

Synthesis and spectral studies of Cobalt(II), Nickel(II) and Copper (II) complexes of 2,6-dimethyl 4-pyrone semicarbazone

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(Received: October 25, 2009; Accepted: December 11, 2009)

ABSTRACT

Complexes of the type $[M(DMPS)_2X_2]$. Where M=cobalt(II) nickel(II) and copper(II) DMPS =2,6-Dimethyl 4-pyrone semicarbazone and X = Cl⁻, Br⁻, I⁻, NO₃⁻ and ClO₄⁻ have been prepared, the ligand and complex have been characterized by elemental analysis IR spectra, electronic spectra, molar mass, conductance, magnetic susceptibility values. DMPS acts as neutral bidentate ligand and coordinate is proposed through azomethine N and carbonyl oxygen atoms of semicarbazone moiety the remaining position of metal ions are satisfied by negative anions such Cl⁻, Br⁻, I⁻, NO₃⁻ or ClO₄⁻ the complexes were proposed to be monomeric octahedral in geometry.

Key words: Schiff base/DMPS/Co(II), Ni(II), Cu(II)/Complexes.

INTRODUCTION

In recent years the complexes of Schiff bases are considered to an important class of chemical compounds used extensively for the treatment of several disease¹⁻⁴. Schiff base complexes have been widely used as analytical reagents⁵⁻⁷. and as corrosion inhibitors⁸. keeping the above applications of Schiff base complexes and in continuation of our earlier work⁹⁻¹⁶. on the Schiff base complexes, preparation and characterization of cobalt (II), nickel(II) and copper (II) complexes with 2,6-dimethyl 4-pyrone semicarbazone are reported here.

EXPERIMENTAL

All the chemicals used were of analytical grade. The complexes were analysed for metal contents by standard procedure¹⁷. IR spectra of ligand and their complexes were recorded on Perkin-Elmer 577 using KBr disc. The electronic spectral data were recorded on a Cary 2390 spectrophotometer. Magnetic susceptibility values

were measured by Gouy method using Hg[Co(NCS)₄] as a calibrant. The molar conductance measurements were done on systronics conductivity meter model 303 using DMF as the solvent Analytical data, electronic spectral data, molar conductance value, magnetic susceptibility value, decomposition temperature and molecular formula of the ligand as well as their complexes are recorded in Table – 1 and the salient features of IR bands are recorded in Table 2.

Preparation of the Ligand

Ethanol solution of 2,6-dimethyl 4-pyrone (0.01M) was treated with semicarbazide hydrochloride (0.01M) dissolved in ethanolic solution of sodium acetate in tetrahydrofuran. The resulting mixtures were heated on water bath for 4 h with frequent stirring. The precipitate was filtered. Washed with ether. The residue was washed with water and recrystallized with DMF. m.p-117±1°C. Yield 70-75%

Preparation of the Complexes

The complexes of cobalt(II), nickel(II) and

copper(II) have been prepared by reacting an ethanolic solution of the ligand 2-6 dimethyl 4-pyrone semicarbazone (DMPS) with ethanolic solution of the corresponding metal halide/nitrate/perchlorate in the molar ratio 2:1 the procedure carried out in each case was of similar nature with a slight variation of timing of reflux. The complexes obtained in each case were washed with ethanol to remove any excess of the ligand. Finally complexes were washed with anhydrous diethyl ether and dried in air oven. Yield 60-65%.

RESULTS AND DISCUSSION

I.R. Spectra, It is established from the literature¹⁸ that semicarbazone ligand can coordinate in a bidentate manner in most cases through azomethine nitrogen and carbonyl oxygen of semicarbazone moiety.

IR spectrum of the ligand DMPS exhibits a medium broad band at 3220 cm⁻¹ assigned^{18,20} to ν_{N-H} . In the spectra of the complexes this band appears without any change indicating that either primary amino or secondary amino groups has not taken part in the coordination with metal ion.

IR spectrum of the ligand exhibits a sharp strong band at 1690 cm⁻¹ assigned^{19,21} to $\nu_{C=O}$. In the spectra of the complexes this band is shifted to higher frequency region and appear at 1725 cm⁻¹ with slightly reduced intensity. The shift of the band and change in intensity suggesting coordination

through carbonyl oxygen of semicarbazone moiety. The linkage with oxygen atom is further supported by the appearance of a new band in the far ir region at 570-520 cm⁻¹ in the complexes assignable^{19,22} to ν_{M-O} . The IR spectrum of the ligand exhibit a band at 1475 cm⁻¹ assigned^{19,23} to ν_{C-N} in the spectra of the complexes this band shows red shift with slightly reduced intensity. The shift of the band and change in intensity proposes coordination of azomethine N with metal ion. The linkage with nitrogen atom is further supported by the appearance of a band in the far in region at 395-360 cm⁻¹ assigned²⁴ to ν_{M-N} the evidence of metal halogen is confirmed by the low molar conductance of the complexes in the range 1.1-4.2 ohm⁻¹ cm² mol⁻¹. This statement is further confirmed by the appearance of a band in far ir region at 325-270 cm⁻¹ which assigned to ν_{M-X} . Nitrate complexes shows characteristic medium intensity bands at 1375 and 1205 cm⁻¹ with a separation of about 170 cm⁻¹ due to monodentately coordinated nitrate group. Combination band at 1640 cm⁻¹ and 1620 cm⁻¹ with a separation of 20 cm⁻¹ confirming the monodentate behaviour of the nitrate group. In the case of perchlorate complexes four bands are observed at 1150 1050, 650 and 600 cm⁻¹ suggesting monodentate coordination of perchlorate group.

Electronic spectra and magnetic susceptibility of the complexes

The electronic spectra of all the complexes have been recorded in the region 10,000-25,000 cm⁻¹, the copper complexes exhibits two broad

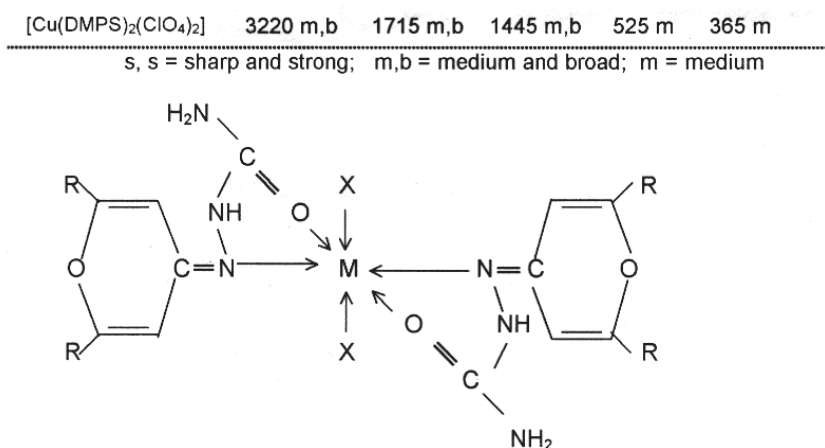


Fig. 1: [M(DMPS)₂X₂]; M=Co(II), Ni(II) and Cu(II); X=Cl, Br, I, NO₃⁻ and ClO₄⁻; R=Methyl

Table 1: Analytical, magnetic susceptibility measurements electronic spectral data, mol. Formula and decomposition temperature of ligand DMPS and its complexes

Compounds	Mol. Formula	% Analysis found (calculated)				μ_{eff} B.M.	λ_{max} electronic Cm^{-1}	$\Omega \text{m Ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$	DT $^{\circ}\text{C}$
		M	C	N	H				
DMPS (Colorless)	181		52.88 (23.20)	23.11 (23.20)	5.93 (6.07)				
[Co(DMPS) ₂ Cl ₂] (Yellowish red)	491.93	12.13 (11.97)	39.13 (39.07)	17.11 (17.07)	4.43 (4.47)	5.11	13200,19600	3.6	276
[Co(DMPS) ₂ Br ₂] (Yellowish red)	580.748	10.06 (10.14)	32.89 (33.66)	14.54 (14.46)	3.74 (3.78)	5.07	13100,19200	3.1	270
[Co(DMPS) ₂ I ₂] (Red)	674.738	8.68 (8.73)	28.58 (28.45)	12.36 (12.44)	3.22 (3.26)	5.14	22540	3.7	278
[Co(DMPS) ₂ NO ₃] ₂] (Deep red)	544.95	10.89 (10.81)	35.16 (35.23)	15.33 (15.41)	3.97 (4.03)	4.89	12400,19700	3.9	271
[Co(DMPS) ₂ ClO ₄] ₂] (Light Green)	619.93	9.58 (9.50)	31.11 (30.97)	13.66 (13.54)	3.51 (3.54)	4.96	22100	4.2	269
[Ni(DMPS) ₂ Cl ₂] (Brown)	491.71	12.02 (11.93)	38.91 (39.04)	16.93 (17.08)	4.41 (4.47)	3.18	10600,15300	2.1	263
[Ni(DMPS) ₂ Br ₂] (Deep Brown)	580.528	10.03 (1.11)	32.93 (33.07)	14.53 (14.46)	3.82 (3.78)	3.11	10000,15100	2.6	235
[Ni(DMPS) ₂ I ₂] (Brownish red)	674.518	8.64 (8.70)	28.31 (28.46)	12.52 (12.45)	3.23 (3.26)	3.13	10300,15200	2.9	241
[Ni(DMPS) ₂ (NO ₃) ₂] (Deep red)	544.71	10.84 (10.77)	35.36 (35.24)	15.49 (15.42)	4.07 (4.03)	3.21	24300	2.7	244
[Ni(DMPS) ₂ ClO ₄] ₂] (Red)	619.71	9.39 (9.47)	31.11 (30.98)	13.46 (13.55)	3.60 (3.55)	3.19	10400,16000	2.4	230
[Cu(DMPS) ₂ Cl ₂] (Blue)	496.54	12.83 (12.79)	38.93 (38.66)	16.82 (16.91)	4.39 (4.43)	1.81	24800	1.2	241
[Cu(DMPS) ₂ Br ₂] (Blue)	585.354	10.77 (10.85)	32.92 (32.80)	14.27 (14.35)	3.71 (3.75)	1.86	11200,14500	1.1	247
[Cu(DMPS) ₂ (NO ₃) ₂] (Blue)	549.54	11.49 (11.56)	35.13 (34.93)	15.34 (15.28)	3.94 (4.00)	1.90	14300	1.3	260
[Cu(DMPS) ₂ ClO ₄] ₂] (Deep red)	624.54	10.11 (10.17)	30.66 (30.74)	3.40 (3.44)	3.48 (3.52)	1.94	11600,14600	1.4	277

DT = Decomposition Temperature

Table 2: Key is spectral bands (cm⁻¹) of ligand DMPS and its metal complexes

Compounds	$\nu_{\text{N-H}}$	$\nu_{\text{C-O}}$	$\nu_{\text{C-N}}$	$\nu_{\text{M-O}}$	$\nu_{\text{M-N}}$	$\nu_{\text{M-X}}$
DMPS	3220 m,b	1690 s,s	1475 s,b			
[Co(DMPS) ₂ Cl ₂]	3220 m	1720 m,b	1440 m,b	535 m	370 m	305 m
[Co(DMPS) ₂ Br ₂]	3220 m	1715 m,b	1450 m,b	525 m	360 m	280 m
[Co(DMPS) ₂ I ₂]	3220 m	1710 m,b	1445 m,b	525 m	380 m	270 m
[Co(DMPS) ₂ NO ₃] ₂	3220 m	1710 m,b	1450 m,b	530 m	375 m	
[Co(DMPS) ₂ ClO ₄] ₂	3220 m	1720 m,b	1445 m,b	535 m	360 m	
[Ni(DMPS) ₂ Cl ₂]	3220 m	1720 m,b	1450 m,b	525 m	370 m	325 m
[Ni(DMPS) ₂ Br ₂]	3220 m	1725 m,b	1445 m,b	535 m	375 m	395 m
[Ni(DMPS) ₂ I ₂]	3220 m	1725 m,b	1440 m,b	520 m	375 m	375 m
[Ni(DMPS) ₂ NO ₃] ₂	3220 m	1715 m,b	1445 m,b	525 m	370 m	
[Ni(DMPS) ₂ ClO ₄] ₂	3220 m	1715 m,b	1450 m,b	525 m	370 m	
[Co(DMPS) ₂ Cl ₂]	3220 m	1710 m,b	1440 m,b	530 m	375 m	315 m
[Cu(DMPS) ₂ Br ₂]	3220 m	1710 m,b	1450 m,b	520 m	380 m	285 m
[Cu(DMPS) ₂ NO ₃] ₂	3220 m	1710 m,b	1445 m,b	520 m	380 m	
[Co(DMPS) ₂ ClO ₄] ₂	3220 m	1715 m,b	1445 m,b	525 m	365 m	

S.S = sharp and strong. m.b = medium and broad: m = medium

bands in the region 11500-11100cm⁻¹ and 14800-14400cm⁻¹ assigned to ²T_{2g}(F) <sup>4E_g and charge transfer bands respectively indicating distorted octahedral²⁷ geometry for the copper(ii) complexes. The magnetic moment values for copper(ii) complexes. i.e. in the range 1.81 to 1.94 B.M. the cobalt(ii) complexes exhibit three bands in the region 13800-12400 cm⁻¹, 19700-19200cm⁻¹ and 22640-22100cm⁻¹ assignable to the transitions ⁴T_{2g}(F) ← ⁴T_{1g} ← TM(F), ⁴A_{2g}(F) ← TM ⁴T_{1g}(F), and ⁴T_{1g}(P), ⁴T_{1g} ← TM(F) respectively. The above mentioned spectral bands indicate octahedral²⁷ geometry for the cobalt(ii) complexes. The octahedral geometry of cobalt(ii) complexes is also supported^{28,29} by magnetic susceptibility values in the range 4.92 to 5.9B.M. the nickel (ii) complexes exhibits three absorption bands in the region 10700-10,000 cm⁻¹, 16000 - 15100 cm⁻¹, and 24800-24200 cm⁻¹, respectively assignable to ³T_{2g}(F) ← ³A_{2g}(F), ³T_{1g}(F) ← ³A_{2g}(F), and ³T_{1g}(P), ← ³T_{2g}(F) transitions respectively. The suggesting octahedral²⁷ geometry for Ni(ii) complexes is further supported^{28,29} by magnetic susceptibility values of the complexes in the range 3.11 B.M. to 3.19 B.M.

Conductivity Measurement

Molar conductance values of the complexes of cobalt(ii) nickel(ii) and copper (ii) were found to be in the range. 1.1-4.2 ohm⁻¹ mol⁻¹ in DMF indicating their non electrolytic nature³⁰. The values of conductance also support the structure assigned on the basis of elemental analysis. IR spectra and magnetic susceptibility values.

CONCLUSIONS

Thus on the basis of the above studies it is concluded that the complexes possess the octahedral geometry around the central metal ion as shown in Fig. 1.

ACKNOWLEDGEMENTS

The authors are grateful to the Principal, L,N,T, College Muzaffarpur for providing laboratory facilities. B.K. Rai is also grateful to U.G.C. for financial support for this project under Minor Research Project.

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