Asian Journal of Chemistry Vol. 5, No. 1 (1993) 35-40

Synthesis and Spectral Studies of Metal Complexes Derived from Aromatic Heterocyclic Schiff bases

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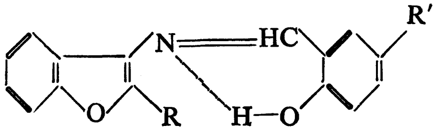
Complexes of the type $MLCl_2$ [M=Co(II), Ni(II) and Cu(II)] where L = Schiff base derived from condensation of salicylaldehyde/substituted salicylaldehyde with ethyl-3-amino-2-benzofurancarboxylate were synthesised. All the complexes were characterised by the elemental analysis, IR, electronic and magnetic susceptibility data. The conductance measurements in DMF indicate the nonelectrolytic/electrolytic nature of the complexes. The IR spectral data suggest that all the ligands act as neutral bidentates towards all the complexes. Based on the IR, electronic and magnetic data polymeric octahedral structures are proposed for all the complexes.

INTRODUCTION

Schiff bases are becoming increasingly important as biochemical, analytical and antimicrobial agents. In recent years Schiff base ligands have received much importance and yet there is much scope for thorough probe on metal complexes with such ligands which are also of biochemical interest. Simple 2, 3-substituted benzofuran derivatives are well known for their biological and pharmacological properties.[1,2] Recently Hiremath *et al*[3] have reported that the metal complexes of benzofuran derivatives also act as potent antimicrobial[3] and antifungal agents[4]. Therefore, in continuation of our efforts to synthesise the metal complexes of biological importance, we report here Co(II), Ni(II) and Cu(II) complexes with ligands derived from the condensation of salicylaldehyde/substituted salicylaldehydes with ethyl-3-amino-2-benzofurancarboxylate.



L	R	R′
I	$COOC_2H_5$	H
II	$COOC_2H_5$	Cl
III	$COOC_2H_5$	CH_3
IV	$COOC_2H_5$	OCH_3

EXPERIMENTAL

All the metal chlorides used were of AR grade. Substituted salicylaldehydes were prepared by Duffs method. Ethyl-3-amino-2-benzofuran carboxylate was prepared by known procedure[5].

Preparation of Schiff base

Ethyl-3-amino-2-benzofuran carboxylate (0.01 mol) in ethanol and corresponding aldehyde (0.01 mol) in the same solvent were refluxed on a water bath for 2 hrs. The reaction mixture on partial evoporation yielded the required Schiff bases in good yields. The separated Schiff bases were filtered, washed with ethanol thoroughly and recrystallised from suitable solvent. [I = $C_{18}H_{15}NO_4$, 123°C; II = $C_{18}H_{14}NO_4Cl$, 146°C; III = $C_{19}H_{17}NO_4$, 132°C; IV = $C_{19}H_{17}NO_5$, 162°C]

Preparation of Complexes

The ligand (0.01 mol) in ethanol was added to the metal chloride (0.01 mol) in the same solvent and refluxed for about 3 hrs on a water bath. The separated complexes were filtered, washed with ethanol and dried over fused calcium chloride. In the case of Ni(II) complexes alcoholic ammonia was added to isolate the complexes.

Chemical Analysis

All the complexes were analysed for the metal, chloride and nitrogen by standard methods.

Physical Measurements

IR spectra in nujol mull were recorded on a Hitachi 270–50 IR spectrophotometer in the range 4000–250 cm^{-1} and electronic spectra in solid state were obtained from I.I.T. Madras. The magnetic moment measurements were carried out by using Gouy method using $Hg[Co(SCN)_4]$ as a calibrant. Conductivity measurements were made on an Elico conductivity bridge model CM82T at room temperature.

RESULTS AND DISCUSSION

The analytical data (Table 1) show 1 : 1 stoichiometry for all the complexes. All the complexes are soluble to a limited extent in DMF and DMSO and insoluble in common organic solvents. This insolubility did not permit us to determine the molecular weights. The molar conductance of all the complexes in DMF (10^{-3}M) solution fall in the range 10–30 ohm^{-1} cm^2 $mole^{-1}$ indicating their non-electrolytic nature.

TABLE 1

ANALYTICAL DATA, MOLAR CONDUCTANCE AND MAGNETIC SUSCEPTIBILITY DATA OF THE COMPLEXES

Ligand	Complex	% Found (calculated)			Λ_m^*	μ_{eff} B.M.
		M	N	Cl		
I	$CoLCl_2$	12.98 (13.42)	3.04 (3.19)	15.84 (16.18)	13.08	4.7
	$NiLCl_2$	13.04 (13.38)	3.09 (3.19)	15.90 (16.18)	21.45	3.2
	$CuLCl_2$	13.90 (14.32)	3.02 (3.16)	16.40 (16.01)	18.35	1.6
II	$CoLCl_2$	12.12 (12.44)	2.68 (2.96)	14.68 (15.00)	29.88	4.8
	$NiLCl_2$	12.04 (12.41)	2.72 (2.96)	14.60 (15.00)	30.04	3.4
	$CuLCl_2$	12.94 (13.29)	2.68 (2.93)	14.37 (14.85)	14.85	1.82
III	$CoLCl_2$	12.89 (13.01)	2.89 (3.09)	15.42 (15.68)	15.89	4.94
	$NiLCl_2$	12.68 (12.97)	2.92 (3.09)	15.20 (15.68)	14.52	3.3
	$CuLCl_2$	13.40 (13.88)	2.98 (3.06)	15.22 (15.52)	19.88	1.63
IV	$CoLCl_2$	12.42 (12.56)	2.78 (2.99)	14.98 (15.14)	13.76	4.92
	$NiLCl_2$	12.12 (12.52)	2.85 (2.99)	15.02 (15.15)	16.84	3.5
	$CuLCl_2$	13.09 (13.41)	2.82 (2.96)	14.73 (15.00)	14.23	1.8

*$ohm^{-1}\ cm^2\ mole^{-1}$

Magnetic Moment :

The magnetic moments for the present Co(II) complexes lie in the range 4.7–4.95 B.M. which agree with the earlier reports of polymeric octahedral Co(II) complexes[6]. Ni(II) complexes possess the magnetic moments in the range 3.2–3.6 B.M. The low value may be due to polymeric nature of the complexes. Cu(II) complexes possess the magnetic moment values in the range 1.6–1.82 B.M., which is well within the range reported for most of the distorted octahedral Cu(II) complexes.

Infrared Spectra

All the ligands exhibit a broad and weak band in the region 2750–2600 cm^{-1} assignable to intramolecularly hydrogen[8] bonded OH. In the corresponding complexes this band appears at a higher frequency side as a strong band in the region 3500–3325 cm^{-1} indicates the presence of free phenolic OH group[9] after the cleavage of intramolecular hydrogen bonding. This suggests that oxygen of OH group has not taken part in coordination.

The band due to C=O stretch in the ligands appears around 1730 cm^{-1} which in complexes suffers a negative shift of 30–100 cm^{-1}, thereby indicating the coordination through carbonyl oxygen atom in all the complexes. A strong band due to C=N stretch (azomethine) in ligands appears around 1620 cm^{-1}, which upon complexation either splits or shifts towards lower frequency side by 30–90 cm^{-1} suggesting the involvement of azomethine nitrogen atom in coordination with the metal ions.

A strong intense band in the region 1200–1210 cm^{-1} is assigned to C—O—C stretch of furan ring[10], which in complexes remains at the same position with low intensity or suffers a slight positive shift of 5–20 cm^{-1} indicating no bonding of furan ring oxygen with the metal ions.

Strong to medium intensity non-ligand bands observed around 500 cm^{-1} and in the region 460–400 cm^{-1} are assigned to M–N and M–O stretches[12,13] respectively in all the complexes. The weak bands in the regions 320–300 and 290–260 cm^{-1} are assigned to terminal and bridging M–Cl stretching vibrations respectively in view of the other reports[14].

Electronic Spectra

The electronic spectra of all complexes were taken in nujol mull. The Co(II) complexes exhibit three bands in the region 8700–8000 cm^{-1}, 12500–12200 and 20000–18000 cm^{-1} corresponding to $^4T_{1g} \rightarrow {}^4T_{2g}(F)$ (ν_1), $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ (ν_2) and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (ν_3) respectively in an octahedral environment. The ligand field parameters like Dq, B′, β, $\beta\%$ etc have been calculated (Table 2) and these are in the range reported for most of the octahedral Co(II) complexes.

All the Ni(II) complexes exhibit two bands in the region 15000–14000 cm^{-1} and 23000–25000 cm^{-1} corresponding to ν_2 and ν_3 transitions respectively in an octahedral field. The ligand field parameters further suggest octahedral geometry around Ni(II) ion.

The Cu(II) complexes exhibit a broad band in the region 16670–13890 cm^{-1}. This suggests that all the complexes have tetragonally distorted octahedral structure. The broadness of the band may be due to dynamic Jahn-Teller distortion.

ACKNOWLEDGEMENTS

The authors are thankful to Dr. S. P. Hiremath, Head of the Department of Chemistry for providing the facilities and I.I.T. for electronic spectra.

TABLE 2

ELECTRONIC SPECTRAL DATA OF THE COMPLEXES

Ligand	Complex	max (cm^{-1})			Dq cm^{-1}	B′ cm^{-1}	β	β%	LFSE Kcal/mole
		ν_1	ν_2	ν_3					
I	$CoLCl_1$	8696	12500	18500	979	726	0.75	24.72	16.78
	$NiLCl_2$	8660*	14200	24000	866	815	0.78	21.63	29.69
	$CuLCl_2$		16670–13890		1458	—	—	—	25.00
II	$CoLCl_2$	8547	12200	20000	970	840	0.87	13.13	16.63
	$NiLCl_2$	8900*	14290	23250	890	723	0.70	30.48	30.51
	$CuLCl_2$		16950–14000		1389	—	—	—	25.00
III	$CoLCl_2$	8475	12200	18180	955	719	0.74	25.65	16.37
	$NiLCl_2$	9150*	14930	25000	915	832	0.80	20.00	31.37
	$CuLCl_2$		16670–13890		1458	—	—	—	25.00
IV	$CoLCl_2$	8622	12350	20000	977	835	0.86	13.65	16.75
	$NiLCl_2$	8900*	14290	23250	890	723	0.70	30.48	30.51
	$CuLCl_2$		16390–14490		1444	—	—	—	24.76

*Calculated value.

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[*Received*: 27 February 1991; *Accepted*: 10 January 1992] AJC–387