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Physico-chemical and Biological Properties of Mn(II), Co(II), Ni(II) and Cu(II) Chelates of Schiff Bases

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Two novel Schiff bases were synthesised using 1-methyl 2-pyrrolidinone/1-methyl-2-pyridone with *o*-phenylene diamine along with their Mn(II), Co(II), Ni(II) and Cu(II) chelates and characterised. The IR, electronic thermogravimetric data, antibacterial and antifungal activities are discussed here.

Key Words: (1-Methyl-2-pyrrolidimino) phenylene diamine, (1-Methyl-2-pyridimino) phenylene diamine, Mn(II), Co(II), Ni(II), Cu(II), Chelates.

INTRODUCTION

Because of the ready accessibility, diverse chemical activity,[1-5] broad spectrum of biological and pharmacological properties[6, 7] such as analgesic, antipyretic, anti-inflammatory, anticancerous, bactericidal and fungicidal has made the study of imines a viable source to signify and magnify the observations and results for the betterment of human life.

As the microbial activity of an active ligand is altered many-folds on coordinating with a suitable metal ion,[8] keeping the above facts in mind and in continuation of our research work[9, 10] on transition metal complexes with Schiff bases, in the present paper synthesis and characterisation of Mn(II), Co(II), Ni(II) and Cu(II) complexes with (1-methyl-2-pyrrolidimino) phenylene diamine ($MPPD_1$-L_1) and (1-methyl-2-pyridimino) phenylene diamine ($MPPD_2$-L_2) are reported.

EXPERIMENTAL

All the chemicals used were of BDH quality. For the preparation of the ligands, the procedure followed is as reported earlier[11]. Melting points were determined in open capillaries. IR spectra (KBr) were recorded on a Perkin-Elmer 621 grating spectrophotometer.

The purity of all compounds was checked by running TLC on silica gel-G plates using chloroform ethyl-acetate (1 : 1) mixture and spots were visualized by iodine vapours. The metal contents of the complexes were determined by standard literature procedures.[12, 13]

RESULTS AND DISCUSSION

The analytical data and physical properties of the ligands and their metal complexes are given in Table-1.

The complexes are solids and are soluble in DMSO and DMF. The low values of conductance in DMF at room temperature show them to be the non-electrolytes.

TABLE-1
ANALYTICAL, MAGNETIC MOMENT, ELECTRONIC SPECTRA AND ELECTRICAL CONDUCTANCE DATA OF THE METAL COMPLEXES

Ligands/Complexes (Colour)	μ_{eff} (B.M.)	Λ_m $\Omega^{-1}cm^{-1}$ $mole^{-1}$	λ_{max} electronic (cm^{-1})	Analysis % Found (Calcd.)			
				M	C	H	N
L_1-$C_{16}H_{22}N_4$	—	—	32260	—	71.11	8.14	20.74
(Golden brown)			27027		(71.21)	(8.25)	(20.81)
L_2-$C_{18}H_{18}N_4$	—	—	32258	—	74.48	6.20	19.31
(Dark brown)			27029		(74.54)	(6.35)	(19.37)
$Mn(L_1)(H_2O)_2$	5.19	2.38	22252	15.21	53.19	6.09	15.51
(Reddish brown)			24675	(15.31)	(53.31)	(6.20)	(15.60)
$Mn(L_2)(H_2O)_2$	5.24	2.20	22250	14.41	56.70	4.72	14.70
(Dull red)			24880	(14.53)	(56.82)	(4.90)	(14.81)
$Co(L_1)(H_2O)_2$	4.85	1.92	10526	16.14	52.61	6.02	15.34
(Greenish brown)			21700	(16.25)	(52.71)	(6.21)	(15.41)
$Co(L_2)(H_2O)_2$	4.75	1.75	9700	15.30	56.11	4.67	14.54
(Greenish brown)			19900	(15.42)	(56.22)	(4.77)	(14.60)
$Ni(L_1)(H_2O)_2$	2.90	8.63	10755	16.09	52.64	6.03	15.35
(Yellowish brown)			23600	(16.17)	(52.72)	(6.15)	(15.50)
$Ni(L_2)(H_2O)_2$	2.80	8.52	10760	15.25	56.14	4.67	14.55
(Dark brown)			23620	(15.30)	(56.31)	(4.72)	(14.67)
$Cu(L_1)(H_2O)_2$	1.96	1.25	13850	17.19	51.95	5.95	15.15
(Faint green)				(17.24)	(51.98)	(6.01)	(15.30)
$Cu(L_2)(H_2O)_2$	1.92	1.15	13790	16.31	55.45	4.62	14.37
(Pale green)				(16.42)	(55.60)	(4.80)	(14.47)

The infrared spectrum of (1-methyl-2-pyrrolidimino) phenylene diamine [L_1] and (1-methyl-2-pyridimino) phenylene diamine [L_2] observed strong and broad peak in 3260–3200 cm^{-1} region which can be assigned to ν(N—H) vibrations[14]. In the spectra of the complexes this band is shifted indicating the involvement of the nitrogen in coordination. Further, a broad band of medium intensity at 1700–1600 cm^{-1} can be assigned to ν(C=N) and was found to exhibit red shift in the complexes suggesting coordination of the azomethine nitrogen. The presence of —CH_3— and —CH— groups is indicated by bands around 1850 and 2970 cm^{-1} respectively. A specific band at 3064 cm^{-1} indicates the presence of —C—H phenyl group in the ligand as well as in all metal complexes. At the same time no band is obtained around 1740–1630 cm^{-1} indicating the complete condensation of the amine and the ketonic groups.

The band around 450 cm^{-1} in all the metal chelates suggests ν(M—N) vibration which further confirms the coordination of nitrogen atoms of these groups with the metal. An additional band at 3460 cm^{-1} suggests the presence of the coordinated water.

The magnetic moments (Table-1) and electronic spectral data are also consistent with an octahedral structure in all the present metal-complexes. The spectrum of the ligand showed two characteristic bands at 32258 cm^{-1} and 27027 cm^{-1}. The shift of these bands exhibited in the spectra of complexes can be taken as a proof of coordination of the ligands to the metal ions.

The octahedral environment of the ligands around the central Mn(II) ion is confirmed by the appearance of broad bands[15] at 22250 cm^{-1} and 24875 cm^{-1} due to $^6A_{1g}(F) \rightarrow {}^4T_{2g}(P)$ and $^6A_{1g}(F) \rightarrow {}^4A_{2g}(P)$. Similarly the $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ and $^6T_{1g}(F) \rightarrow T_{1g}(P)$ transitions expected for Co(II) complexes are very clear at 10530–9500 cm^{-1} and 22000–20000 cm^{-1} respectively. The bands at 10755 cm^{-1} in Ni(II) complexes are assignable to $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ transition and another at 23600 cm^{-1} to $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ transition of an octahedral geometry.

The distorted octahedral geometry for Cu(II) complex is indicated by the band[16] around 14000 cm^{-1} range for $^2E_g \rightarrow {}^2T_{2g}$ due to J.T. distortion.

The decomposition temperature ranges for the metal chelates are summarised in Table-2.

TABLE-2
THERMAL DECOMPOSITION DATA OF THE LIGAND MPPD$_1$ (L_1) AND ITS BIVALENT METAL-CHELATES

Complex	Stage	$T_{range\ in\ TG}$ (°C)	$T_{peak\ in\ TG}$ (°C)	Loss of mass %		Probable assignments
				From TG	Theoretical	
$Mn(L_1)(H_2O)_2$	I	70–260	170	23.00	22.28	Loss of $2H_2O$ + phenylene diamine part
	II	270–520	420	66.00	64.72	Loss of remaining part
$Co(L_1)(H_2O)_2$	I	110–300	190	20.00	19.68	Loss of $2H_2O$ + phenylene diamine part
	II	310–520	480	40.00	34.25	Loss of remaining part
$Ni(L_1)(H_2O)_2$	I	100–300	230	13.00	11.62	Loss of $2H_2O$
	II	300–450	410	20.00	21.08	Loss of phenylene diamine part
	III	450–550	490	51.00	51.21	Loss of remaining part
$Cu(L_1)(H_2O)_2$	I	80–150	150	3.50	3.80	Loss of H_2O
	II	160–530	530	36.50	36.60	Loss of phenylene diamine part
	III	530–620	600	45.00	42.60	Loss of remaining part

The title compounds were screened for their antimicrobial activity against some pathogenic bacteria. Organisms used include both gram positive and gram negative strains like *E. coli, S. aureus, S. typhi, B. subtilis, A. aerogenes* and *B. megatherium.* The solvent used was DMF. Sensitivity plates were seeded with a bacterial inoculum of 1×10^6 CIU/mL and each well (diameter 10 mm) was

loaded with 0.1 mL of test compound solution of variable concentration in DMF. The zones of inhibition were recorded after incubation for 24 h using vernier callipers. (Table-3).

TABLE-3
BACTERIOLOGICAL ACTIVITY ANALYSIS OF LIGANDS AND THEIR METAL CHELATES

Organism	Ligands		Chelates							
			Mn(II)		Co(II)		Ni(II)		Cu(II)	
	L_1	L_2	L_1	L_2	L_1	L_2	L_1	L_2	L_1	L_2
E. coli	+	+	+	+	++	+	+	–	+	+
S. aureus	–	+	++	+	–	–	+	+++	+	+
S. typhi	–	–	–	+	–	–	–	+	++	+++
B. subtilis	–	++	+	++	+	–	+	++	+	+
A. aerogenes	+	+	+	+	++	–	+	++	++	+
B. megatherium	+	–	++	+	+	–	+	++	+	+++

(–) Inactive (less than 1 mm), (+) Weakly active (12–16 mm), (++) moderately active (17–20 mm), (+++) highly active (21–30 mm)

The fungicidal activities of the ligands and their corresponding metal chelates were evaluated by testing them against *Alternaria alternata* and *Aspergillus niger* at different concentrations. The results of the fungicidal screening is recorded in Table-4, which shows that the ligands are moderately active against *A. alternata* and the activity increases as the concentration increases. In addition, the metal complexes are found to be more active on complexation which is in agreement with those reported earlier.[17]

TABLE-4
FUNGICIDAL SCREENING DATA OF LIGANDS AND THEIR METAL CHELATES

	Average % inhibition of spore germination after 72 h					
	Alternaria alternata (conc. in ppm)			*Aspergillus niger* (conc. in ppm)		
	100	500	1000	100	500	1000
$MPPD_1$	25	38	61	21	32	53
$MPPD_2$	27	36	64	22	31	50
Mn-$MPPD_1$	52	57	62	49	47	57
Mn-$MPPD_2$	49	52	60	41	50	56
Co-$MPPD_1$	39	42	70	37	39	62
Co-$MPPD_2$	42	48	71	39	45	66
Ni-$MPPD_1$	32	45	69	30	41	56
Ni-$MPPD_2$	36	52	72	31	49	61
Cu-$MPPD_1$	48	50	59	45	42	51
Cu-$MPPD_2$	51	54	58	47	44	53

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