

Physico-chemical study of Co(II), Ni(II) and Cu(II) complexes of nitrogen and sulphur containing Schiff base

B.K. RAI^{1*} and CHANDAN KUMAR²

¹Department of Chemistry, LNT College, Muzaffarpur - 842 002 (India).

²B. R. A. Bihar University, Muzaffarpur, Bihar (India).

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ABSTRACT

A series of complexes of the type $[M(DDMS)_2X_2]$ where M = Co(II), Ni(II) and Cu(II), X = Cl⁻, Br⁻, I⁻ and NO₃⁻; DDMS = 3, 4 dihydro- 5, 6- dimethoxy isocoumarin semicarbazone. Schiff base ligand DDMS obtained by the condensation of 3, 4 dihydro 5, 6 dimethoxy isocoumarine and semicarbazide hydrochloride. The ligand as well as complexes have been characterized by elemental analysis, molar conductance, molar mass, magnetic susceptibility, electronic and IR spectral data. Elemental analyses confirm the stoichiometry of the complexes is 1:2 [Metal:ligand]. Study of IR spectral data proposes DDMS acts as neutral bidentate ligand and coordination takes place through azomethine N and carbonyl oxygen of semicarbazone moiety. The remaining positions of metal ions are satisfied by negative ions, such as Cl⁻, Br⁻, I⁻ and NO₃⁻. The molar conductance measurement in DMF indicates the non electrolytic nature of the complexes. The study of electronic spectral data and magnetic susceptibility measurement proposes the geometry of complexes are octahedral in nature.

Key words: DDMS/Co(II), Ni(II) and Cu(II)/ Complexes/ Spectral study.

INTRODUCTION

Semicarbazone constitute one of the most important class of nitrogen and oxygen donor ligands¹. They form variety of metal complexes indicates the spectacular progress in bioinorganic and coordination chemistry². They exhibit remarkable antimicrobial potency such as antimalarial, antitumour, antiviral, anticancer, antibacterial and antifungal activities. They were also used as potential drugs and fungicidal agent³⁻¹⁰. Their antibacterial and antifungal activity are due to their ability to form chelates with transition metal ions. In view of the above applications of Schiff base and their metal complexes and in continuation of our earlier work¹¹⁻¹⁹ in this field, in the present paper we report the synthesis, characterization of Co(II), Ni(II) and Cu(II) complexes with Schiff base ligand DDMS[3,4-dihydro-5,6-dimethyl isocoumarin semicarbazone].

EXPERIMENTAL

This paper was presented in 46th Annual convention of Indian Chemical Society at Vellore on 02-06 Dec,2009.

All the chemicals and reagents were of reagent grade. All the solvent used in this work were used without any further purification. The IR spectra of the ligand and complexes were recorded on Perkin-Elmer model-577 spectrophotometer using KBr disc. Electronic spectra of the complexes were taken in DMF on a Cary-2390 spectrophotometer. Magnetic susceptibility value were measured by Gouy method using Hg[Co(NCS)₄] as a calibrant. Molar conductance values were made using Systronics conductivity meter model 303 in DMF.

Preparation of ligand DDMS

The Schiff base were prepared by the

condensation reaction of equimolar amounts of ketone and amine in ethanolic medium. Ethanolic solution of 3, 4-dihydro-5,6-dimethyl isocoumarin (0.01 M) was condensed with semicarbazide hydrochloride (0.01 M) dissolved in 10% ethanolic solution of sodium acetate in tetrahydrofuran. The resulting mixture was refluxed on water bath for 3-4 h with occasional stirring. The solution was cooled, kept for a night, filtered and dried in air oven. Yield 60%; m.p. $117 \pm 1^\circ\text{C}$.

Preparation of complexes

The complexes of Co(II), Ni(II) and Cu(II) were prepared by reacting respective metal halides dissolved in minimum amount of ethanol with ethanolic solution of ligand DDMS in molar ratio 1:2. The resulting solution were refluxed on water bath with occasional stirring for 2-3 h. The procedure carried out in each case were similar nature with slight variation of timing of reflux. On cooling solid coloured complexes separated out which was filtered, washed with ethanol, dried and recrystallised with ethanol. Yield in all cases 60-65%.

The following general method were adopted for the preparation of nitrate complexes. The metal complexes were synthesized by refluxation-precipitation method. The hot ethanolic solution of ligand DDMS (0.002 M) were mixed with ethanolic solution of respective metal nitrate (0.001 M). The resulting solution were heated on a water bath for 2 to 3 h. The procedure carried out in each case of similar nature with a slight variation of timing of reflux. The volume of the solution were reduced $\frac{1}{4}$ th of its original volume and poured in ice cold water to yield precipitate. The precipitate were allowed to stand for 24 h, then filtered off, washed with hot ethanol and dried in oven at 120°C . The yield were 60-65%.

The melting points of all the complexes were determined by open capillary method. The complexes were analysed for metal contents by standard procedures²⁰. IR spectra of the ligand and complexes were recorded using KBr disk on Perkin Elmer-577 spectrophotometer in the region $200-4000\text{ cm}^{-1}$. Magnetic susceptibilities were measured by Gouy method using $\text{Hg}[\text{Co}(\text{NCS})_4]$ as a calibrant.

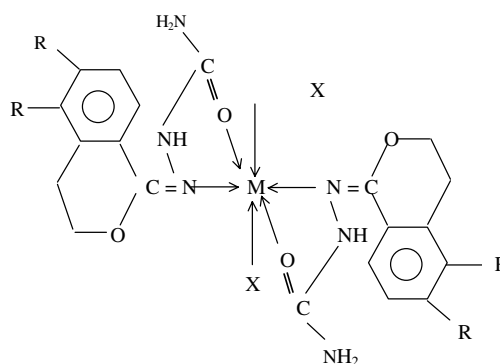
The electronic spectra were recorded on

a Cary-2390 spectrophotometer. Molar conductance measurements were made on Systronics conductivity meter 303 using DMF as a solvent. Analytical, colour, mol. wt. electronic spectra, conductivity, magnetic susceptibility data and decomposition temperature are recorded in Table-1. The salient features of IR spectral bands are recorded in Table-2.

RESULTS AND DISCUSSION

IR spectrum of DDMS exhibits a strong broad band at 3270 cm^{-1} assigned^{21,22} to $\nu_{\text{N-H}}$ modes of the terminal amino of semicarbazone moiety of isocoumarin. In the spectra of the complexes this band appear without any change indicating that coordination not takes place through N-atom of amino group. IR spectrum of the ligand exhibits a strong and broad band at 1580 cm^{-1} assigned^{21,23} to $\nu_{\text{C=N}}$. This band is shifted to lower frequency region with slightly reduced intensity indicating coordination of azomethine²⁵ N of the semicarbazone moiety. The linkage with N atom is further confirmed by the appearance of another band in the far ir region at $470-435\text{ cm}^{-1}$ assigned^{24,28} to $\nu_{\text{M-N}}$. The spectrum of the ligand exhibits a strong and broad band 1720 cm^{-1} which is assigned^{21,29} to $\nu_{\text{C=O}}$. On complexation, this band suffered a downward shift, suggesting coordination of the metal ion through the carbonyl oxygen atom of semicarbazone moiety.

The coordination through oxygen atom of semicarbazone moiety are further confirmed by the presence of a far ir band at $540-500\text{ cm}^{-1}$ assigned



M = Co(II) and Ni(II); X = Cl⁻, Br⁻, I⁻ and NO₃⁻; M = Cu(II); X = Cl⁻, Br⁻, I⁻ and NO₃⁻ [M(DDMS)₂X₂], R = Methoxy

Fig. 1:

Table 1: Analytical, colour, mol. formula, magnetic susceptibility, molar conductance, electronic spectra and decomposition temperature of the ligand DDMS and its metal complexes

Compounds (Colour)	Mol. weight	Yield %	% Metal	% Analysis found (calculated)			μ_{eff} B.M.	Ω_m ohm ⁻¹ cm ² mol ⁻¹	DT°C	λ_{max} electronic cm ⁻¹
				C	N	H				
DDMS (Colourless)	265.00	60		54.21 (54.33)	15.75 (15.84)	5.59 (5.66)				
[Co(DDMS) ₂ Cl ₂]	659.93	62	8.85 (8.92)	43.50 (43.64)	12.64 (12.72)	4.48 (4.54)	5.12	6.7	207	12160, 18300, 22140
[Co(DDMS) ₂ Br ₂]	748.738	63	7.77 (7.86)	38.27 (38.46)	11.10 (11.21)	3.82 (4.00)	4.84	6.4	201	12190, 8330, 22160
Brownish red [Co(DDMS) ₂ I ₂]	842.75	64	6.90 (6.99)	34.03 (34.17)	9.88 (9.96)	3.47 (3.55)	4.89	7.1	212	12020, 18407, 21312
Brown [Co(DDMS) ₂ (NO ₃) ₂]	712.93	65	8.17 (8.26)	41.28 (40.39)	11.69 (11.78)	4.12 (4.20)	4.97	7.6	210	12210, 18340, 21600
Deep brown [Ni(DDMS) ₂ Cl ₂]	659.71	62	8.80 (8.89)	43.54 (43.69)	12.64 (12.73)	4.48 (4.54)	3.20	8.3	232	10900, 13200, 20240
Green [Ni(DDMS) ₂ Br ₂]	748.51	60	7.76 (7.84)	38.33 (38.47)	11.13 (11.27)	3.84 (4.09)	3.24	8.1	216	10960, 13980, 20290
Green [Ni(DDMS) ₂ I ₂]	842.53	60	6.89 (6.96)	34.01 (34.18)	9.88 (9.96)	3.49 (3.56)	3.16	8.9	202	10660, 14160, 20410
Greenish red [Ni(DDMS) ₂ (NO ₃) ₂]	712.71	63	8.14 (8.23)	40.26 (40.40)	11.63 (11.78)	4.14 (4.26)	3.10	9.4	203	10600, 14060, 20600
Green [Cu(DDMS) ₂ Cl ₂]	664.54	64	9.48 (9.56)	43.24 (43.33)	12.52 (12.64)	4.47 (4.51)	1.94	10.1	212	14040, 26190
Blue [Cu(DDMS) ₂ Br ₂]	753.348	61	8.36 (8.43)	38.11 (38.22)	11.04 (11.15)	3.80 (3.98)	1.96	10.3	217	14360, 26360
Blue [Cu(DDMS) ₂ (NO ₃) ₂]	717.54	60	8.77 (8.85)	40.01 (40.13)	11.59 (11.70)	4.12 (4.18)	1.89	9.6	222	14270, 26280

DT = Decomposition Temperature

to ν_{M-O} . The coordination through metal-halogen is confirmed by the appearance of a band in the region 325-275 cm^{-1} assigned^{24,26} to ν_{M-X} (Cl, Br and I). The evidence of metal halogen coordination is further confirmed by the low value of molar conductance in the range 6.4-10.3 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$.

The presence of two bands at 1570 and 1450 cm^{-1} with a separation of 120 cm^{-1} suggest mono-coordinated nature of nitrate group^{30,31}.

Electronic spectra and magnetic susceptibility of the complexes

The Co(II) complexes display three band

in the region 12020-12210 cm^{-1} , 18300-18407 cm^{-1} and 22160-21312 cm^{-1} assigned to the transitions ${}^4T_{2g}(F) \leftarrow {}^4T_{1g}(F)$, ${}^4A_{2g}(F) \leftarrow {}^4T_{1g}(F)$ and ${}^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$ respectively which indicate octahedral^{32,33} geometry of Co(II) complex which further supported³⁴⁻³⁶ by high m_{eff} value in the range 4.84-5.12 B.M. The Ni(II) complexes exhibits three bands in the region 10600-10960 cm^{-1} , 13200-14160 cm^{-1} and 20240-20600 cm^{-1} assigned to ${}^3T_{2g}(F) \leftarrow {}^3A_{2g}(F)$, ${}^3T_{1g}(F) \leftarrow {}^3A_{2g}(F)$ and ${}^3T_{1g}(F) \leftarrow {}^3A_{2g}(F)$ respectively, suggesting octahedral^{33,37} geometry of Ni(II) complexes. The proposed geometry of Ni(II) complexes are further supported^{34,35,38} by m_{eff} value of Ni(II) complexes in the range 3.10-3.24 B.M. The Cu(II) complexes exhibit two ligand field bands in

Table 2: Key ir spectral bands (cm^{-1}) of ligand DDMS and its metal complexes

Compounds	ν_{N-H}	$\nu_{C=O}$	$\nu_{C=N}$	ν_{M-O}	ν_{M-N}	ν_{M-X}
DDMS	3270 s,b	1720 s,b	1580 s,b			
[Co(DDMS) ₂ Cl ₂]	3270 s,b	1695 m,b	155 m,b	505 m	440 m	310 m
[Co(DDMS) ₂ Br ₂]	3270 s,b	1695 m,b	1550 m,b	515 m	445 m	285 m
[Co(DDMS) ₂ I ₂]	3270 s,b	1690 m,b	1555 m,b	520 m	435 m	280 m
[Co(DDMS) ₂ (NO ₃) ₂]	3270 s,b	1690 m,b	1550 m,b	525 m	440 m	
[Ni(DDMS) ₂ Cl ₂]	3270 s,b	1695 m,b	1555 m,b	540 m	470 m	325 m
[Ni(DDMS) ₂ Br ₂]	3270 s,b	1700 m,b	1555 m,b	535 m	465 m	300 m
[Ni(DDMS) ₂ I ₂]	3270 s,b	1695 m,b	1555 m,b	535 m	460 m	275 m
[Ni(DDMS) ₂ (NO ₃) ₂]	3270 s,b	1690 m,b	1560 m,b	540 m	470 m	
[Cu(DDMS) ₂ Cl ₂]	3270 s,b	1690 m,b	1555 m,b	500 m	455 m	320 m
[Cu(DDMS) ₂ Br ₂]	3270 s,b	1690 m,b	1560 m,b	510 m	450 m	290 m
[Cu(DDMS) ₂ (NO ₃) ₂]	3270 s,b	1685 m,b	1560 m,b	520 m	455 m	
[Cu(DDMS) ₂ (ClO ₄) ₂]	3270 s,b	1685 m,b	1560 m,b	525 m	445 m	

m = medium, s = strong, b = broad

the region at 14040-14360 cm^{-1} and 26070-26360 cm^{-1} assigned to the transitions ${}^2T_{2g} \leftarrow {}^2E_g$ and charge transfer band which suggest distorted octahedral^{33,39} geometry for the Cu(II) complexes. The magnetic susceptibility value of Cu(II) complexes lie in the range 1.87-1.96 B.M.^{34,35,40}

Molar Conductance of the Complexes

Molar conductance value of the complexes are measured in the solvent DMF and the complexes were found to be non electrolytic⁴¹ in nature. The molar conductance value of complexes are lies in the range 6.4-10.3 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$.

CONCLUSION

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

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