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STUDIES ON METAL COMPLEXES OF 3–N METHYLANILINOMETHYL–5–o–CHLOROPHENYL–1,3,4–OXADIAZOLE–2–THIONE

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ABSTRACT

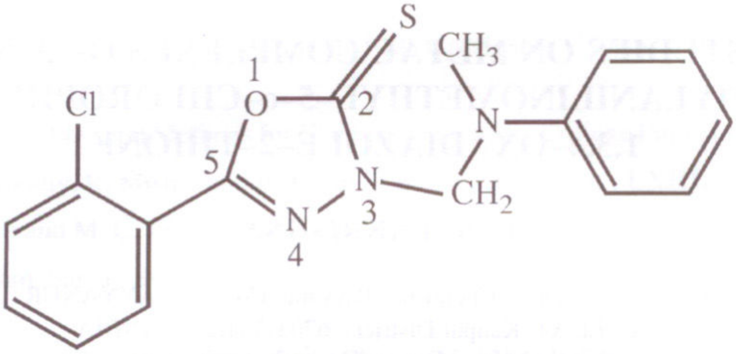
A new series of complexes of Fe (III), Co (II), Ni (II), Cu (I), Zn (II), Cd (II), Hg (II), Pb (II) and Ag (I) with 3–N–methylanilinomethyl–5–o–chlorophenyl–1,3,4–oxadiazole–2–thione have been synthesized. Characterization of these complexes were carried out mainly by using elemental analyses, magnetic susceptibility measurements, thermogravimetric and UV–Vis, IR, ^{1}H NMR spectral studies. Though the ligand is potentially polydentate, in the complexes studied, it behaves as a monodentate ligand – bonding either through N(4) of the oxadiazole moiety or through S of the thione group – or as a bidentate bridging ligand. Tetrahedral structures for Fe (III), Co (II), Ni (II), Cu (I), Zn (II), Hg (II) and Pb (II) complexes, tetrahedral polymeric structure for Cd (II) and linear structure for Ag(I) complex have been proposed. Antibacterial studies of the ligand and Fe (III), Co (II), Ni (II), Cu (I) and Zn (II) complexes were also carried out.

Key words : Antibacterial studies, Mannich base, Metal complexes, Oxadiazoles.

INTRODUCTION

Metal complexes of Mannich bases have been studied extensively in recent years due to the selectivity and sensitivity of ligands towards various metal ions. Substituted 1,3,4–oxadiazole–2–thione and their metal complexes have gained attention due to their wide range of biological activities[1–5]. Some of the 1,3,4–oxadiazole derivatives are found to be acting as corrosion inhibitors in mild steel in acid medium[6]. In the literature, there is only one report on the metal complexes of oxadiazole Mannich bases and their fungicidal activity[7]. Therefore, it was thought worthwhile to synthesize metal complexes of some substituted oxadiazole thione Mannich bases and to investigate their bonding characteristics.

The present communication deals with the synthesis, characterization and biological activities of some metal complexes of 3–N–methylanilinomethyl–5–o–chlorophenyl–1,3,4–oxadiazole–2–thione (L).



(L)

Figure 1

EXPERIMENTAL

All the chemicals used were of AnalaR or Chemically pure grade. Metal salts (chlorides, nitrates and sulphates) and the reagents used were of Excelar or SQ quality of Qualigens Fine Chemicals, India. The solvents used were purified by standard methods. Spectroscopic grade solvents were used for spectral studies. The parent oxadiazole, 5–o–chlorophenyl–1,3,4–oxadiazole–2–thione, was prepared by the literature method[8]. The Mannich base was then prepared by stirring a solution of the thione (0.01 mol), formaldehyde (0.0015 mol) and N–methylaniline (0.01 mol) in 40 mL ethanol for one hour and keeping it overnight. The solid compound formed was separated and washed several times with ethanol. The product was recrystallised from ethanol and then dried (M.P. = 65°C, Yield 70%).

The Fe (III), Co (II), Ni (II), Cd (II), Cu (I) and Hg (II) complexes were prepared by adding a hot ethanolic solution of respective metal chlorides to a refluxing solution of the ligand in ethanol, maintaining the stoichiometric metal–ligand ratios. The solid complexes separated out almost immediately, except in Fe (III) and Ni (II), were filtered off, washed repeatedly with hot ethanol and dried. In the case of Fe (III) and Ni (II), complexes separated out only after raising the pH of the medium by adding sodium acetate (~1.50 g) and maintaining the reaction mixture at the refluxing temperature for half an hour. For preparing the Zn (II) complex, a hot aqueous solution of Zn (II) sulphate was used, while for Pb (II) and Ag (I) complexes, the starting materials were aqueous solution of respective metal nitrates.

C, H and N contents of the ligand and the complexes were determined micro analytically. Metal, sulphur and chlorine contents were determined by standard procedures[9]. The molar conductance were measured using a Systronics microprocessor–based conductivity meter (model–306, Systronics, India). Magnetic susceptibilities were determined with a Gouy assembly at room temperature, using $Hg[Co(NCS)_4]$ as the calibrant. Electronic spectra were recorded on a Perkin – Elmer Lambda 15 UV/VIS spectrophotometer in DMF solution. IR spectra were recorded (KBr) on a Perkin – Elmer FT1000 spectrophotometer and ^1H NMR (DMSO – d_6 + $CDCl_3$) on a Perkin–Elmer R–32 spectrometer at 90 MHz. Thermograms were recorded on a Perkin – Elmer 7 Series Thermal Analysis System. The complexes were heated in air at the rate of 10°C rise of temperature per minute.

RESULTS AND DISCUSSION

The ligand was characterized by Mass, NMR and IR spectral data. The mass spectrum of the ligand showed molecular ion peak at m/z, 331 consistent with the molecular formula $C_{16}H_{14}N_3OClS$. The ^1H NMR of the ligand showed signals at δ 3.30 (s, 3H, > NCH_3), δ 5.74 (s, 2H, –N–CH_2–N–) and δ 7.00 – 7.91 (m, 9H, Ar–H). IR spectrum of the ligand shows a strong band at 1595 cm^{-1} and has been assigned to ν(C=N) of oxadiazole ring. ν(C=S) of the ligand was assigned at 1186 cm^{-1}. In the ligand, ν(C–O–C) of oxadiazole ring appears at 1421 cm^{-1} [10].

Table 1. Analytical data and molar conductance of the complexes

Complex	Analysis, % found (Calcd.)						Molar conductance ($S\ cm^2mol^{-1}$)
	Metal	C	H	N	S	Cl	
Ligand	–	57.89 (57.93)	4.20 (4.22)	12.67 (12.67)	9.63 (9.65)	10.69 (10.70)	–
$[CoL_2Cl_2]$	7.47 (7.43)	48.40 (48.44)	3.50 (3.56)	10.48 (10.60)	7.96 (8.07)	17.54 (17.89)	10.93
$[NiL_2Cl_2]2H_2O$	7.00 (7.08)	46.20 (46.35)	4.00 (3.89)	10.12 (10.14)	7.64 (7.72)	17.10 (17.12)	31.12
$[CuL.Cl(H_2O)_2]$	13.48 (13.62)	41.10 (41.16)	3.81 (3.89)	8.97 (9.00)	6.67 (6.86)	15.33 (15.20)	9.19
$[AgL(NO_3)]$	21.40 (21.52)	38.25 (38.30)	2.79 (2.81)	11.15 (11.17)	6.60 (6.38)	6.98 (7.07)	9.81
$[ZnL_2SO_4]$	7.81 (7.93)	46.55 (46.59)	3.40 (3.42)	10.10 (10.19)	11.89 (11.65)	8.86 (8.60)	14.34
$[CdLCl_2]$	21.85 (21.83)	37.21 (37.30)	2.70 (2.74)	8.15 (8.16)	6.20 (6.22)	20.60 (20.60)	23.64
$[HgL_2Cl_2]$	21.48 (21.46)	41.00 (41.10)	3.00 (3.02)	8.90 (8.99)	6.64 (6.85)	15.09 (15.18)	29.00
$[PbL_2(NO_3)_2]$	20.50 (20.84)	38.60 (38.63)	2.80 (2.84)	11.21 (11.27)	6.61 (6.44)	7.10 (7.13)	23.46
$[FeL_2Cl_2]Cl.5H_2O$	6.14 (6.10)	41.90 (41.96)	4.15 (4.19)	9.10 (9.18)	6.74 (6.99)	19.43 (19.37)	83.62

The analytical data support the proposed formulations for the complexes. (Table 1). The non–electrolytic nature of the complexes, except the Fe (III) complex, is ascertained by low conductivity values which are much lower than those reported for 1 : 1 electrolytes in the same solvent. For the Fe (III) complex, the conductance value (83.62 S cm^2mol^{-1}) is an indication of its 1 : 1 electrolytic nature[11].

Magnetic properties

The cobalt complex, $[CoL_2Cl_2]$ shows a magnetic moment value of 4.54 BM. The higher than the spin only value for the magnetic moment is to be expected for Co (II) complex in tetrahedral environment[12]. The copper complex, $[CuLCl(H_2O)_2]$ is found to be diamagnetic. That is complete reduction of Cu (II) → Cu (I) takes place during complex formation. It was observed during the synthesis of this complex that excess of ligand is required than the stoichiometric ratio and this proves that a part of the ligand which is in excess may reduce Cu (II) → Cu (I) and the cation thus formed complex with remaining ligand. This was confirmed by the synthesis of the same complex by prior reduction of Cu (II) salt by sulphur dioxide. For $[NiL_2Cl_2]2H_2O$, the measured magnetic moment value is 3.75 BM which is higher than spin–only value. Hence, orbital contribution may be expected from tetrahedral $^3T_1$ ground state. For Fe (III) complex, the measured magnetic moment value 5.92 BM is close to spin–only value for a d^5 system. As expected Zn (II), Cd (II), Hg (II), Pb (II) and Ag (I) complexes are diamagnetic.

Electronic spectra

The electronic spectrum of the ligand in DMF showed an absorption maximum at 32,150 cm^{-1} ($\varepsilon = 1901\ mol^{-1}\ cm^{-1}$) due to $n \rightarrow \pi^*$ transition and this remained almost unchanged in the complexes also. The electronic spectrum of Co (II) complex is dominated by a high energy intense band at 16,900–17,800 cm^{-1}. This transition corresponds to $^4A_2 \rightarrow {}^4T_1(P) = 12Dq + 15B$ (ν_3) and is responsible for the blue colour of the synthesized complex[13]. For a tetrahedral Co (II) complex, two more transitions are theoretically possible,

$$^4A_2 \longrightarrow {}^4T_2 = 10Dq \quad ...\nu_1$$
$$^4A_2 \longrightarrow {}^4T_1 = 18Dq \quad ...\nu_2$$

Bands due to these transitions fall in IR and near IR regions and hence, are not observed. By using the single transition energy, it is not possible to calculate crystal field parameters for Co (II) complex. However, the measured magnetic moment of Co (II) complex can be related to 10 Dq, by the relationship,

$$\mu_{eff} = \mu_s (1 - 4)\ \lambda/10Dq)$$

Substituting μ_{eff}= 4.54 BM, μ_s= 3.87 BM, λ= –180 cm^{-1}, 10Dq value of 4160 cm^{-1} was estimated for Co (II) complex. This value falls in the range expected for tetrahedral Co (II) complexes and hence, the assignment is apparently correct[14].

For Ni (II) complex, there is an intense band at 16,400 cm^{-1}. It is documented in the literature[15] that tetrahedral Ni (II) complex show high intenisty bands in the region 16,500 – 14,000 cm^{-1} and are attributed to $^3T_1(F) \rightarrow {}^3T_1(P)$ transition (ν_3). A near IR band with appreciable intensity is also recorded at 9300 cm^{-1}. This is assigned to $^3T_1$ (F) $\rightarrow$ $^3A_2$ (F) – ν_2 transition. The ligand field parameters ν_3/ν_2 = 1.76, B = 887 cm^{-1} and β = 0.85 are quite consistent with tetrahedral geometry.

In the case of Fe (III) complex, a number of weak spin forbidden bands are observed in the range 18,800 – 20,500 cm^{-1}. These transitions are characteristic of tetrahedral Fe (III) complex[12] and hence, tetrahedral geometry is proposed for the Fe (III) complex.

Thermal analysis

Thermogravimetric study of the Ni (II) and Fe (III) complexes have been carried out. In the case of Ni (II) complex, a weight loss of 4.10% (theoretical 4.35%) in the temperature below 150 °C[15,16] indicates the presence of two molecules of water of crystallization. This was followed by a single step mass–loss in the temperature range of 200–500 °C, corresponding to all organic matter. The mass of the solid residue obtained was 9.00% of the initial mass, which corresponds to NiO (theoretical = 9.01%).

In the case of the Fe (III) complex, up to 150°C, the thermogram showed 9.50% weight loss (theoretical 9.83%) and this corresponds to five molecules of water of crystallization[15,16]. The complex showed maximum mass loss in the temperature range 200 – 500°C, corresponding to the loss of all organic matter. Final mass of residue in this case corresponds to Fe_2O_3 (17.00%, theoretical = 17.45%).

^{1}H NMR

In the complexes, ^{1}H NMR signals, especially the singlet due to –N–CH_2–N–(compared to ligand spectrum) shifts downfield, indicating the involvement of oxadiazole moiety in complexation.

IR Spectra

In the complexes of Co (II), Ni (II), Cu (I), Fe (III), Zn (II) and Pb (II), the shift in band positions, compared to those presents in the ligand molecule, are similar, thereby indicating the presence of similar type of bonding. The ν(C–O–C) of oxadiazole ring shift downward by 10–20 cm^{-1} in complexes, indicating the involvement of oxadiazole ring in complexation[17]. The ν(C=N) of these complexes shift downward by about 20 cm^{-1}, suggesting the bonding to metal through N–atom at 4–position. Though oxadiazole ring has two nitrogen atoms, at position 3 and 4, it is almost likely that the one at 4–position is involved in bonding by taking into consideration of the steric factors. In the case of Hg (II) and Ag (I) complexes, the ν(C=N) almost remains unaffected from its position in the ligand. But the ν(C=S) shows a significant downward shift (~15 cm^{-1}), thereby indicating that the bonding might have taken through the thione S atom[10].

But in the Cd (II) complex, shifts in both ν(C=N) and ν(C=S) were observed. This means that in this case, both the N–atom and S–atom are involved, with the oxadiazole moiety acting as either a bidentate chelating ligand or a bidentate bridging ligand. The most likely mode of bonding could be as a bidentate bridging ligand.

A broad band in the range 3400–3455 cm^{-1} in Ni (II), Fe (III) and Cu (I) complexes are due to ν(OH)[18]. This gives evidence for water of crystallization in Ni (II) and Fe (III) complexes. In the Cu (I) complex, a band at 860 cm^{-1} supports the existence of coordinated water molecule[19]. In Ag (I) and Pb (II) complexes, bands at 1358 cm^{-1} ($\nu_{as}(NO_2)$, 1310 cm^{-1} vs(NO_2) and 1030 cm^{-1} ν(NO) are due to monodentate nitrate group[20,21]. Bands at 1105 cm^{-1} and 1032 cm^{-1} are due to chelating sulphato group in Zn (II) complex[22]. The low frequency bands in the 455–465, 435–445 and 370–380 cm^{-1} region are tentatively assigned to ν(M–N), ν(M–O) and ν(M–S), respectively.

Antibacterial activity

Antibacterial activity shown by the ligand and the complexes are given in Table 2. Concentration of compound is 5 mg/10 mL in DMF. Organisms studied are Bacillus subtilis (B.Sub), Staphylococcus aureus (S.au), Escherichia coli (E. coli) and Pseudomonas aeruginosa (Ps.au).

Table 2. Results of antibacterial activity screening[a]

Compound	Diameter of zone of inhibition (mm)			
	B. sub[b]	*S. au*	*E. coli*	*Ps. au*
LIGAND	12	18	29	12
$[FeL_2Cl_2]Cl.5H_2O$	18	21	49	24
$[CoL_2Cl_2]$	12	20	28	12
$[NiL_2Cl_2]2H_2O$	14	18	28	14
$[CuLCl(H_2O)_2]$	12	19	29	12
$[ZnL_2SO_4]$	14	20	28	12

a – Concentration of compound is 5 mg/10 mL in DMF.

b – *B. sub : Bacillus subtilis, S.au : Staphylococcus aureus, E. coli : Escherichia coli, Ps.au : Psuedomona aeruginosa.*

Our results of investigation on the antibacterial activity revealed that the Fe (III) complex exhibits much higher activity towards all the organisms studied than the ligand. The results indicated that the Fe (III) complex showed enhanced antibacterial activity towards B.sub, E–coli and Ps. au. The other metal complexes did not show any significant increase in activity as compared to the ligand.

CONCLUSIONS

The ligand molecule, acts a monodentate ligand in all the studied cases except in Cd (II) complex, bonding either through N(4) or through S–depending up on the nature of the metal ions. In the Cd (II) complex, it appears to act as a bidentate bridging ligand. Tetrahedral structures for Fe (III), Co (II), Ni (II), Zn (II), Cu (I), Hg (II) and Pb (II) complexes, tetrahedral polymeric structure for Cd (II) and linear structure for Ag (I) complex have been tentatively proposed.

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