



Synthesis and Structural Aspect of Some Transition Metal Complexes with Schiff Base Ligand Derived from 2, 6 Diethyl 4-pyrone

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ABSTRACT

A series of transition metal complexes of Co(II), Ni(II) and Cu(II) having the general composition $[M(DEPS)_2X_2]$; where, M = Co(II), Ni(II) and Cu(II), DEPS = 2, 6 Diethyl 4-pyrone semicarbazone, X = Cl⁻, Br⁻, I⁻ and NO₃⁻ have been prepared. The prepared complexes were characterized by elemental analyses, molar conductance, magnetic susceptibility measurements, IR and electronic spectral studies. From the perusal of IR spectral data, it is proposed that the Schiff base DEPS behaves as a bidentate ligand and coordination proposes through azomethine N and carbonyl oxygen atom of semicarbazone moiety. The remaining positions of metal ions are satisfied by negative ions, such as Cl⁻, Br⁻, I⁻ and NO₃⁻. Electronic, spectral data and magnetic susceptibility measurement indicate octahedral geometry around central metal ion.

Key words : DEPS/ Schiff base/ Co(II), Ni(II) and Cu(II) complexes.

INTRODUCTION

Study of Schiff base ligand is an excellent chelation ligand which can exhibit variety in the structure of their metal complexes. Transition metal complexes of N and O chelation centre have attracted considerable attention because of their interesting physicochemical properties and pronounced biological activities. Schiff bases and their metal complexes have used as hypertensive, hypothermic, anticancer²⁻⁴, antifungal, antibacterial & antitubercular reagents⁵⁻⁸. Transition metal

complexes are of great significance on account of their unique coordination and structural properties and their utilities as bio-inorganic models⁹⁻¹³. In recent years, extensive research in chemistry of metal chelates involving chelating Schiff base containing nitrogen, oxygen and sulphur donor sites have steadily grown in many areas including synthesis, structure elucidation, reaction kinetics, redox behaviour and biological reactions. The biological aspects of Schiff base complexes, owing to their biopotency, have been major cause of tremendous progress of research in this field. The

catalytic and biocidal activities of Schiff base compounds are enhanced by coordination with transition metal ions. Keeping the above facts in mind and in continuation of our earlier recent research works¹⁴⁻¹⁹ in this field, we now report the synthesis and characterization of coordination compound of Co(II), Ni(II) and Cu(II) with 2, 6-diethyl 4-pyrone semicarbazone.

EXPERIMENTAL

All the chemicals used were of analytical grade. The complexes were analysed for metal contents by standard procedures²⁰. 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 $\text{Hg}[\text{Co}(\text{NCS})_4]$ 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-diethyl 4-pyrone (0.01M) was treated with semicarbazide hydrochloride (0.01 M) 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- $126 \pm 1^\circ\text{C}$. Yield 60-65%.

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-diethyl 4-pyrone semicarbazone (DEPS) 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 70-75%.

RESULTS AND DISCUSSION

I.R.Spectra

IR spectrum of the ligand DEPS exhibits a medium broad band at 3220 cm^{-1} assigned^{14,15} to $\nu_{\text{N-H}}$. 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 1740 cm^{-1} assigned²¹ to $\nu_{\text{C=O}}$. In the spectra of the complexes, this band is shifted to higher frequency region and appear at 1770 cm^{-1} with slightly reduced intensity. The shift of the band and change in intensity suggest 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 $540-510\text{ cm}^{-1}$ in the complexes assignable¹⁹ to $\nu_{\text{M-O}}$. The IR spectrum of the ligand exhibits a band at 1500 cm^{-1} assigned²² to $\nu_{\text{C=N}}$. 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 ir region at $395-370\text{ cm}^{-1}$ assigned¹⁹ to $\nu_{\text{M-N}}$. The evidence of metal halogen is confirmed by the low molar conductance of the complexes in the range $1.6-3.6\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$. This statement is further confirmed by the appearance of a band in far ir region at $320-275\text{ cm}^{-1}$ which assigned¹⁹ to $\nu_{\text{M-X}}$. Nitrate complexes show characteristic medium intensity bands at 1375 and 1245 cm^{-1} with a separation of about 130 cm^{-1} due to monodentately coordinated nitrate²³ group.

The electronic spectral and magnetic susceptibility value tentatively proposes octahedral geometry of Co(II), Ni(II) and Cu(II) complexes.

Conductivity measurement

Molar conductance values of the complexes of Cobalt(II), Nickel(II) and Copper(II) were found to be in the range $1.6-3.6\text{ ohm}^{-1}\text{ mol}^{-1}$ in

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

Compounds (Colour)	Molar mass	Yield %	% Analysis found (calculated)				μ_{eff} B.M.	DT °C	Ω_m ohm -1 cm ² mol ⁻¹	λ_{max} electronic cm ⁻¹
			M	C	N	H				
DEPS (Colourless)	209	64		57.24 (57.41)	19.89 (20.09)	7.07 (7.17)				
[Co(DEPS) ₂ Cl ₂] (Yellow)	547.93	67	10.66 (10.75)	43.60 (43.80)	15.26 (15.33)	5.37 (5.47)	5.14	286	3.4	13100, 19700, 22840
[Co(DEPS) ₂ Br ₂] (Yellow)	636.745	63	9.14 (9.25)	37.52 (37.69)	13.04 (13.19)	4.62 (4.71)	8.10	279	3.6	13160, 19570, 22810
[Co(DEPS) ₂ I ₂] (Red)	730.738	70	7.91 (8.06)	32.69 (32.84)	11.38 (11.49)	4.06 (4.10)	4.89	273	3.1	13260, 19540, 22440
[Co(DEPS) ₂ (NO ₃) ₂] (Red)	600.93	65	9.69 (9.80)	39.80 (39.93)	13.81 (13.97)	4.92 (4.99)	4.94	281	3.3	12800, 19370, 22780
[Ni(DEPS) ₂ Cl ₂] (Brown)	547.71	60	10.60 (10.71)	43.62 (43.82)	15.21 (15.33)	5.40 (5.47)	3.17	240	3.2	10800, 15430, 24360
[Ni(DEPS) ₂ Br ₂] (Brown)	636.528	70	9.13 (9.22)	37.58 (37.70)	13.08 (13.19)	4.62 (4.71)	3.11	239	2.8	10560, 15470, 24100
[Ni(DEPS) ₂ I ₂] (Dee p red)	730.518	69	7.90 (8.03)	32.67 (32.85)	11.38 (11.49)	4.02 (4.10)	3.04	247	2.4	10470, 15610, 24140
[Ni(DEPS) ₂ (NO ₃) ₂] (Red)	600.71	70	9.68 (9.77)	39.81 (39.95)	13.84 (13.98)	4.90 (4.99)	3.09	248	2.6	10510, 15280, 24220
[Cu(DEPS) ₂ Cl ₂] (Blue)	552.54	66	11.38 (11.49)	43.28 (43.41)	15.08 (15.20)	5.36 (5.42)	1.93	270	1.8	11700, 17360
[Cu(DEPS) ₂ Br ₂] (Blue)	641.358	67	9.81 (9.90)	37.35 (37.42)	13.02 (13.09)	4.59 (4.67)	1.90	265	1.17	11450, 17270
[Cu(DEPS) ₂ (NO ₃) ₂] (Blue)	605.54	63	10.35 (10.49)	39.50 (39.63)	13.82 (13.87)	47.48 (47.54)	1.94	273	1.6	11670, 17220

DT = Decomposition Temperature

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

Compounds	$\nu_{\text{N-H}}$	$\nu_{\text{C=O}}$	$\nu_{\text{C=N}}$	$\nu_{\text{M-O}}$	$\nu_{\text{M-N}}$	$\nu_{\text{M-X}}$
DEPS	3260 s,b	1740 s,b	1500 s,b			
[Co(DEPS) ₂ Cl ₂]	3260 s,b	1765 m,b	1480 m,b	540 m	395 m	310 m
[Co(DEPS) ₂ Br ₂]	3260 s,b	1770 m,b	1475 m,b	535 m	390 m	285 m
[Co(DEPS) ₂ I ₂]	3260 s,b	1770 m,b	1475 m,b	535 m	385 m	275 m
[Co(DEPS) ₂ (NO ₃) ₂]	3260 s,b	1760 m,b	1475 m,b	535 m	390 m	
[Ni(DEPS) ₂ Cl ₂]	3260 s,b	1760 m,b	1480 m,b	525 m	395 m	320 m
[Ni(DEPS) ₂ Br ₂]	3260 s,b	1765 m,b	1480 m,b	520 m	390 m	290 m
[Ni(DEPS) ₂ I ₂]	3260 s,b	1765 m,b	1480 m,b	520 m	395 m	280 m
[Ni(DEPS) ₂ (NO ₃) ₂]	3260 s,b	1765 m,b	1480 m,b	525 m	370 m	
[Cu(DEPS) ₂ Cl ₂]	3260 s,b	1765 m,b	1475 m,b	510 m	395 m	320 m
[Cu(DEPS) ₂ Br ₂]	3260 s,b	1770 m,b	1475 m,b	510 m	390 m	290 m
[Cu(DEPS) ₂ (NO ₃) ₂]	3260 s,b	1765 m,b	1475 m,b	515 m	380 m	

m = medium, s = strong, b = broad

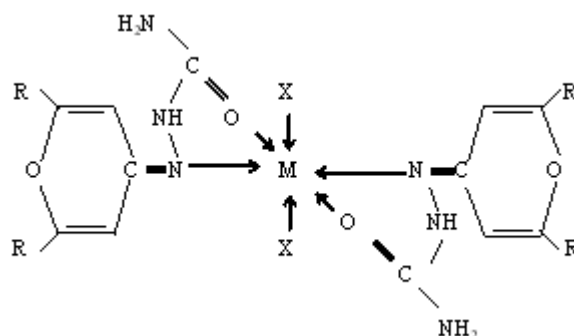


Fig.1: [M(DEPS)₂X₂]; M = Co(II), Ni(II) and Cu(II); X = Cl⁻, Br⁻, I⁻, NO₃⁻ and ClO₄⁻; R = Ethyl

DMF indicating their nonelectrolytic²² nature. 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.

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