multiplet)	2.54 (singlet)	1.25 - 1.27 (doublet)

Electronic spectra. Assignments for various transitions are based on the supporting literature from standard references [22, 23]. Aziprotryn is a white, crystalline compound and has no absorption characteristics in the visible region. The spectra of metal complexes show characteristic bands in the visible region that can be assigned to various d-d transitions in support of the proposed stereochemistry of the complexes (Table 5).

Table 5. Electronic spectral data of the complexes of aziprotryn.

Compound	Electronic spectra bands (ν_{max}, cm^{-1})
Co(II) complex	18760, 15150, 14500, 13890
Ni(II) complex	14390
Cu(II) complex	14490, 12600

The blue Co(II) complex shows an intense absorption band at 18760 cm^{-1} with multiple structures at 15150 cm^{-1}, 14490 cm^{-1} and 13890 cm^{-1}. Such a band pattern is assignable to a tetrahedral geometry [24]. The intense absorption band at 18760 cm^{-1} is assignable to the transition $^4A_2 \rightarrow {}^4T_1$ (P) of tetrahedral geometry while the multiple structures are due to spin forbidden transitions from the $^4A_2$ state to several doublet states which have notable intensity due to spin-orbit coupling. The other two expected transitions in the near infrared region $^4A_2 \rightarrow {}^4T_2$, and $^4A_2 \rightarrow {}^4T_1$ (F) were not observed due to instrument limitations.

The pale green Ni(II) complex shows a high intensity broad band located at 14390 cm^{-1} that can be assigned to $^3T_1$ (F) → $^3T_1$ (P) in tetrahedral geometry. Two other bands corresponding to $^3T_1$ (F) → $^3T_2$ (F) and $^3T_1$ (F) → $^3A_2$ (F) transitions, which generally are observed in the near infrared region, could not be seen due to instrument limitation.

The spectrum of the Cu(II) complex is typical with a strong broad band in the region of 14490 to 12600 cm^{-1} expected for square planar geometry shifting towards an elongated octahedron due to two solvent molecules located at larger distance in solutions. This is a general observation with respect to several square planar complexes of Cu(II), which transform into distorted octahedral geometries in solution [25, 26]. In fact, in well resolved spectra such as those of Cu(II) complexes, three band structures are seen whose frequencies shift to lower frequency with increasing solvent interaction along the z-axis. The broad bands observed in the present case can be assigned to a combination of the expected transitions $^2B_1 \rightarrow {}^2A_2$, $^2B_1 \rightarrow {}^2B_2$, and $^2B_1 \rightarrow {}^2E$. A square planar geometry is proposed for the solid Cu(II) complex. Zn (II) being a d^{10} system, is not expected to show any d-d transitions. Based on its composition, a tetrahedral geometry is proposed for the complex $[Zn(AZP)(H_2O)Cl]Cl$.

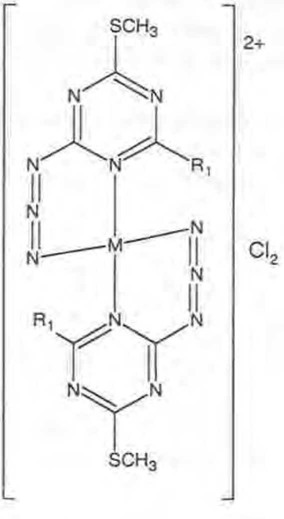


Figure 4. Metal complexes of aziprotryn. R_1 = $NHCH(CH_3)_2$ and M represents Co(II), Ni(II) and Cu(II) cations.

CONCLUSION

On the basis of analytical, conductance and spectral data, it is concluded that aziprotryn behaves as a neutral bidentate NN donor towards Co(II), Ni(II), Cu(II) and Zn (II) by involving the terminal nitrogen of the azido group and one adjacent ring nitrogen in coordination (Figure 4). Tetrahedral geometry for Co(II), Ni(II) and Zn(II) complexes and square planar geometry for

Cu(II) are proposed. Preliminary studies of the anti-bacterial activities of the metal complexes of AZP and other derivatives against *Escherichia coli* and *Staphylococus aureus* showed promising results and further studies in this line are in progress.

ACKNOWLEDGEMENT

The authors are grateful to the Chairman, Department of Chemistry, Addis Ababa University for the laboratory facilities and instrumentation. The Department of Analytical Chemistry of Lund University is acknowledged for materials support. This work was made possible by financial support received from the Swedish International Development Agency (SIDA).

REFERENCES

1. Raju, V.J.T.; Ranbaore, V.; Atre, V.; Ganorker, M.C. *J. Indian Chem. Soc.* **1982**, 59, 199.
2. Ramarao, N.; Rao, P.V.; Raju, V.J.T.; Ganorker, M.C. *Indian J. Chem.* **1985**, 24A, 877.
3. Syamala, B.S.; Lakshmi, P.V.A.; Raju, V.J.T.; Reedy, P.U.M. *Biometals* **1985**, 5, 23.
4. Rani, D.S.; Lakshmi, P.V.A.; Raju, V.J.T. *Transition Met. Chem.* **1994**, 19, 75.
5. Pacakova, V.; Stulik, K.; Jiskra, J. *J. Chromatogr. A* **1996**, 754, 17.
6. Esser, H.O.; Dupius, G.; Vogel, C.; Marco, G. J. in *Herbicides: Chemistry, Degradation and Mode of Action*, 2nd ed., Kearney, P.C.; Kaufman, D.D. (Eds.); Marcel Dekker: New York; **1976**; Vol. II, pp 129-208.
7. Smolin, E.M.; Rapoport, L. *Chemistry of Heterocyclic Compounds*, Vol. 13, Wiley-Interscience: New York; **1959**, pp 293, 301, 285, 351.
8. Knusli, E.; Schappi, W.; Berrer, D. (to J.R. Giegy S.A.), *Swiss Pat.* **1961**, 393, 344; *U.S. Pat.* **1961**, 13, 145, 208.
9. Knusli, E. (to Geigy S. A.), *Swiss Pat.* **1960**, 389, 633.
10. Schulz, H.; Schwarze, W. (to Degussa), *Ger. Pat.* **1962**, 172, 684.
11. Pusino, A.; Gessa, C.; Kozlowski, H. *Pestic. Sci.* **1988**, 24, 1.
12. Kelvin, H.; Atwood, D.A. *Inorg. Chem.* **1998**, 37, 224.
13. Soma, R.; Frank, R.S.; John, N.B.; Quain, H.; Veron, J.R.; Sanat, K.M. *Inorg. Chim. Acta* **1994**, 227, 175.
14. Godwin, H.A.; Sylva, R.N.; Vagg, R.S.; Watton, E.C. *Aust. J. Chem.* **1969**, 22, 1605.
15. Vogel, A.I. *A Textbook of Quantitative Organic Analysis*, 4th ed., Longman: London; **1978**, pp 138-172.
16. Vogel, A.I. *A Textbook of Quantitative Inorganic Analysis*, 4th ed., Longman: London; **1978**, pp. 433-435.
17. Arora, C.L.; Sekhon, G.S. *Asian J. Chim.* **1993**, 5, 475.
18. Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed., Wiley-Interscience: New York; **1986**, p. 291.
19. Cotton, F.A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 3rd ed., Wiley Eastern: New Delhi; **1972**, p 353.
20. Beck, W.; Fehlhammer, W.P.; Pollman, P.; Schuierer, E.; Felds, K. *Chem. Ber.* **1967**, 100, 2335.
21. Ref. 19, p 229.
22. Lever, A.B.P. *Inorganic Electronic Spectroscopy*, 2nd ed., Elsevier: Amsterdam; **1984**.
23. Figgis, B.N. *Ligand Fields*, Wiley Eastern: New Delhi; **1986**.

24. Ref. 20, p 881.
25. Belford, R.L. *J. Chem. Phys.* **1975**, 26, 1165.
26. Huhey, J.E. *Inorganic Chemistry*, 3rd ed., Harper and Row: New York; **1983**, pp 368-412.