



## Biocidal and Spectroscopic Study of the Co(II), Ni(II) and Cu(II) Complexes with Schiff Bases

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### ABSTRACT

Schiff base complexes of general formula  $[M(\text{MDES})_2X_2]$  where M = Co(II), Ni(II) and Cu(II), MDES = 1-methyl- 2, 6 diethyl piperidone semicarbazone and X = Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup> and NO<sub>3</sub><sup>-</sup>, have been synthesized. The ligand as well as metal complexes were characterized by elemental analyses, IR spectra, electronic spectra, molar conductivity and magnetic susceptibility measurements. On the basis of above observations it has been observed that ligand acts as neutral bidentate manner and coordination proposed through azomethine nitrogen and carbonyl oxygen of semicarbazone moiety. The remaining coordination centres are satisfied by anions such as Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup> and NO<sub>3</sub><sup>-</sup>. On the basis of electronic spectral data and magnetic susceptibility data the geometry of the complexes tentatively proposed octahedral. Antibacterial activity of ligand and complexes were also determined.

**Key words:** MDES, Schiff Base, Mixed ligand, Metal complexes, Antibacterial activity.

### INTRODUCTION

The chemistry of Schiff base and their metal complexes have been extensively studied in recent years owing to their pharmacological properties<sup>1-6</sup>. Schiff base ligands have been extensively investigated with respect to their numerous applications in organic synthesis as well as in pharmacology. Schiff base ligands have been successfully used in several catalytic asymmetric

reactions<sup>7-8</sup>. Schiff base metal complexes of nitrogen, oxygen and sulphur donor atoms are found to be effective catalysts for oxidation reactions<sup>9-10</sup>. In particular, the selective oxidation of alcohol into carbonyl compounds by metal complexes are well documented in the literature<sup>11-13</sup>. Schiff base complexes have served as a selective antimetastatic agent<sup>14</sup>, as anticancer drugs against<sup>15-17</sup> colorectal tumors. Recently, Schiff base transition metal complexes are reported by several

workers<sup>18-23</sup>. Receiving impetus from the above observations and in continuation of our research programme<sup>24-28</sup> on complexes of Schiff base ligand, the present paper, illustrates the synthesis and structural investigation of Schiff base complexes of Co(II), Ni(II) and Cu(II) with 1-methyl-2,6-diethyl piperidone semicarbazone (MDES).

### EXPERIMENTAL

All the chemicals used were BDH reagents. Melting points were determined in open capillaries and are uncorrected. The metal contents of all the complexes were analysed using standard procedure<sup>29</sup>. The IR spectra of the ligand and complexes were recorded on Beckmann IR-20 spectrophotometer using KBr pellets. The electronic spectra of the complexes were recorded on a Cary 2390 Spectrophotometer. Magnetic moment was measured by Gouy balance using  $\text{Hg}[\text{Co}(\text{NCS})_4]$  as a calibrant. The molar conductance were done on Toshniwal conductivity bridge using DMF as a solvent. Analytical data, colour, molar conductivity, electronic spectral data, magnetic susceptibility, decomposition temperature and molar mass are recorded in Table - 1 and salient features of IR spectra are recorded in Table - 2.

#### Preparation of the ligand

Ethanol solution of 1-methyl-2,6-diethyl piperidone was treated with ethanolic solution of semicarbazide/thiosemicarbazide in 1:1 molar ratio. The resulting reaction mixture was heated on water bath for 5-6 h, when polycrystalline colourless solid began to separate out after allowing the solution to stand overnight. It was filtered washed with ethanol and dried in an electric oven, yield 65-70%, mp  $171 \pm 1^\circ\text{C}$ .

#### Preparation of the complexes

The complexes of Co(II), Ni(II) and Cu(II) have been formed by reacting an ethanolic solution of corresponding metal halide/metal nitrate with ethanolic solution of ligand 1-methyl-2,6-diethyl piperidone semicarbazone (MDES) in the molar ratio 1:2. The procedure carried out in each case was of similar nature with a slight variation of timing of reflux. The coloured complexes obtained in each case were cooled, filtered and washed with ethanol several times to remove any excess of the ligand.

Finally, complexes were washed with anhydrous diethyl ether and dried in electric oven. Yield 65-70%.

### RESULTS AND DISCUSSION

The IR spectra of the ligands as well as complexes have been measured in the region  $4000-200\text{ cm}^{-1}$ . The IR spectra of the ligand shows strong band at  $1480\text{ cm}^{-1}$  assignable<sup>30-32</sup> to the  $\nu_{\text{C}=\text{N}}$ . In the spectra of the complexes, this band shows red shift with slightly reduced intensity. The shift of the band and change in intensity suggest coordination of the azomethine nitrogen with metal ion. The linkage with azomethine N is further supported by the appearance of a far ir band in the region  $420-400\text{ cm}^{-1}$  in the complexes assigned<sup>29-33</sup> to  $\nu_{\text{M}-\text{N}}$ . The next IR spectra of the ligand shows a sharp and strong band at  $1665\text{ cm}^{-1}$  assigned<sup>29,34</sup> to  $\nu_{\text{C}=\text{O}}$ . In the spectra of the complexes this band also shows red shift appearing in the region at  $1700\text{ cm}^{-1}$  indicating coordination through carbonyl oxygen of semicarbazone moiety. The coordination with carbonyl oxygen atom is further supported by the appearance of a band in the far ir region at  $520-500\text{ cm}^{-1}$  assigned<sup>29,30,32,33,35</sup> as  $\nu_{\text{M}-\text{O}}$ . The coordination through metal halogen is indicated by the appearance of a band in the region  $325-270\text{ cm}^{-1}$  assigned<sup>29,30,32,33</sup> to  $\nu_{\text{M}-\text{X}}$  (Cl<sup>-</sup>, Br<sup>-</sup> or I<sup>-</sup>). The evidence of metal halogen is further supported by the low value of molar conductance of the complexes in the range  $2.3-5.8\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$ . The nitrate complexes exhibit two additional ir bands at  $1580\text{ cm}^{-1}$  and  $1460\text{ cm}^{-1}$  with a separation of  $120\text{ cm}^{-1}$  suggests monocoordinated behaviour of nitrate group<sup>33,36</sup>.

On the basis of above ir spectral bands assignments, it is proposed that ligand MDES behaves as neutral bidentate manner and coordination takes place through azomethine nitrogen and carbonyl oxygen atom of semicarbazone moiety. The remaining coordination sites are occupied by anions such as Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup> and  $\text{NO}_3^-$ .

The electronic spectral and magnetic susceptibility values tentatively proposes octahedral geometry of Cobalt(II), Nickel(II) and Copper(II) complexes.

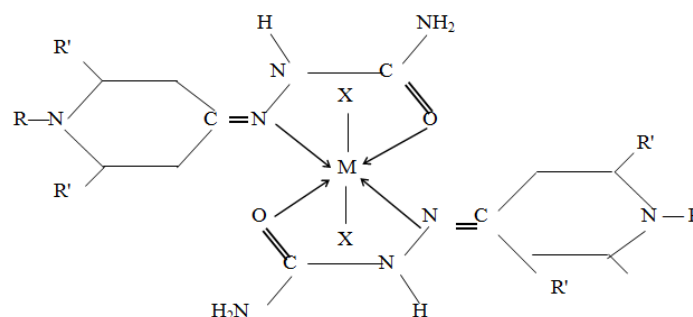
**Table 1: Analytical, colour, molar mass, magnetic susceptibility, conductivity measurement and decomposition temperature of ligand MDES and its metal complexes**

Compounds (Colour)	Molar mass	% Analysis found (calculated)				$\mu_{\text{eff}}$ B.M	$\lambda_{\text{max}}$ cm <sup>-1</sup>	electronic $W_m$	ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup>	Decompo- sition Temp °C
		M	C	N	H					
MDES (Colourless)	224		58.87 (58.92)	24.96 (25.00)	6.87 (6.92)					
[Co(MDES) <sub>2</sub> Cl <sub>2</sub> ] (Yellowish red)	577.93	10.13 (10.19)	45.65 (45.68)	19.33 (19.40)	6.87 (6.92)	5.16	13600	7.4	271	
[Co(MDES) <sub>2</sub> Br <sub>2</sub> ] (Yellowish red)	666.74	8.75 (8.83)	39.55 (39.61)	16.75 (16.79)	5.90 (5.99)	5.11	13900	7.8	280	
[Co(MDES) <sub>2</sub> I <sub>2</sub> ] (Dark brown)	760.73	7.70 (7.74)	34.65 (34.70)	14.68 (14.72)	5.19 (5.25)	4.87	14300	7.1	301	
[Co(MDES) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ] (Dark brown)	630.93	9.30 (9.34)	41.80 (41.84)	17.70 (17.75)	6.25 (6.33)	4.93	20000	7.3	289	
[Ni(MDES) <sub>2</sub> Cl <sub>2</sub> ] (Light yellow)	577.71	10.10 (10.16)	45.62 (45.69)	19.31 (19.38)	6.86 (6.92)	3.04	11200	8.3	316	
[Ni(MDES) <sub>2</sub> Br <sub>2</sub> ] (Light yellow)	666.53	8.74 (8.80)	39.55 (39.60)	16.75 (16.80)	5.92 (6.00)	3.01	11900	8.1	312	
[Ni(MDES) <sub>2</sub> I <sub>2</sub> ] (Yellowish brown)	760.51	7.65 (7.71)	34.67 (34.71)	14.65 (14.72)	5.18 (5.25)	3.12	11300	8.8	317	
[Ni(MDES) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ] (Brownish yellow)	630.71	9.24 (9.30)	41.79 (41.85)	17.67 (17.75)	6.30 (6.34)	3.09	11600	8.4	303	
[Cu(MDES) <sub>2</sub> Cl <sub>2</sub> ] (Blue)	582.54	10.82 (10.90)	45.25 (45.31)	19.15 (19.22)	6.80 (6.86)	1.87	11300	8.7	269	
[Cu(MDES) <sub>2</sub> Br <sub>2</sub> ] (Bluish green)	611.35	9.40 (9.46)	39.25 (39.31)	16.60 (16.68)	5.90 (5.95)	1.94	12100	9.1	263	
[Cu(MDES) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ] (Deep blue)	635.54	9.91 (9.99)	41.47 (41.53)	17.57 (17.62)	7.15 (7.22)	1.96	12000	8.2	279	

**Table 2: Key IR spectral bands of ligand MDES and its metal complexes**

Compounds	$\nu_{C=O}$	$\nu_{C=N}$	$\nu_{M-O}$	$\nu_{M-N}$	$\nu_{M-X}$
MDES	1665 s,b	1480 s,m			
[Co(MDES) <sub>2</sub> Cl <sub>2</sub> ]	1700 m,b	1455 m,b	505 m	400 m	305 m
[Co(MDES) <sub>2</sub> Br <sub>2</sub> ]	1695 m,b	1460 m,b	510 m	420 m	280 m
[Co(MDES) <sub>2</sub> I <sub>2</sub> ]	1690 m,b	1455 m,b	515 m	410 m	270 m
[Co(MDES) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ]	1695 m,b	1450 m,b	510 m	415 m	
[Ni(MDES) <sub>2</sub> Cl <sub>2</sub> ]	1700 m,b	1460 m,b	500 m	400 m	325 m
[Ni(MDES) <sub>2</sub> Br <sub>2</sub> ]	1695 m,b	1455 m,b	495 m	395 m	295 m
[Ni(MDES) <sub>2</sub> I <sub>2</sub> ]	1690 m,b	1455 m,b	500 m	400 m	275 m
[Ni(MDES) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ]	1695 m,b	1460 m,b	395 m	395 m	
[Cu(MDES) <sub>2</sub> Cl <sub>2</sub> ]	1695 m,b	1455 m,b	495 m	410 m	315 m
[Cu(MDES) <sub>2</sub> Br <sub>2</sub> ]	1700 m,b	1450 m,b	500 m	420 m	285 m
[Cu(MDES) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ]	1690 m,b	1455 m,b	495 m	415 m	

m = medium, s = strong, b = broad



M = Co(II) and Ni(II); X = Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup> and NO<sub>3</sub><sup>-</sup>; M = Cu(II); X = Cl<sup>-</sup>, Br<sup>-</sup> and NO<sub>3</sub><sup>-</sup>; R = Methyl; R' = Ethyl

**Fig.1: [M(MDES)<sub>2</sub>X<sub>2</sub>]**

### Molar conductivity

Molar conductance value of the complexes are measured in the solvent DMF and the complexes were found to be non electrolytic<sup>39</sup> in nature. The molar conductance value of the complexes are lies in the range 7.1-9.1 ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>.

### Antimicrobial activity

Antimicrobial activity of the ligand MDES and their metal complexes of Co(II), Ni(II) and Cu(II) have been screened by disc plate method<sup>40</sup>. On comparison with reference to antibiotic, the complexes were found to be more effective than ligand due to chelation theory<sup>41</sup>.

### CONCLUSION

Thus on the basis of above observations the complexes of Cobalt(II), Nickel(II) and Copper(II) tentatively propose an octahedral geometry as shown in Fig.-1.

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