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Hydrazone and Hydrazide Chelates of Ni(II) and Cu(II)

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Co-ordination compounds of general formulae ML_2 and ML_2B_2 [where M = Ni(II) or Cu(II), L = mono deprotonated *o*-vaniline hydrazone (OVHyH), *o*-vaniline phenyl hydrazone (OVPhHyH) salicylidine hydrazide ($SAHyH_2$) and salicylidine phenyl hydrazide ($SAPhHyH_2$), B = α,β or γ-picoline] have been synthesised and characterised based on the elemental analysis, conductance, magnetic and spectral data.

INTRODUCTION

Hydrazones and hydrazides of aldehydes and ketones are reported[1–5] for the formation of Schiff's bases and their metal complexes. In the present study a series of Schiff's bases are *o*-vaniline hydrazone (OVHyH), *o*-vaniline phenyl hydrazone (OvPhHyH), salicylidine hydrazide ($SAHyH_2$) and salicylidine phenyl hydrazide ($SAPhHyH_2$). In this paper the preparation and characterisation of compounds of the type ML_2 and ML_2B_2 on the basis of elemental analysis, conductance, magnetic moments and spectral data are reptorted.

EXPERIMENTAL

The hydrazones were prepared by heating acetic acid solutions of aldehydes and ketones (0.05 M) with equimolar aqueous solution of hydrazine hydrate, phenyl hydrazine hydrochloride. The hydrazides were prepared by heating methanolic solution of methyl salicylate and aqueous solution of hydrazine hydrate/phenyl hydrazine hydrochloride.

Preparation of ML_2 type compounds

Aqueous metal salt solutions (0.01 M) were treated with methanolic solution of ligands (0.02 M) and digested on a water bath for about 30–45 min. The solid, coloured compounds were filtered, washed with methanol and dried over fused calcium chloride.

Preparation of ML_2B_2

Solid compounds as prepared above were taken in fusion tubes and treated with 4–5 drops of α,β or γ-picoline. The fusion tubes were heated ones water bath for 5 min and left in the cupboard for 2–3 days. The solid compounds were washed with small portion of methanol, filtered and dried over vacuum desiccator.

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.

Magnetic moments of solid complexes were determined at room temperature on a Gouy balance using solid copper(II) sulphate pentahydrate ($\chi_g = 5.9 \times 10^{-6}$ CGS unit) as a calibrant. The conductivities of all the complexes were determined using Systronics conductivity metre bridge in 10^{-3} M DMF solution. IR spectra and electronic spectra/UV reflectance spectra were recorded at chemical laboratories of IIT, New Delhi and CDRI, Lucknow.

RESULTS AND DISCUSSION

The physico-chemical investigation (Table-1) establishes metal-ligand ratio to be 1 : 2 ($M : L_2$ and $M : L_2 : B_2$) where L = mono-deprotonated ligands and B = α,β or γ-picoline. The ligand thus behaves as a monobasic acid at lower pH^{4-6}.

TABLE-1
ANALYTICAL DATA OF METAL COMPLEXES

S. N.	Formula	Colour	Elemental analysis (%), Found (Calcd)			
			C	H	N	Metal
1.	$Ni(OVHy)_2$	Yellow	50.12 (49.48)	4.24 (4.63)	14.26 (14.43)	14.55 (14.94)
2.	$Ni(OVPhHy)_2$	Yellowish green	62.44 (62.22)	4.76 (4.81)	10.28 (10.74)	10.68 (11.85)
3.	$Ni(SAHyH)_2$	Green	46.80 (46.60)	3.82 (3.88)	14.53 (15.55)	16.08 (16.11)
4.	$Ni(SAPhHyH)_2$	Faint green	61.01 (60.93)	4.19 (4.29)	10.27 (10.93)	11.11 (11.32)
5.	$Ni(OVHy)_2$ (α,β or γ-Picoline)$_2$	Deep green	56.85 (56.72)	5.76 (5.81)	15.21 (15.27)	10.51 (11.63)
6.	$Ni(OVPhHy)_2$ (α,β or γ-Picoline)$_2$	Green	64.98 (64.95)	5.67 (6.69)	11.91 (11.96)	8.24 (8.26)
7.	$Ni(SaHyH)_2$ (α,β or γ-Picoline)$_2$	Faint green	55.11 (54.98)	5.12 (5.36)	15.98 (16.09)	11.01 (11.11)
8.	$Ni(SAPhHyH)_2$ (α,β or γ-Picoline)$_2$	Grass green	64.28 (64.09)	5.24 (5.34)	12.39 (12.46)	8.55 (8.60)
9.	$Cu(OVHy)_2$	Gray	48.85 (48.79)	4.51 (4.57)	14.15 (14.23)	16.05 (16.13)
10.	$Cu(OVPhHy)_2$	Chocolate	61.62 (61.59)	4.72 (4.76)	10.21 (10.26)	11.61 (11.64)
11.	$Cu(SAHyH)_2$	Green	46.42 (45.96)	3.76 (3.83)	15.28 (15.32)	17.11 (17.37)
12.	$Cu(SAPhHyH)_2$	Deep green	62.86 (62.71)	4.38 (4.42)	11.15 (11.25)	12.68 (12.76)
13.	$Cu(OVHy)_2$ (α,β or γ-Picoline)$_2$	Green	56.24 (56.16)	5.68 (5.76)	15.08 (15.12)	11.25 (11.43)
14.	$Cu(OVPhHyH)_2$ (α,β or γ-Picoline)$_2$	Gray	64.61 (64.55)	5.58 (5.63)	11.81 (11.83)	8.88 (8.94)
15	$Cu(SAHyH)_2$ (α,β or γ-Picoline)$_2$	Chocolate	58.28 (58.18)	5.42 (5.60)	11.18 (11.21)	12.61 (12.71)
16.	$Cu(SAPhHyH)_2$ (α,β or γ-Picoline)$_2$	Gray	63.68 (63.57)	5.21 (5.29)	12.32 (12.36)	9.28 (9.34)

TABLE-2
MAGNETIC MOMENT AND ELECTRONIC SPECTRAL DATA OF COMPLEXES

S.N.	Formula	Magnetic moment (BM)	Electronic spectral band (cm^{-1})		
			$^1A_{1g}\rightarrow{}^1A_{2g}$	$^1A_{1g}\rightarrow{}^1B_{1g}$	$^1A_{1g}\rightarrow{}^1E_g$
1.	Ni(OVHy)$_2$	Diamagnetic	15550	19960	25100
2.	Ni(OVPhHy)$_2$	Diamagnetic	15510	19910	25105
3.	Ni(SAHyH)$_2$	Diamagnetic	15460	19900	25090
4.	Ni(SAPhHyH)$_2$	Diamagnetic	15500	19885	25000
			$^3A_{2g}\rightarrow{}^3T_{2g}$	$^3A_{2g}\rightarrow{}^3T_{1g}$ (F)	$^3A_{2g}\rightarrow{}^3T_{1g}$
5.	Ni(OVHy)$_2$ (α,β or γ-Picoline)$_2$	2.98–3.02	10650	16200	26150
6.	Ni(OVPHy)$_2$ (α,β or γ-Picoline)$_2$	2.96–2.98	10550	16050	26050
7.	Ni(SAHyH)$_2$ (α,β or γ-Picoline)$_2$	2.98–3.04	10200	15650	26850
8.	Ni(SAPhHyH)$_2$ (α,β or γ-Picoline)$_2$	3.02–3.10	10150	15650	26850
9.	Cu(OVHy)$_2$	1.86	16000		
10.	Cu(OVPhHy)$_2$	1.84	15000–16500		
11.	Cu(SAHyH)$_2$	1.82	15580–16600		
12.	Cu(SAPhHyH)$_2$	1.83	16100		
13.	Cu(OVHy)$_2$ (α,β or γ-Picoline)$_2$	1.91	13750–14300		
14.	Cu(OVPhHy)$_2$ (α,β or γ-Picoline)$_2$	1.93	13650–14200		
15.	Cu(SAHyH)$_2$ (α,β or γ-Picoline)$_2$	1.92	13800–14450		
16.	Cu(SAPhHyH)$_2$ (α,β or γ-Picoline)$_2$	1.94	13600–14190		

The magnetic moments of Cu(II) complexes vary between 1.82–1.86 BM for ML_2 type compound and 1.91–1.94 BM for ML_2B_2 type of compound indicating one unpaired electron and no metal-metal bond. Magnetic moment values of Cu(II) complexes are not diagnostic for geometry of compound, although Ray *et al.*[8] and Bhattacharya *et al.*[9] proposed μ_{eff} for Cu(II) in the range of 1.80–1.88 BM to be indicative of square-planar geometry and 1.91–2.2 BM for psuedo octahedral configuration of the complexes. The observed moment suggests[10, 11] square-planar geometry for ML_2 type and psuedo-octahedral/distorted octahedral geometry for ML_2B_2 type complexes.

Ni(II) complexes of the type NiL_2 are diamagnetic in nature indicating the square-planar geometry[12] and those of NiL_2B_2 [2.98–3.10 BM] to be of octahedral geometry[13].

TABLE-3

KEY IR SPECTRAL BANDS (cm^{-1}) OF LIGANDS AND THEIR METAL COMPLEXES

Formula	ν(M—N)	ν(M—O)	ν(O—H)	$\nu(NH_2)$	ν(C═N)	ν(C—O)	ν(O—Me)	ν(C═O)
OVHyH	—	—	3250	3420	1650	1280	1010	—
OVPhHyH	—	—	3230	3410	1650	1280	1010	—
$SAHyH_2$	—	—	3260	3405	—	1270	—	1660
$SAPhHyH_2$	—	—	3240	3420	—	1270	—	1665
$Ni(OVHy)_2$	450	500	—	3420	1630	1290	1010	—
$Ni(OVPhHy)_2$	455	520	—	3410	1640	1300	1010	—
$Ni(SAHyH)_2$	450	510	—	3410	—	1280	—	1660
$Ni(SAPhHyH)_2$	445	505	—	3415	—	1280	—	1665
$Ni(OVHy)_2$ (α,β or γ-Picoline)$_2$	455	510	—	3405	1630	1300	1010	—
$Ni(OVPhHy)_2$ (α,β or γ-Picoline)$_2$	450	515	—	3400	1640	1295	1010	—
$Ni(SAHyH)_2$	450	520	—	3400	—	1295	—	1660
$Ni(SAPhHyH)_2$	450	500	—	3410	—	1280	—	1665
$Cu(OVHy)_2$	445	510	—	3420	1630	1295	1010	—
$Cu(OVPhHy)_2$	450	505	—	3405	1640	1295	1010	—
$Cu(SAHyH)_2$	455	500	—	3410	—	1285	—	1660
$Cu(SAPhHyH)_2$	450	510	—	3415	—	1280	—	1665
$Cu(OVHy)_2$ (α,β or γ-Picoline)$_2$	445	500	—	3400	1630	1295	1010	—
$Cu(OVPhHy)_2$ (α,β or γ-Picoline)$_2$	450	505	—	3405	1640	1295	1010	—
$Cu(SAHyH)_2$ (α,β or γ-Picoline)$_2$	455	520	—	3410	—	1280	—	1660
$Cu(SAPhHyH)_2$ (α,β or γ-Picoline)$_2$	450	500	—	3400	—	1285	—	1665

Cu(II) square-planar complexes can have the following spin-allowed transitions $^2B_{1g} \rightarrow {}^2B_{2g}$, $^2B_{1g} \rightarrow {}^2A_{1g}$, $^2B_{2g} \rightarrow {}^2E_g$. As the energy gaps between these transitions are not large, a complex broad band[14] is observed at about 16000 cm^{-1} for CuL_2 type of complexes. Accordingly these complexes are assigned square- planar geometry. For picoline adducts combination bands $^2B_{1g} \rightarrow {}^2A_{1g}$, $^2B_{1g} \rightarrow {}^2B_{2g}$ and $^2B_{1g} \rightarrow {}^2E_g$ are observed around 13000 cm^{-1}. The electronic spectral values together with magnetic moment data suggest a distorted octahedral geometry[15].

NiL_2 type of complexes give three spin-allowed transitions at 15000 cm^{-1}, 20000 cm^{-1} and 25000–26000 cm^{-1}. These transitions are assigned $^1A_{1g} \rightarrow {}^1A_{2g}$, $^1A_{1g} \rightarrow {}^1B_{1g}$ and $^1A_{1g} \rightarrow {}^1E_g$ respectively; accordingly NiL_2 type of complexes are assigned square-planar geometry[16]. For NiL_2B_2 type complexes three spin-allowed transitions are observed in the UV reflectance spectra of the complexes. These transitions are assigned $^3A_{2g} \rightarrow {}^3T_{2g}$ (10000 cm^{-1}), $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ (16000 cm^{-1}) and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ (26000 cm^{-1}). Accordingly NiL_2B_2 type complexes are assigned[17] octahedral geometry.

Comparison of the infrared spectral bands of ligands and their complexes give very useful information about the nature of 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[18].

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. Bands observed around 1650 cm^{-1}, assigned as ν(C═N) (Schiff residue) in the free ligand, get lowered by about 15–25 cm^{-1} indicating their involvement in co-ordination[19].

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, suggesting non-participation of methoxy group in coordination.

The coordination through oxygen and nitrogen is further confirmed by occurrence 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.

The IR spectral studies indicate that keto form persists in free ligand. The IR spectra bands for their complexes too show the band due to >C═O upon complexation. The bands due to >C═O remain unaffected, thus suggesting non-involvement of >C═O group upon complexation.

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