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Synthesis and Characterization of Mononuclear and Binuclear Complexes of Ni(II) and Cu(II) derived from Aromatic Hydrazones

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In the present work, the synthesis and characterization of mononuclear and binuclear complexes of Ni(II) and Cu(II) derived from aromatic hydrazones is described.

Key Words: Mononuclear and binuclear complexes, Ni(II), Cu(II), Hydrazones.

INTRODUCTION

Several authors reported the hydrazones of aldehydes and ketones[1–4] for the formation of Schiff's bases and their metal complexes. In continuation of the work of Jha *et al.*[5] we have prepared some new hydrazones, *viz.*, *o*-hydroxy-5-methyl salicylidene hydrazone (OHMSAHYH), *o*-hydroxy-5-methyl acetophenone hydrazone (OHMAPHYH), 2-Hydroxy-4-methoxy acetophenone hydrazone (OHMEAPHYH), *o*-hydroxy-5-methyl acetophenone phenyl hydrazone (OHMAPHYPH), *o*-hydroxy-4-methoxy salicylidene phenyl hydrazone (OHMESAHYPH) and *o*-hydroxy-5-methyl salicylidene phenyl hydrazone (OHMSAHYPH) and the mononuclear as well as binuclear complexes of Ni(II) and Cu(II) have been synthesized and characterized on the basis of elemental analysis, conductance, magnetic moments and spectral data.

EXPERIMENTAL

Preparation of ML_2 compounds: The corresponding aqueous metal salt solutions (0.01 M) were treated with methanoic solutions of ligands (0.02 M) and digested on water bath for about half an hour. The solid, coloured compounds were filtered, washed with methanol and dried over fused calcium chloride.

Preparation of ML_2B_2 compounds: The above prepared ML_2 solid compounds were taken in fusion tubes and treated with 3–4 drops of α,β,γ-picoline. The fusion tubes were heated on a water bath for about 5 min and left for 3–4 d. The solid compounds were washed with methanol, filtered and dried over vacuum desiccators.

Preparation of $M_2L_2X_2$ or $M_2L_2(NO_3)_2$ type complexes: The ML_2 type complexes were dissolved in hot ethanol and treated with aqueous hydrated MX_2 or $M(NO_3)_2$ type compound in the ratio (1 : 1). Both solutions were taken in a conical flask attached with Liebig condenser. The solutions were refluxed for about 6 h. The solid compounds were cooled, filtered, washed with ethanol and water and dried in vacuum desiccators.

Preparation of $M_2L_2X_2B_4$ type complexes: The above prepared $M_2L_2X_2$ complexes were taken in fusion tubes and treated with 3–4 drops of α,β,γ-picoline and heated on a water bath for 5 min and left for 3–4 d. The solid compounds were washed with a small portion of methanol, filtered and dried over vacuum desiccators.

The metal complexes were decomposed with fuming nitric acid and metal content was determined with the method reported in literature[6, 7]. C, H and N were determined at CDRI, Lucknow.

The magnetic moments of solids complexes were determined at room temperature on a Gouy balance using solid copper(II) sulphate pentahydrate as a calibrant. The conductivities of all the complexes were determined by using Systronics conductivity meter bridge in 10^{-3} M in DMF solution. IR spectra, electronic spectra and UV reflectance spectra were recorded at CDRI, Lucknow.

RESULTS AND DISCUSSION

On the basis of analytical data (Table-1) it has been noted that Ni(II) and Cu(II) form mononuclear complexes of the formulae NiL_2, CuL_2, NiL_2B_2 and CuL_2B_2 and binuclear complexes of the formulae NiL_2X_2, $Cu_2L_2X_2$, $Ni_2L_2(NO_3)_2$, $Cu_2L_2(NO_3)_2$, $Cu_2L_2X_2B_4$ type, where L denotes:

(1) *o*-hydroxy 5-methyl salicylidene hydrazone (OHMSAHYH)
(2) *o*-hydroxy 5-methyl acetophenone hydrazone (OHMAPHYH)
(3) 2-Hydroxy 4-methoxy acetophenone hydrazone (OHMEAPHYH)
(4) *o*-hydroxy 5-methyl acetophenone phenyl hydrazone (OHMAPHYPH)
(5) *o*-hydroxy 4-methoxy salicylidene phenyl hydrazone (OHMESAHYPH)
(6) *o*-hydroxy 5-methyl salicylidene phenyl hydrazone (OHMSAHYPH)

X = Cl and B = α, β, γ-picoline.

TABLE-1
ANALYTICAL DATA OF Ni(II) AND Cu(II) COMPLEXES OF HYDRAZONES

S.No.	Formula	Colour	Element analysis (%), Found (Calcd.)			
			C	H	N	M
1.	$Ni(OHMAPHY)_2$	Yellow	60.93 (56.25)	5.37 (5.72)	16.95 (14.50)	17.75 (15.10)
2.	$Ni(OHMEAPHY)_2$	Pale yellow	55.70 (51.92)	5.18 (5.28)	15.62 (13.46)	16.39 (13.94)
3.	$Ni(OHMSAHY)_2$	Light yellow	50.93 (53.93)	4.37 (5.05)	16.95 (15.73)	17.75 (16.29)
4.	$Ni(OHMAPHYP)_2$	Light yellow	60.63 (67.16)	5.58 (5.59)	10.82 (10.44)	11.33 (10.82)
5.	$Ni(OHMEAPHYP)_2$	Deep yellow	63.72 (63.30)	4.70 (5.27)	11.29 (09.84)	12.12 (10.32)
6.	$Ni(OHMSAHYP)_2$	Pink	69.70 (66.04)	5.55 (5.11)	10.82 (11.00)	11.33 (11.54)
7.	$Ni(\alpha, \beta, \gamma\text{-pic})_2\cdot(OHMSAHY)_2$	Green	50.54 (67.71)	5.90 (5.01)	17.00 (13.16)	11.05 (09.09)

S.No.	Formula	Colour	Element analysis (%), Found (Calcd.)			
			C	H	N	M
8.	Ni(α, β, γ-pic)$_2$·(OHMEAPHYP)$_2$	Yellowish green	68.10 (65.68)	8.90 (6.02)	12.91 (11.49)	9.11 (8.03)
9.	Cu(OHMAPHY)$_2$	Green	50.12 (55.45)	5.32 (5.64)	17.63 (14.37)	18.89 (16.31)
10.	Cu(OHMEAPHY)$_2$	Green	52.88 (51.24)	5.14 (5.21)	17.40 (13.26)	15.30 (15.07)
11.	Cu(OHMSAHY)$_2$	Light green	50.11 (53.10)	5.33 (4.97)	16.64 (15.48)	18.88 (17.57)
12.	Cu(OHMAPHYP)$_2$	Green	64.78 (66.47)	5.11 (5.53)	11.54 (10 34)	12.90 (11.73)
13.	Cu(OHMEAPHYP)$_2$	Light Green	64.82 (62.82)	5.66 (5.23)	11.70 (09.77)	12.00 (10.99)
14.	Cu(OHMAPHYP)$_2$	Light green	62.79 (65.49)	5.10 (5.06)	11.52 (12 28)	12.90 (10.91)
15.	Cu(α, β, γ-pic)$_2$·(OHMSAHY)$_2$	Gray	60.92 (59.65)	5.82 (6.11)	16.80 (16.06)	12.75 (12.04)
16.	Cu(α, β, γ-pic)$_2$·(OHMSAHYP)$_2$	65.43 (67.55)	05.50 (05.92)	12.55 (12.44)	— —	09.71 (09.33)
17.	Ni$_2$(OHMAPHY)$_2$Cl$_2$	36.40 (41.99)	03.68 (04.27)	12.33 (10.88)	15.33 (13.78)	25.61 (22.82)
18.	Ni$_2$(OHMEAPHY)$_2$Cl$_2$	39.35 (31.39)	04.15 (04.10)	11.40 (14.51)	14.68 (14.67)	23.67 (24.13)
19.	Ni$_2$(OHMSAHY)$_2$(NO$_3$)$_2$	32.25 (35.59)	02.20 (03.33)	10.23 (15.57)	— —	22.41 (21.76)
20.	Ni$_2$(OHMAPHY)$_2$Cl$_2$[α, β, γ-pic]$_4$	52.00 (54.39)	04.92 (05.96)	13.11 (13.35)	08.85 (08.45)	14.20 (14.00)
21.	Ni$_2$(OHMEAPHY)$_2$Cl$_2$[α, β, γ-pic]$_4$	53.98 (52.39)	05.22 (05.74)	13.15 (12.86)	08.20 (08.14)	14.11 (13.49)
22.	Ni$_2$(OHMSAHY)$_2$(NO$_3$)$_2$[α, β, γ-pic]$_4$	48.90 (50.03)	04.95 (05.32)	13.12 (16.21)	— —	14.11 (13.59)
23.	Cu$_2$(OHMAPHY)$_2$(NO$_3$)$_2$	34.58 (37.42)	04.24 (03.81)	14.40 (14.55)	— —	23.20 (22.02)
24.	Cu$_2$(OHMEAPHY)$_2$(NO$_3$)$_2$	34.57 (35.46)	03.60 (03.61)	04.23 (13.79)	— —	23.11 (20.86)
25.	Cu$_2$(OHMAPHY)$_2$Cl$_2$	56.11 (41.22)	11.99 (04.19)	04.12 (10.68)	15.13 (13.53)	27.13 (24.25)
26.	Cu$_2$(OHMEAPHY)$_2$Cl$_2$	38.51 (38.84)	03.92 (03.95)	11.40 (10.07)	14.48 (12.75)	39.53 (22.85)
27.	Cu$_2$(OHMAPHY)$_2$Cl$_2$[α, β, γ-pic]$_4$	52.00 (53.77)	05.92 (05.89)	13.47 (13.20)	08.74 (08.36)	15.33 (14.98)
28.	Cu$_2$(OHMEAPHY)$_2$(NO$_3$)$_2$[α, β, γ-pic]$_4$	49.23 (48.87)	05.32 (05.35)	05.42 (15.00)	— —	14.25 (13.61)

TABLE-2
MAGNETIC MOMENT AND ELECTRONIC SPECTRAL DATA OF COMPLEXES

Sl. No.	Formula	μ_{eff} (BM)	Electronic spectral band (cm^{-1})		
			$^1A_{1g} \rightarrow {}^1A_{2g}$	$^1A_{1g} \rightarrow {}^1B_{1g}$	
1.	$Ni(OHMAPHY)_2$	Diamag.	15550	19960	
2.	$Ni(OHMEAPHY)_2$	Diamag.	15460	19900	
3.	$Ni(OHMSAHY)_2$	Diamag.	15550	19960	
4.	$Ni(OHMAPHYP)_2$	Diamag.	15500	19895	
5.	$Ni(OHMEAPHYP)_2$	Diamag.	15510	19910	
6.	$Ni(OHMSAHYP)_2$	Diamag.	15500	19885	
			$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$
7.	$Ni(\alpha, \beta, \gamma\text{-pic})_2\cdot(OHMAPHY)_2$	2.99–3.02	10650	16150	26150
8.	$Ni(\alpha, \beta, \gamma\text{-pic})_2\cdot(OHMAPHY)_2$	2.99–3.02	10550	15650	26850
			$^2B_{1g} \rightarrow {}^2A_{1g}$ to $^2B_{1g} \rightarrow {}^2E_g$		
9.	$Cu(OHMAPHY)_2$	1.84	16000 (Single band)		
10.	$Cu(OHMEAPHY)_2$	1.81	15584, 16600		
11.	$Cu(OHMSAHY)_2$	1.83	16000		
12.	$Cu(OHMAPHYP)_2$	1.83	15000, 16500		
13.	$Cu(OHMEAPHYP)_2$	1.82	16000		
14.	$Cu(OHMSAHYP)_2$	1.83	15000, 16500		
			$^2E_g \rightarrow {}^2T_{2g}$, [$^2B_{1g} \rightarrow {}^2A_{1g}$ $^2B_{1g} \rightarrow {}^2B_{2g}$]		
15.	$Cu(\alpha, \beta, \gamma\text{-pic})_2\cdot(OHMSAHY)_2$	1.89–1.91	13750–14500		
16.	$Cu(\alpha, \beta, \gamma\text{-pic})_2\cdot(OHMSAHYP)_2$	1.91–1.92	13750–14500		
			$^1A_{1g} \rightarrow {}^1A_{2g}$	$^1A_{1g} \rightarrow {}^1B_{1g}$	
17.	$Ni_2(OHMAPHY)_2Cl_2$		15550	19960	
18.	$Ni_2(OHMEAPHY)_2Cl_2$		15510	19910	
19.	$Ni_2(OHMSAHY)_2(NO_3)_2$		15460	19900	
			$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$		
20.	$Ni_2(OHMAPHY)_2Cl_2[\alpha, \beta, \gamma\text{-pic}]_4$	2.40–2.42	10650, 16180, 26150		
21.	$Ni_2(OHMEAPHY)_2Cl_2[\alpha, \beta, \gamma\text{-pic}]_4$	2.21–2.42	10550, 16050, 26050		
22.	$Ni_2(OHMSAHY)_2(NO_3)_2[\alpha, \beta, \gamma\text{-pic}]_4$	2.32–2.41	10200, 15650, 26850		

Sl. No.	Formula	μ_{eff} (BM)	Electronic spectral band (cm^{-1})
			$^2B_{1g} \rightarrow {}^2E_g$
23.	$Cu_2(OHMAPHY)_2(NO_3)_2$	1.12	15384, 16304
24.	$Cu_2(OHMEAPHY)_2(NO_3)_2$	1.14	15364, 16304
25.	$Cu_2(OHMAPHY)_2Cl_2$	1.16	14600, 15100
26.	$Cu_2(OHMEAPHY)_2Cl_2$	1.20	15000–16500
			$^2E_g \rightarrow {}^2T_{2g}$
27.	$Cu_2(OHMAPHY)_2\ Cl_2$ [α, β, γ-pic]$_4$	1.12	13790, 14000
28.	$Cu_2(OHMEAPHY)_2(NO_3)_2$ [α, β, γ-pic]$_4$	1.39	13000, 14000

TABLE-3
KEY IR SPECTRAL BANDS (cm^{-1}) OF MONONUCLEAR METAL COMPLEXES

Formula	ν(M–N)	ν(M–O)	ν(NH_2)	ν(C=N)	ν(C–O)	ν(O–Me)	ν(C=O)
$Ni(OHMAPHY)_2$	450	500	3420	1630	1290	1010	—
$Ni(OHMEAPHY)_2$	455	520	3410	1640	1300	1010	—
$Ni(OHMSAHY)_2$	450	510	3410	—	1280	—	1660
$Ni(OHMAPHYP)_2$	445	505	3415	—	1280	—	1665
$Ni(OHMEAPHYP)_2$	450	520	3400	—	1295	—	1660
$Ni(OHMSAHYP)_2$	450	500	3410	—	1280	—	1665
Ni(α, β, γ-pic)$_2$·$(OHMSAHY)_2$	455	510	3405	1630	1300	1010	—
Ni(α, β, γ-pic)$_2$·$(OHMEAPHYP)_2$	450	515	3400	1640	1295	1010	—
$Cu(OHMAPHY)_2$	445	510	3420	1630	1295	1010	—
$Cu(OHMEAPHY)_2$	450	505	3405	1640	1295	1010	—
$Cu(OHMSAHY)_2$	455	500	3410	—	1285	—	1660
$Cu(OHMAPHYP)_2$	450	510	3415	—	1280	—	1665
$Cu(OHMEAPHYP)_2$	445	500	3400	1630	1295	1010	—
$Cu(OHMSAHYP)_2$	450	505	3405	1640	1295	1010	—
$Cu(OHMAPHY)_2Cl_2$ [α, β, γ-pic]$_2$	455	520	3410	—	1280	—	1660
$Cu(OHMSAHYP)_2(NO_3)_2$ [α, β, γ-pic]$_2$	450	500	3400	—	1285	—	1665

Thus, diamagnetic NiL_2 is proposed to have square-planar geometry[8]. Complexes of the type NiL_2B_2 have been found to be paramagnetic having magnetic moment values betwen 2.99–3.02 B.M. suggesting six-coordinated octahedral structure for these complexes[9–11].

The binuclear complexes of the type $Ni_2L_2X_2$ and $Ni_2L_2(NO_3)_2$ are diamagnetic in nature accordingly suggested to have square-planar geometry. For the binuclear complexes of the type $Ni_2L_2X_2B_4$ and $Ni_2L_2(NO_3)_2B_4$ μ_{eff} ranges between 2.21 and 2.40 B.M. These are less than the expected range of magnetic moments (3.1–3.3 B.M.) for octrahedral Ni(II). The magnetic data can be interpreted in terms of the presence of antiferromagnetic exchange[12–15] through hydrazine-nitrogen bridge.

Magnetic moment values of Cu(II) complexes, CuL_2, have been found to be 1.81–1.84 B.M. which is in the range of the square-planar complexes, whereas for CuL_2B_2 type the magnetic moments have been found to be 1.89–1.92 B.M. which is in the range of the octahedral geometry[16–19].

The magnetic moment data found for the binuclear CuL_2X_2 and $Cu_2L_2B_4$ are in the range of 1.2–1.16 B.M. and 1.12–1.39 B.M. which is due to one unpaired electron. The data agree well with a dimetric model[20].

Diamagnetic complexes NiL_2 and $Ni_2L_2X_2$ show the bands around 15550 and 20000 cm^{-1} indicating square-planar structure for these complexes[21].

According to observed band position in the reflection spectra of NiL_2B_2 and $Ni_2L_2X_2B_4$ a pseudo-octahedral geometry is proposed.

CuL_2 and $Cu_2L_2X_2$ show a broad band at about 15000–16650 cm^{-1} which may be assigned due to the combination of transition in square-planar field[22–26].

$$^2B_{1g} \rightarrow {}^2B_{2g}(\nu_1), \quad {}^2B_{1g} \rightarrow {}^2A_{1g}(\nu_2), \quad {}^1B_{1g} \rightarrow {}^1E_g(\nu_3)$$

In CuL_2B_2 and $CuL_2X_2B_4$ a broad band has been observed at 13750–14300 cm^{-1} due to the combination of

$$^2B_{1g} \rightarrow {}^2A_{1g}(\nu_1), \quad {}^2B_{1g} \rightarrow {}^2B_{2g}(\nu_2), \quad {}^2B_{1g} \rightarrow {}^2E_g(\nu_3)$$

This is indicative of distorted octahedral geometry for the complexes of the $Cu_2L_2B_2$ type and $Cu_2L_2X_2B_4$ type.

Comparison of the infrared spectral bands of ligands and their complexes gives very useful information about the nature of the bonding as well as binding sites. A broad band observed in free ligand at around 3200 cm^{-1} due to ν(O–H) is absent in its complexes indicating coordination of phenolic oxygen by deprotonation[27].

A weak band present in free ligand at about 3400 cm^{-1} due to ν(N–H) remains unaffected upon complexation indicating non-involvement of primary amine residue. Bonds observed around 1650 cm^{-1} assigned as ν(C=N) (Schiff's residue) in the free ligands get lowered by about 15–25 cm^{-1} indicating their involvement in coordination[28].

A band present at 1010 cm^{-1} in the infrared spectrum of the ligand is assigned to ν(C—O) due to methoxy group. The band remains unchanged in all the complexes, sugesting non-participation of methoxy group in coordination.

The coordination through oxygen and nitrogen is further confirmed by the occurence of new bands at 500 and 450 cm^{-1} in the spectra of complexes which are assigned to ν(M–O) and ν(M–N) stretching frequencies respectively.

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