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A Few Bivalent Metal Complexes with 2-Acetyl Thiophene Thiosemicarbazone

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Metal complexes of the type [MLX_2] [where M = Co(II), Ni(II) and Cu(II), L = 2-acetyl thiophene thiosemicarbazone (ATTS), ($X = Cl^-$, Br^-, NO_3^- and ClO_4^-) have been synthesised in neutral medium and characterised. The IR spectrum of the complexes suggest the coordination of the metal ion to the ligand through azomethine nitrogen, thiol-sulphur and sulphur atom of cyclic thioether. The ligand acts as a bi-bidentate chelating agent resulting in polymeric structure of the complexes. The octahedral geometry of the complexes has been proposed on the basis of elemental analysis, magnetic susceptibility measurements and spectral studies. Fungicidal screening of the complexes shows them active against *Aspergillus niger, Fusarium oxysporium* and *Helminthosporium oryzae.*

INTRODUCTION

Metal complexes with ligands containing sulphur and nitrogen donor atoms have been found useful as potential drugs[1–4]. Considering the importance of such complexes, in the present paper we report the synthesis and characterization of Co^{2+}, Ni^{2+} and Cu^{2+} complexes with 2-acetyl thiophene thiosemicarbazone (ATTS) and their fungicidal screening.

EXPERIMENTAL

All the chemicals and solvents used were of analytical grade and the solvents were used without further purification. The ligand 2-acetyl thiophene thiosemicarbazone was prepared by adopting literature method[5] and analysed[6].

Preparation of complexes: The ligand and the appropriate metal salt in the molar ratio 1 : 1 was dissolved separately in ethanol and mixed in a conical flask. The contents were refluxed on a water bath for 2 to 3 h, till the solids were separated, after which the contents were kept on a water bath for about 30 minutes. It was then cooled, filtered, washed with ethanol followed by ether. The solids were dried and then analysed[7]. The colour and analytical data are recorded in Table-1.

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TABLE-1
ANALYTICAL DATA OF THE LIGAND AND ITS METAL COMPLEXES

Complexes	Colour	% Found (calcd)			μ_{eff}* (B.M.)
		M	N	S	
ATTS	White	—	25.35	18.75	
			(25.65)	(19.17)	
$[Cu(ATTS)Cl_2]$	Green	19.80	13.05	9.99	1.72
		(20.00)	(13.22)	(10.08)	
$[Cu(ATTS)Br_2]$	Green	15.05	9.99	7.69	1.75
		(15.60)	(10.33)	(7.87)	
$[Cu(ATTS)(NO_3)_2]$	Marine grey	17.00	18.59	8.45	1.85
		(17.14)	(18.89)	(8.64)	
$[Cu(ATTS)(ClO_4)_2]$	Leaf brown	14.00	9.30	7.05	1.01
		(14.25)	(9.42)	(7.18)	
$[Co(ATTS)Cl_2]$	Purple	18.69	13.39	10.19	4.91
		(18.62)	(13.42)	(10.23)	
$[Co(ATTS)Br_2]$	Purple	14.40	10.35	7.86	5.15
		(14.66)	(10.45)	(7.96)	
$[Co(ATTS)(NO_3)_2]$	Light grey	15.95	19.05	8.55	5.30
		(16.10)	(19.13)	(8.74)	
$[Co(ATTS)(ClO_4)_2]$	Minosa	13.21	9.25	7.16	4.81
		(13.36)	(9.52)	(7.25)	
$[Ni(ATTS)Cl_2]$	Light blue	18.56	13.20	10.08	2.82
		(18.77)	(13.43)	(10.23)	
$[Ni(ATTS)Br_2]$	Light green	14.45	10.25	7.79	2.91
		(14.61)	(10.46)	(7.96)	
$[Ni(ATTS)(NO_3)_2]$	Green	15.90	19.00	8.63	3.10
		(16.05)	(19.14)	(8.75)	
$[Ni(ATTS)(ClO_4)_2]$	Light green	13.00	9.39	7.05	3.12
		(13.31)	(9.53)	(7.26)	

ATTS = 2-acetyl thiophene thiosemicarbazone; *At room temp.

Carbon, hydrogen and nitrogen were estimated by semimicro combustion method by MLN Micro Elementary CHN analyser. Conductance was measured in 10^{-3} M DMF solution of the freshly prepared complexes using Toshniwal conductivity bridge. The IR spectra of the ligand and the complexes were recorded in KBr pellets with Perkin-Elmer Model 398. The magnetic susceptibility values of the metal complexes were measured by Gouy method using $Hg[Co(CNS)_4]$ as a calibrant at room temperature. The absorption spectra of the ligand and complexes were recorded by Carl-Zeiss (ZN) Zena model spectrophotometer and Backmann-35 double beam spectrophotometer using appropriate solvents for soluble complexes and mull for insoluble complexes.

RESULTS AND DISCUSSION

All the complexes are amorphous, high melting and insoluble in water as well as in common organic solvents. However, the complexes are slightly soluble in

DMF and DMSO. Low conductivity values indicate that complexes are non-electrolytes. The analytical data indicate 1 : 1 metal-ligand stoichiometry for all complexes.

TABLE-2
ELECTRONIC TRANSITIONS AND CRYSTAL FIELD PARAMETERS OF COMPLEXES

Complexes	Electronic spectral bands (cm^{-1})	Assignments	Ligand field parameters in cm^{-1}					
			D	B	C	F_2	F_4	β
ATTS	33,330	$\pi \rightarrow \pi^*$	—	—	—	—	—	—
	37,040	$\pi \rightarrow \pi^*$						
$[Co(ATTS)Cl_2]$	16,950	$^4T_{1g} \rightarrow {}^4A_{2g}(F)(\nu_2)$	9570	957	4430	1590	126.6	0.98
	21,050	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)(\nu_3)$						
	29,050	C.T.						
$[Co(ATTS)Br_2]$	17,240	$^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)(\nu_2)$	9580	958	4437	1592	126.8	0.98
	21,280	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)(\nu_3)$						
	29,410	C.T.						
$[Co(ATTS)(NO_3)_2]$	16,670	$^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)(\nu_2)$	8997	947	4387	1574	125.3	0.97
	20,830	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)(\nu_3)$						
	29410	C.T.						
$[Co(ATTS)ClO_4)_2]$	16,390	$^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)(\nu_2)$	8880	888	4115	1476	117.6	0.92
	20,000	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)(\nu_3)$						
	28,570	C.T.						
$[Ni(ATTS)Cl_2]$	15,270	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)(\nu_2)$	9850	896	4218	1499	120.5	0.96
	25,970	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)(\nu_3)$						
$[Ni(ATTS)Br_2]$	15,150	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)(\nu_2)$	9963	940	4427	1572	126.2	0.90
	26,320	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)(\nu_3)$						
$[Ni(ATTS)(NO_3)_2]$	15,040	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)(\nu_2)$	9725	884.1	4163	1479	119.0	0.85
	25,640	$^3A_{2g} \rightarrow {}^3T_{1g}(P)(\nu_3)$						
$[Ni(ATTS)(ClO_4)_2]$	15,380	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)(\nu_2)$	10160	9237	4350	1545.2	124.3	0.89
	26,320	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)(\nu_3)$						
$[Cu(ATTS)Cl_2]$	16,500	$^2E_g \rightarrow {}^2T_{2g}$						
	27,800	C.T.						
$[Cu(ATTS)Br_2]$	16,000	$^2E_g \rightarrow {}^2T_{2g}$						
	28,570	C.T.						
$[Cu(ATTS)NO_3)_2]$	15,800	$^2E_g \rightarrow {}^2T_{2g}$						
	27,030	C.T.						
$[Cu(ATTS)(ClO_4)_2]$	15,800	$^2E_g \rightarrow {}^2T_{2g}$						
	27,700	C.T.						

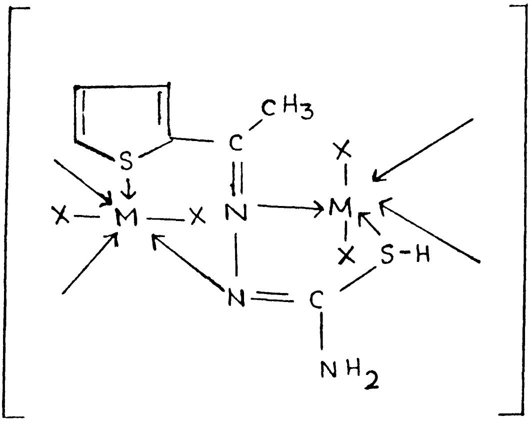
The ligand 2-acetyl thiophene thiosemicarbazone (ATTS) is believed to exist in solution as a tautomeric equilibrium between the thione and thiol form. The ligand ATTS exhibits a strong band at 3400 cm^{-1} which may be due to the asymmetric strectching vibration of the terminal NH_2 group. It further exhibits three IR bands of strong intensity at 3280 cm^{-1}, 3240 cm^{-1} and 3120 cm^{-1} which may be due to ν_{asym}(N—H) of terminal NH_2 group and ν_{sym}(N—H) of NH_2 and NH group respectively[9]. It has been reported that the first two bands are due to the terminal NH_2 group and the third one is due to the secondary NH group[10]. The band at 3400 cm^{-1} is not affected during chelation, which indicates that terminal NH_2 does not take part in coordination. All other bands display blue shift with lower intensity. These observations indicate the participation of the hydrazine nitrogens in complex formation. The absence of any bands between 2650–2450 cm^{-1} in the ligand spectrum indicating that there is no S—H group in the free ligand in solid state[9, 11].

The band of strong intensity at *ca.* 1620 cm^{-1} appearing in the spectrum of the ligand as well as in the metal complexes can be assigned to deformation vibration of terminal NH_2 group which does not take part in bonding. The band of strong intensity at 1592 cm^{-1} with a shoulder at 1605 cm^{-1} in the ligand spectrum may be assigned to azomethine stretch[12, 13]. In all the complexes it undergoes red-shift by 15–20 cm^{-1} indicating the participation of azomethine nitrogen in coordination. The IR spectra of ATTS show characteristic bands at 1550 cm^{-1} ν(N—C—N—), 1430 cm^{-1} ν(C=S) and 1310 cm^{-1} ν(NH—C=S) arising from the thione form of the ligand in solid state. This is further supported by the presence of C=S band at 760 cm^{-1}. In the IR spectrum of the complexes bands due to ν(N—C—N), ν(C=S) and ν(NH—C=S) disappear and new bands for azomethine ν(C=N—N=C)[14, 15] and ν(C—S) appear at 1585 cm^{-1} and 720 cm^{-1} respectively[16], indicating the coordination of metal ion through azomethine nitrogen and thiol sulphur. Further, a band at 830 cm^{-1} assigned to ν(C—S) of thiazole ring[17] is located in the spectrum of ATTS, but this band is observed at *ca.* 805 cm^{-1} in the spectrum of the complexes suggesting participation of the thiazole sulphur in coordination. In the lower frequency region new bands at 480–470 cm^{-1} and 425–420 cm^{-1} are assigned to ν(M—N)[18] and ν(M—S)[19] respectively.

Coordination of NO_3^- group to the metal ion is indicated by the presence of a bond at 1020 cm^{-1}. Three additional bands of the perchlorate complexes at *ca.* 1240 cm^{-1}, 1115 cm^{-1} and 970 cm^{-1} can be attributed to ν_8, ν_6 and ν_1 vibration of the coordinated ClO_4^- group respectively.

These important features of the spectra of the ligand and metal complexes provide a consistent picture and lead us to suggest the most probable structure of the complexes as shown in Fig. 1.

The copper(II) complexes exhibit the normal magnetic moments 1.72–2.10 B.M. The electronic spectra of the complexes show asymmetric bands around 15,500 cm^{-1} with a weak shoulder at 16,500 cm^{-1} (Table-2) which can be assigned to $^2E_g \rightarrow {}^2T_{2g}$ transitions in an approximately octahedral ligand field. Charge transfer bands are also observed for the complexes around 27,780 cm^{-1}. The



nature of the spectral bands and the paramagnetic behaviour of the Cu(II) complexes indicate a distorted octahedral configuration around copper ion.[20]

The observed magnetic moments of the Co(II) complexes are in the range 4.80–5.20 B.M. which are in accordance with the values expected for octahedral Co(II) complexes. The electronic spectra show a band system in the region 17,000–16,000 cm^{-1} and 21,000–20,000 cm^{-1} respectively which possess the characteristic features of known octahedral Co(II) complexes[21] (Table–2). The spectral transitions of the octahedral components of Co(II) complex assigned to ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)(\nu_2)$ and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)(\nu_3)$ respectively. Besides these charge transfer bands are also observed around 29,000 cm^{-1}.

The visible absorption spectra of Ni(II) complexes show broad asymmetric bands at *ca.* 15,000 and 21,000 cm^{-1} followed by a strong band at 26,000 cm^{-1} (Table–2). In an octahedral approximation the first two bands can be assigned to ${}^3A_{2g}(F) \rightarrow {}^3A_{1g}(F)$ amd ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}$ transitions. The high frequency bands correspond to ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}$ transitions. The magnetic moments of the Ni(II) complexes lie in the range 2.80–3.20 B.M. which is observed for most octahedral Ni(II) complexes[22].

Fungicidal Activity

The antifungal activity of the ligands and its metal complexes was tested against *Helminthosporium oryzae, Fusarium oxysporium* and *Aspergillus niger* by the method of Horsfall[23]. The evaluation was carried out at 1000 ppm in dioxane. The amount of germination or growth inhibition was determined after inoculation of the fungal spores onto Czapexdox agar-agar medium containing the test sample. The whole system was kept in an incubator for five days at 30 ± 1°C. The percentage inhibition was calculated as follows:

$$\% \text{ of inhibition} = \frac{100(P - Q)}{P}$$

where P = area of colony growth without test sample. Q = area of colony growth with test sample. When metal salts such as copper chloride, cobalt chloride are used as fungicides they cause damage to the level[24], whereas the coordination compounds do little damage. Among the complexes being reported here, the copper(II) complexes possess the highest fungitoxicity. The fungitoxicity of the complexes has been attributed to the presence of the N—C=S moiety[25].

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