

NOTE

Complexes of Co(II), Ni(II) and Cu(II) with a Bidentate Schiff Base and Some Nitrogen Donor Neutral Ligands

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Complexes of the type $[MLL'_2X_2]$ where M = Co(II), Ni(II), Cu(II); L = *m*-nitrobenzaldehyde semicarbazone (MNBS); L' = pyridine (Py), γ -picoline (γ -Pic) and quinoline (Qn) X = Cl⁻, Br⁻ and NO₃⁻ were synthesized. The infrared spectra indicate the coordination of both the ligands to metal ion. Magnetic moment and electronic spectral data provide existence of octahedral geometry in all the complexes.

In the present communication we wish to report the studies on some complexes of Co(II), Ni(II) and Cu(II) with the *m*-nitrobenzaldehyde semicarbazone and some nitrogen donor neutral ligands.

The Schiff base (*m*-nitrobenzaldehyde semicarbazone) was prepared as reported earlier.¹ The complexes were prepared by mixing the ethanolic solution of metal salts, Schiff base and neutral nitrogen donor ligands (pyridine, γ -picoline, quinoline) in 1 : 1 : 2 molar ratio. The resulting complexes were filtered, washed with ethanol, then with ether and dried *in vacuo*. The elemental analyses were carried out by standard methods. The molecular weights of the complexes were measured by rast's camphor method. Molar conductances were measured using 10⁻³ M solution (nitrobenzene) in a Systronic 304 direct reading conductivity meter. Magnetic moments were determined by Gouy method. IR spectra were recorded on a Shimadzu-480 spectrophotometer. Electronic spectra were recorded on a Shimadzu 160-A spectrophotometer. The analytical and physical data of the isolated complexes are given in Table-1.

The elemental analysis suggests the formula $[MLL'_2X_2]$ for all the complexes where M = Co(II), Ni(II), Cu(II); L = *m*-nitrobenzaldehyde semicarbazone (MNBS); L' = neutral nitrogen donor ligands pyridine (Py), γ -picoline (γ -Pic), quinoline (Qn); X = Cl⁻, Br⁻ and NO₃⁻. All the complexes have melting point above 200°C. The molecular weight measurements indicate that all the complexes are monomeric in nature. Low molar conductance values (4.2–8.3 mhos) indicate that all the complexes are non-electrolyte.

TABLE-I
ANALYTICAL AND PHYSICAL DATA OF Co(II), Ni(II) AND Cu(II) COMPLEXES

Compound (Colour)	Mol. wt (Found/calcd)	Analysis % found/(calcd)			μ_{eff} (B.M.)
		M	N	Cl/Br	
[Cu(MNBS)(γ -pic) ₂ Cl ₂] (Sky blue)	511.30 (528.50)	11.90 (12.01)	16.02 (15.89)	13.01 (13.43)	1.72
[Cu(MNBS)(Qn) ₂ Cl ₂] (Grey)	588.20 (600.50)	10.43 (10.57)	14.12 (13.98)	11.99 (11.82)	1.81
[Cu(MNBS)(Py) ₂ Cl ₂] (Blue)	490.60 (500.50)	12.46 (12.68)	16.88 (16.78)	14.22 (14.18)	1.99
[Cu(MNBS)(γ -pic) ₂ Br ₂] (Blue)	607.30 (617.50)	10.22 (10.28)	13.71 (13.60)	25.88 (25.91)	1.73
[Cu(MNBS)(Qn) ₂ Br ₂] (Greenish brown)	673.80 (689.50)	9.02 (9.20)	12.27 (12.18)	23.03 (23.20)	1.93
[Cu(MNBS)(Py) ₂ Br ₂] (Pea green)	583.20 (591.50)	10.61 (10.73)	14.48 (14.20)	26.97 (27.04)	1.89
[Cu(MNBS)(γ -pic) ₂ (NO ₃) ₂] Light green	590.10 (581.50)	10.83 (10.92)	14.56 (14.44)	—	1.74
[Cu(MNBS)(Qn) ₂ (NO ₃) ₂] (Dark blue)	648.30 (653.50)	9.28 (9.71)	12.97 (12.85)	—	1.95
[Cu(MNBS)(Py) ₂ (NO ₃) ₂] (Purple)	548.80 (553.50)	11.41 (11.47)	15.25 (15.17)	—	1.91
[Co(MNBS)(γ -pic) ₂ Cl ₂] (Pink)	531.97 (523.93)	11.36 (11.24)	16.21 (16.03)	13.66 (13.55)	4.23
[Co(MNBS)(Qn) ₂ Cl ₂] (Blue)	583.30 (595.93)	9.96 (9.88)	14.22 (14.09)	12.02 (11.91)	4.19
[Co(MNBS)(Py) ₂ Cl ₂] (Bluish pink)	504.30 (495.93)	11.86 (11.88)	16.87 (16.93)	14.36 (14.31)	4.33
[Co(MNBS)(γ -pic) ₂ Br ₂] (Light pink)	622.88 (612.93)	9.75 (9.60)	13.83 (13.70)	25.91 (26.10)	4.26
[Co(MNBS)(Qn) ₂ Br ₂] (Blue)	699.32 (684.93)	8.53 (8.60)	12.16 (12.26)	23.04 (23.36)	4.38
[Co(MNBS)(Py) ₂ Br ₂] (Dark blue)	593.70 (584.93)	10.11 (10.07)	14.44 (14.36)	27.12 (27.35)	4.01
[Ni(MNBS)(γ -pic) ₂ Cl ₂] (Greenish white)	531.92 (523.70)	11.39 (11.20)	16.31 (16.03)	13.63 (13.55)	3.66
[Ni(MNBS)(Qn) ₂ Cl ₂] (Yellow)	608.37 (595.70)	9.93 (9.85)	14.22 (14.10)	12.06 (11.91)	3.29
[Ni(MNBS)(Py) ₂ Cl ₂] (Light green)	483.20 (495.70)	11.68 (11.84)	16.68 (16.94)	14.38 (14.32)	3.23
[Ni(MNBS)(Qn) ₂ (NO ₃) ₂] (Parrot green)	651.80 (648.70)	9.31 (9.04)	13.83 (12.94)	—	3.55
[Ni(MNBS)(Py) ₂ (NO ₃) ₂] (Light green)	563.90 (548.70)	10.77 (10.69)	15.32 (15.30)	—	3.48

The IR spectrum of the ligand shows a broad band at 3400 cm^{-1} due to $\nu(\text{NH})$ mode of NH_2 group², which remain unchanged in the complexes indicating the presence of free —NH_2 group. The Schiff base shows a broad band at 1630 cm^{-1} which may be assigned to $\nu(\text{C}=\text{N})$ mode of azomethine nitrogen³ which exhibits a negative shift by $15\text{--}20\text{ cm}^{-1}$ on coordination to the metal ion through azomethine nitrogen in the complexes. The strong absorption band appearing at 1720 cm^{-1} attributed to the stretching vibration of the $\nu(\text{C}=\text{O})$ band in the ligand⁴ which shifts to lower frequency by $60\text{--}70\text{ cm}^{-1}$ further attributes the coordination through oxygen of $\text{C}=\text{O}$ group. In the IR spectra of nitrate complexes appearance of bands at $1030, 1280, 940$ and 1530 cm^{-1} confirms the presence of coordinated NO_3^- group.⁵ The bands at 1620 and 1580 cm^{-1} due to γ -picoline, quinoline and pyridine suggest the coordination of the ligand to the metal ion through heterocyclic nitrogen atom.⁶

The Cu(II) complexes have normal magnetic moment values in the range $1.72\text{--}1.99\text{ B.M.}$ ⁷ The electronic spectra of these complexes show a broad band around 15337 cm^{-1} which may be assigned to the transition ${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}$.⁸ Besides a broad band at *ca.* 26737 cm^{-1} is observed which may be due to charge transfer band. The Ni(II) complexes have magnetic moment values $3.23\text{--}3.66\text{ B.M.}$ ⁷ The electronic spectra of Ni(II) complexes show three well resolved bands at *ca.* $9800, 17574$ and 24038 cm^{-1} assigned to ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F}), {}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$ and ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$ transitions respectively under an octahedral environment around Ni(II) ion.⁸ The Co(II) complexes have magnetic moment values between $4.01\text{--}4.38\text{ B.M.}$ ⁷ expected for high spin octahedral Co(II) complexes and the electronic spectra show two bands at *ca.* 9100 and 18500 cm^{-1} which may be assigned to the transition ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$ and ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})$ which suggest octahedral geometry.⁸

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