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Spectroscopic study of cobalt(II), nickel(II) and copper (II) complexes of a biologically active Schiff bases

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ABSTRACT

A series of Cobalt(II), Nickel(II) and Copper(II) complexes have been synthesized with newly derived biologically active Schiff base ligand, 4-iso-propyl-1-methyl cyclohexane-2-one semicarbazone. The elemental analyses of the ligand as well as metal complexes indicate complexes having 1:2 stoichiometry of the type $[M(IPMCS)_2X_2]$, where M = cobalt(II), nickel(II) and copper(II), IPMCS = 4-isopropyl 1- methyl cyclohexane semicarbazone and X = Cl^-, Br^-, I^- and NO_3^-. The complexes have been characterized by IR spectral, electronic spectra, magnetic susceptibility and molar conductance data. The study of IR spectra of the ligand as well as metal complexes suggest linkage of metal ion through azomethine nitrogen and carbonyl oxygen atom of semicarbazone moiety. On the basis of electronic spectral and magnetic susceptibility values the complexes are proposed to be octahedral geometry. The molar conductivity also reveals that the complexes are non electrolytic in nature.

Key words: IPMCS/ copper(II)/ nickel(II)/ copper(II)/ complexes.

INTRODUCTION

The Schiff base transition metal complexes have been extensively studied in recent years owing to their potential biological activities[1-5]. They exhibit biological properties[6] such as analgesic, antiinflammatory, anticancerous and antimicrobial[7]. The microbial activity of the Schiff bases are altered many-folds on coordination with metal ions[8]. Keeping in mind the biological importance of Schiff base complexes and in continuation of our earlier work[8-24] on complexes with Schiff base ligands, an attempt has been made to prepare the complexes of cobalt(II), nickel(II) and copper(II) with Schiff base 4-iso-propyl-1-methyl cyclohexane-2-one semicarbazone.

EXPERIMENTAL

All the chemicals used are of analytical grade. The analytical data and physical properties of the complexes are listed in Table-1. The analytical data correspond well with the general composition $[M(IPMCS)_2X_2]$ where IPMCS = 4-iso-propyl-1-methyl cyclohexane-2-one semicarbazone and X = Cl^-, Br^-, I^- and NO_3^-. The low value of molar conductance of the complexes support their non electrolytic nature.

Analytical data (C,H,N) were collected on Perkin Elmer-2400 CHNS/O elemental analyser. IR spectra of the samples (Table-2) in 4000-200 cm^{-1} range were recorded on Perkin Elmer 577 spectrophotometer using KBr discs. Magnetic susceptibility values were measured by Gouy balance using mercury $Hg[Co(NCS)_4]$ as the calibrant. Electronic spectral data were recorded out on Shimadzu 160 A spectrophotometer. The molar conductance measurement were carried out on Systronics conductometer model 303 using D.M.F. as a solvent.

Preparation of the ligand

Ethanolic solution of 4-iso-propyl-1-methyl cyclohexane-2-one (0.01 M) was treated with semicarbazide hydrochloride (0.01 M) dissolved in minimum amount of sodium acetate in tetrahydrofuran. The resulting mixtures were heated on a water bath for 2-3 h with frequent stirring. The precipitate formed were then cooled, filtered and washed with cold ethanol and recrystallised with tetrahydrofuran to furnish 4-iso-propyl-1-methyl cyclohexane-2-one semi-carbazone as colourless needles. Yield 60-65% m.p. 136±1°C.

Preparation of the complexes

The complexes were prepared by reacting the respective metal salts of cobalt(II), nickel(II) and copper(II) in ethanol with the ethanolic solution of the ligand 4-iso-propyl-1-methyl cyclohexane-2-one semicarbazone [IPMCS] in molar ratio 1:2. The resulting reaction mixtures were refluxed on a water bath for 2-3 h. The procedure carried out in each case was similar with slight variation of timing of reflux. The solid complexes were filtered, washed with ethanol, dried and recrystallised with tetrahydrofuran. Yield in all cases was 60-65%.

RESULTS AND DISCUSSION

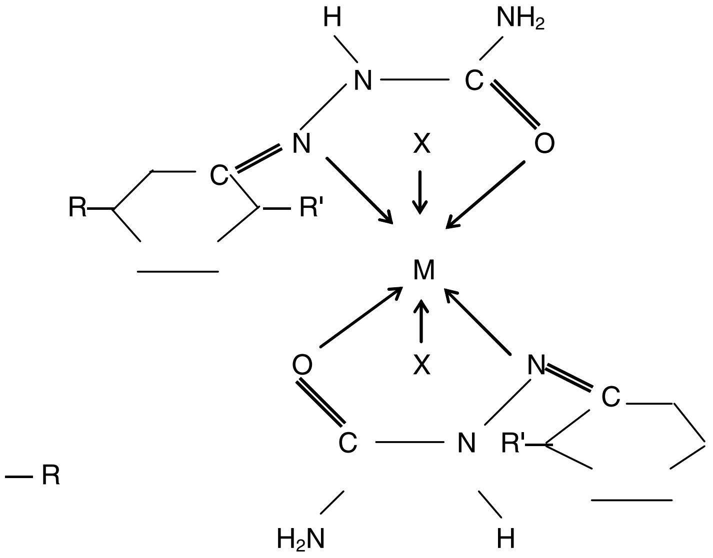
IR spectra

IR spectrum of the ligand exhibits a broad band of medium intensity at 3220 cm^{-1} which assigned[25] to ν_{N-H}. The spectra of the complexes this band is unaffected indicate non involvement of nitrogen atom of either amino or imino group in the coordination. IR spectrum of the ligand also shows a sharp and medium band at 1480 cm^{-1} assigned[26-28] to $\nu_{C=N}$. In the spectra of the complexes, this band is shifted to a lower frequency region with slightly reduced intensity. The shift of the band and change in intensity suggests linkage of azomethane N with metal ion.

The next IR spectrum of the ligand exhibit strong and broad band at ~1660 cm^{-1} which is assigned[26,27,29] to $\nu_{C=O}$. On complexation this band suffers a upward shift suggests coordination of the metal ion through carbonyl oxygen of semicarbazone moiety.

Coordination through azomethine N and oxygen atom of semicarbazone group is further

m = medium, s = strong, b = broad



M = Co(II) and Ni(II); X = Cl^-, Br^-, I^- and NO_3^-; M = Cu(II); X = Cl^-, Br^-, and NO_3^-;
R = CH_3 ; R' = Isopropyl

Fig. 1: [M(IPMCS)X_2]

Table 1: Analytical, colour, mol. wt., magnetic susceptibility, conductivity measurement and decomposition temperature of ligand IPMCS and its metal complexes

Compounds (Colour)	Mol. wt.	% Analysis found (calculated)				μ_{eff} B.M.	Ω_m ohm^{-1} cm^2 mol^{-1}	DT °C	λ_{max} electronic cm^{-1}
		M	C	N	H				
IPMCS	209		63.24	19.98	8.97			136	
(Colourless)			(63.15)	(20.00)	(9.09)				
$[Co(IPMCS)_2Cl_2]$	547.93	10.67	48.29	15.22	7.04	5.18	1.6	217	13500
(Brown)		(10.75)	(48.18)	(15.33)	(6.93)				19800‘
$[Co(IPMCS)_2Br_2]$	636.74	9.34	41.55	13.24	6.02	5.17	1.9	203	13700
(Brown)		(9.25)	(41.46)	(13.19)	(5.96)				20000
$[Co(IPMCS)_2I_2]$	730.73	7.98	36.21	11.55	5.26	5.20	1.8	211	13200
(Brown)		(8.06)	(36.12)	(11.49)	(5.20)				19100
$[Co(IPMCS)_2(NO_3)_2$	600.43	9.91	43.81	14.03	6.28	4.97	1.9	212	12900
] (Yellowish Brown)		(9.80)	(43.93)	(13.97)	(6.32)				19600
$[Ni(IPMCS)_2Cl_2]$	547.71	10.62	48.29	15.26	7.04	3.11	3.4	243	11200
(Green)		(10.71)	(48.20)	(15.33)	(6.93)				15100 23200
$[Ni(IPMCS)_2Br_2]$	636.52	9.29	41.90	13.28	6.04	3.13	3.1	249	11400
(Green)		(9.22)	(41.47)	(13.19)	(5.96)				15300 23500
$[Ni(IPMCS)_2I_2]$	730.52	7.99	36.22	11.56	5.28	3.20	3.2	252	11200
(Green)		(8.03)	(36.13)	(11.49)	(5.20)				15600 23800
$[Ni(IPMCS)_2(NO_3)_2]$	600.71	9.84	44.09	14.03	6.39	3.16	3.8	257	11000
(Yellowish)		(9.77)	(43.94)	(13.98)	(6.32)				15800 24000
$[Cu(IPMCS)_2Cl_2]$	552.54	11.54	47.63	15.28	6.92	1.86	3.6	230	12500
(Blue)		(11.40)	(47.77)	(15.20)	(6.87)				17300
$[Cu(IPMCS)_2Br_2]$	641.35	10.01	41.27	13.14	6.01	1.84	3.4	237	12800,
(Blue)		(9.90)	(41.16)	(13.09)	(5.92)				19000
$[Cu(IPMCS)_2(NO_3)_2]$	605.54	10.56	43.62	13.94	6.20	1.92	3.5	239	12900,
(Blue)		(10.49)	(43.59)	(13.87)	(6.27)				17200

DT = Decomposition Temeperature

Table 2: Salient features of IR spectral bands of ligand IPMCS and its metal complexes

Compounds	$\nu_{C=N}$	$\nu_{C=O}$	ν_{M-O}	ν_{M-N}
IPMCS	1480 s,m	1660 s,b		
$[Co(IPMCS)_2Cl_2]$	1455 m,b	1695 m,b	530 m	415 m
$[Co(IPMCS)_2Br_2]$	1450 m,b	1700 m,b	535 m	410 m
$[Co(IPMCS)_2I_2]$	1455 m,b	1695 m,b	540 m	405 m
$[Co(IPMCS)_2(NO_3)_2]$	1455 m,b	1700 m,b	545 m	395 m
$[Ni(IPMCS)_2Cl_2]$	1450 m,b	1695 m,b	550 m	405 m
$[Ni(IPMCS)_2Br_2]$	1450 m,b	1695 m,b	555 m	410 m
$[Ni(IPMCS)_2I_2]$	1455 m,b	1690 m,b	560 m	415 m
$[Ni(IPMCS)_2(NO_3)_2]$	1455 m,b	1690 m,b	550 m	420 m
$[Cu(IPMCS)_2Cl_2]$	1455 m,b	1695 m,b	540 m	410 m
$[Cu(IPMCS)_2Br_2]$	1455 m,b	1700 m,b	540 m	415 m
$[Cu(IPMCS)_2(NO_3)_2]$	1450 m,b	1695 m,b	540 m	410 m

m = medium, s = strong, b = broad

confirmed by the appearance of bands in the far-ir region at 560-530 cm^{-1}, 425-395 cm^{-1} which may be assigned[30,31] to $\nu_{M—O}$, $\nu_{M—N}$ respectively. The evidence of metal halogen linkage is confirmed by the low value[32] of molar conductance of the complexes in the range 1.6-3.8 ohm^{-1}, cm^2, mol^{-1}. Nitrate complexes show characteristic medium intensity bands at 1280 and 1120 cm^{-1} with a separation of 165 cm^{-1} due to monodentately coordinated nitrate group.

The electronic spectral and magnetic susceptibility values (Table-2) suggest octahedral geometry of the complexes.

CONCLUSION

Thus on the basis of the above studies it may be concluded that the complexes of Co(II), Ni(II) and Cu(II) possess octahedral geometry around the central metal ions as show in Fig.-1.

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