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Characterisation of Some Copper(II), Nickel(II) and Cobalt(II) Coordination Compounds with Schiff Bases Derived from 1,2-Diphenyl-1-Hydroxyiminoethan-2-One and Aromatic Amines

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A number of coordination compounds of the types $[M(L^{1-7})_2]$, $[M(HL^{1-7})_2Cl_2]$ [M = Co(II), Ni(II) or Cu(II)] and $[CuL^{1-7}Cl]$, where HL^{1-7} = Schiff bases derived by condensing 1,2-diphenyl-1-hydroxyiminoethan-2-one with aniline (HL^1), 2-methylaniline (HL^2), 3-methylaniline (HL^3), 4-methylaniline (HL^4), 2-nitroaniline (HL^5), 3-nitroaniline (HL^6) or 4-nitroaniline (HL^7) have been synthesised and characterised on the basis of elemental analyses, magnetic susceptibility, infrared and electronic spectral data.

INTRODUCTION

Transition metal complexes with Schiff bases derived from hydroxyiminoalkanones and aromatic amines have been amongst the most widely studied coordination compounds in the recent past[1-3]. The hardness or softness of an acidic or basic site is not an inherent property of the particular atom at the site but can be influenced by the substituent atoms[4]. The addition of electron donating soft, polarisable substituents can soften an otherwise hard centre and the presence of electron-withdrawing substituents can reduce the softness of a site. Accordingly we have undertaken a programme of synthesising coordination compounds with Schiff bases derived from hydroxyiminoalkanones and anilines with electron donating substituent on it as in toluidines or electron-withdrawing substituents on it as in nitroanilines. We have reported very recently characterisation of some copper(II), nickel(II) and cobalt(II) coordination compounds with Schiff bases derived from 3-hydroxyiminobutan-2-one with aniline and toluidines[5]. In continuation of our own work in the field, in the present communication we report a series of compounds of the types $[M(L^{1-7})_2]$, $[M(HL^{1-7})_2Cl_2]$, [M = Co(II), Ni(II) and Cu(II)] and $[CuL^{1-7}Cl]$ where HL^{1-7} are the Schiff bases derived from 1,2-diphenyl-1-hydroxyiminoethan-2-one and aniline, toluidines or nitroanilines.

EXPERIMENTAL

1,2-Diphenyl-1-hydroxyiminoethan-2-one was prepared starting from 1,2-diphenylethan-1,2-dione (Loba) as reported in the literature[6]. Solid aromatic amines (BDH) such as nitroanilines and *p*-toluidines were recrystallised and liquid aromatic amines such a *ortho*- and *meta*-toluidines were redistilled before use. Metal salts were S. Merck reagents. An *'in situ'* method was adopted for the preparation of the compounds. For the preparation of the coordination compounds of the type $[M(HL^{1-7})_2Cl_2]$, ketone, amines and metal chlorides were mixed together in the molar ratio 2 : 2 : 1 in a dry ethanolic medium and the mixture was warmed. The compounds were separated as coloured crystalline products immediately. All the compounds have been prepared under similar experimental conditions. For preparing the coordination compounds of the type $[M(L^{1-7})_2]$, metal acetates, ketone and amines were mixed together in an aqueous solution in the ratio 1 : 2 : 2 made slightly alkaline by adding sodium acetate to the solution. Copper(II) compounds of the type $[Cu(L^{1-7})_2]$ were warmed in a dry ethanolic medium with copper(II) chlorides to give a series of binuclear or tetranuclear coordination compounds of the type $[CuL^{1-7}Cl]$.This behaviour was found to be absent in the nickel(II) and cobalt(II) compounds.

The compounds were analysed by standard procedures[7]. Infrared spectra and electronic spectra of the complexes were obtained from RSIC, CDRI, Lucknow. Magnetic susceptibilities at room temperature were measured by a Guoy balance using $Hg[Co(CNS)_4]$ as the calibrant. The analytical data, colour and magnetic moment data of the compounds obtained are listed in Table 1. The formula of the compounds obtained on the basis of % composition are shown in the first coloumn of Table 1.

RESULTS AND DISCUSSION

The broad bands of medium intensity in the regions 3300-3200 cm^{-1} in the spectra of ligands are assigned to ν_{O-H} of the oxime group. This band is almost unperturbed in the spectra of the compounds $[M(HL^{1-7})_2Cl_2]$ indicating ligands to coordinate in an uncharged state. The position and nature is suggestive of intermolecular hydrogen bonding supporting *trans*- structure for the compounds. The spectra of compounds $[M(L^{1-7})_2]$ do not contain this band indicating ligands to satisfy primary valencies of the metal ions in addition to secondary valencies.

The Schiff bases exhibit a sharp band in the region 1620-1635 cm^{-1} which have been assigned to the $\nu_{C=N}$ of the oxime group. This band shifts to a lower frequency by 15–25 cm^{-1} on complexation due to the reduction of electron density in the azomethine links.

The Schiff bases show a sharp and intense band in the region 1510–1500 cm^{-1} which can be assigned to $\nu_{C=N}$ of alkylimino group >C=N–R. In metal compounds these bands show a red shift indicating involvement of nitrogen of the group in coordination. The sharp and intense bands in the region 1100–1000 cm^{-1} in the spectra of ligands as well as metal compounds $[M(HL^{1-7})_2Cl_2]$ and

TABLE 1

ANALYTICAL AND PHYSICAL DATA OF METAL COORDINATION COMPOUNDS OF THE TYPES $[\mathrm{M(HL^{1-7})_2Cl_2}]$, $[\mathrm{ML_2^{1-7}}]$ AND $[\mathrm{CuL^{1-7}Cl}]$.

Compounds	Colour	Found (Calc.) %		μ_{eff} (B.M.)
		M	N	
$\mathrm{Ni(HL^{1})_2Cl_2}$	Violet	8.04	7.65	3.10
		(8.05)	(7.67)	
$\mathrm{Ni(HL^{2})_2Cl_2}$	Yellow	7.70	7.35	3.20
		(7.73)	(7.37)	
$\mathrm{Ni(HL^{3})_2Cl_2}$	Pale Yellow	7.74	7.34	3.15
		(7.73)	(7.37)	
$\mathrm{Ni(HL^{4})_2Cl_2}$	Grey	7.72	7.40	3.25
		(7.73)	(7.37)	
$\mathrm{Ni(HL^{5})_2Cl_2}$	Green	7.16	10.21	3.00
		(7.15)	(10.22)	
$\mathrm{Ni(HL^{6})_2Cl_2}$	Yellowish green	7.14	10.24	2.95
		(7.15)	(10.22)	
$\mathrm{Ni(HL^{7})_2Cl_2}$	Dark green	7.14	10.20	3.05
		(7.15)	(10.22)	
$\mathrm{Co(HL^{1})_2Cl_2}$	Pink	8.11	7.65	4.80
		(8.08)	(7.69)	
$\mathrm{Co(HL^{2})_2Cl_2}$	Brown	7.72	7.37	4.90
		(7.75)	(7.37)	
$\mathrm{Co(HL^{3})_2Cl_2}$	Dark brown	7.77	7.40	4.86
		(7.70)	(7.37)	
$\mathrm{Co(HL^{4})_2Cl_2}$	Reddish brown	7.69	7.35	4.98
		(7.76)	(7.37)	
$\mathrm{Co(HL^{5})_2Cl_2}$	Pink	7.20	10.21	4.70
		(7.17)	(10.22)	
$\mathrm{Co(HL^{6})_2Cl_2}$	Orange red	7.15	10.25	4.75
		(7.17)	(10.22)	
$\mathrm{Co(HL^{7})_2Cl_2}$	Reddish brown	7.20	10.22	4.65
		(7.17)	(10.22)	
$\mathrm{Cu(HL^{1})_2Cl_2}$	Grey	8.62	7.63	1.80
		(8.64)	(7.62)	
$\mathrm{Cu(HL^{2})_2Cl_2}$	Green	8.31	7.29	1.85
		(8.30)	(7.33)	
$\mathrm{Cu(HL^{3})_2Cl_2}$	Dark green	8.33	7.32	1.82
		(8.30)	(7.33)	
$\mathrm{Cu(HL^{4})_2Cl_2}$	Greenish yellow	8.35	7.34	1.90
		(8.30)	(7.32)	
$\mathrm{Cu(HL^{5})_2Cl_2}$	Blue	7.69	10.20	1.73
		(7.68)	(10.16)	
$\mathrm{Cu(HL^{6})_2Cl_2}$	Light green	7.70	10.15	1.75
		(7.68)	(10.16)	

Compounds	Colour	Found (Calc.) %		μ_{eff} (B.M.)
		M	N	
$Cu(HL^7)_2Cl_2$	Bluish green	7.65 (7.68)	10.16 (10.16)	1.70
NiL^1_2	Pink	8.92 (8.94)	8.55 (8.53)	Diamagnetic
NiL^2_2	Red	8.50 (8.55)	8.21 (8.15)	”
NiL^3_2	Reddish brown	8.52 (8.55)	8.19 (8.15)	”
NiL^4_2	Grey	8.57 (8.55)	8.13 (8.15)	”
NiL^5_2	Green	7.86 (7.84)	11.25 (11.22)	”
NiL^6_2	Yellowish green	7.83 (7.84)	11.20 (11.22)	”
NiL^7_2	Greyish green	7.80 (7.84)	11.24 (11.22)	”
CoL^1_2	Blue	9.11 (8.97)	8.55 (8.52)	2.05
CoL^2_2	Brown	8.60 (8.58)	8.00 (8.15)	2.15
CoL^3_2	Brown	8.56 (8.58)	8.10 (8.15)	2.10
CoL^4_2	Grey	8.55 (8.58)	8.19 (8.15)	2.20
CoL^5_2	Reddish brown	7.91 (7.86)	11.15 (11.21)	2.00
CoL^6_2	Orange red	7.85 (7.86)	11.20 (11.21)	2.02
CoL^7_2	Brown	7.88 (7.86)	11.22 (11.21)	1.95
CuL^1_2	Green	9.58 (9.60)	8.50 (8.46)	1.88
CuL^2_2	Blue	9.20 (9.19)	8.00 (8.09)	1.98
CuL^3_2	Yellowish green	9.15 (9.19)	8.10 (8.09)	1.90
CuL^4_2	Brownish green	9.20 (9.19)	8.00 (8.09)	2.00
CuL^5_2	Green	8.45 (8.43)	11.10 (11.14)	1.82
CuL^6_2	Greyish green	8.47 (8.43)	11.13 (11.14)	1.85
CuL^7_2	Steel grey	8.44 (8.43)	11.15 (11.14)	1.80

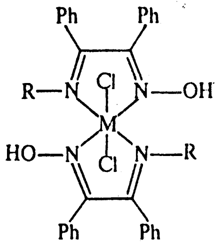
Compounds	Colour	Found (Calc.) %		μ_{eff} (B.M.)
		M	N	
$Cu_2L^1_2Cl_2$	Grey	16.00 (15.96)	7.21 (7.03)	1.60
$Cu_2L^2_2Cl_2$	Yellowish green	15.40 (15.38)	6.85 (6.78)	1.62
$Cu_2L^3_2Cl_2$	Greyish green	15.35 (15.38)	6.75 (6.78)	1.67
$Cu_2L^4_2Cl_2$	Dark green	15.41 (15.38)	6.80 (6.78)	1.65
$Cu_2L^5_2Cl_2$	Steel grey	14.25 (14.31)	9.53 (9.46)	1.58
$Cu_2L^6_2Cl_2$	Sky blue	14.30 (14.31)	9.44 (9.46)	1.60
$Cu_2L^7_2Cl_2$	Dirty yellow	14.29 (14.31)	9.43 (9.46)	1.70

$[M(L^{1-7})_2]$ are assigned to ν_{N-O}. In the spectra of compounds $[CuL^{1-7}Cl]$, this band shows a significant blue shift indicating involvement of oxygen atoms of N–O group also in coordination.

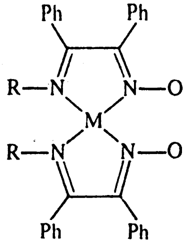
The spectra of the coordination compounds $[M(HL^{1-7})_2Cl_2]$, $[M(L^{1-7})_2]$ and $[CuL^{1-7}Cl]$ differ significantly from each other in the far infrared region. $[ML_2^{1-7}]$ compounds show a single significant band in the region, 550–520 cm^{-1} which is assigned to ν_{M-N}. $[M(HL^{1-7})_2Cl_2]$ show two bands in the far infrared region, one in the region 550–520 cm^{-1} due to ν_{M-N} and another one in the region 370–365 cm^{-1} due to ν_{M-Cl}. These features suggest the ligands to behave in a tetradentate manner. Compounds $[CuL^{1-7}Cl]$ exhibit a group of three bands in the far-infrared region, one in the range 550–520 cm^{-1}, another one in the region 370–360 cm^{-1} and third one in the region 325–307 cm^{-1}, which can be assigned to ν_{Cu-N}, ν_{Cu-Cl} and ν_{Cu-O}.

On the basis of above discussions, $[M(HL^{1-7})_2Cl_2]$, $[M(L^{1-7})_2]$ and $[CuL^{1-7}Cl]$ can be assigned structures I–III which are supported by electronic spectra as well as magnetic moment and conductivity data also, as described in the forthcoming paragraphs.

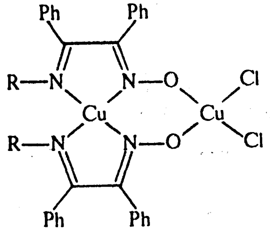
The magnetic moment of the nickel(II) compounds of the type $[Ni(HL^{1-7})_2Cl_2]$ lies in the range 2.95 to 3.30 B.M. at 25°C and is indicative of octahedral structure. The compounds exhibit three well resolved bands, one in the region 12,400–14,100 cm^{-1}, the next one in the vicinity of 17000 cm^{-1} followed by a strong intense band at 25500 cm^{-1} attributed to $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)(\nu_1)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)(\nu_2)$ and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)(\nu_3)$ transitions respectively under an octahedral environmental around Ni(II) ion. The cobalt(II) compounds of the type $[Co(HL^{1-7})_2Cl_2]$ possess magnetic moment values in the range 4.65–4.98 B.M. at room temeperature which suggests octahedral arrangement of the ligands around the central cobalt(II) ion. The compounds exhibit two bands at



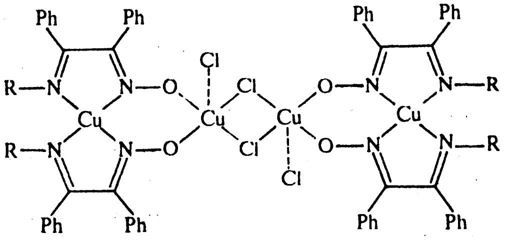
R —C_6H_5, $-C_6H_4(CH_3)$
or $-C_6H_4(NO_2)$
(I)



R as in (I)
(II)



R as in (I)
III (a)



R as in (I)
III (b)

15,100 cm^{-1} and 18,000 cm^{-1} which may be assigned to the transition $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)(\nu_1)$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)(\nu_2)$ respectively in the octahedral field. A charge transfer band is also observed at 24,500 cm^{-1}. The copper(II) compounds of the type $[Cu(HL^{1-7})_2Cl_2]$ have magnetic moment values in the range 1.70–1.90 B.M. which is usually for octahedral copper(II) compounds. They show a broad band around 14,500 cm^{-1} which can be assigned to the transition $^2E_g \rightarrow {}^2T_{2g}$. All the coordination compounds of nickel(II), cobalt(II) and copper(II) of the type $[M(HL^{1-7})_2Cl_2]$ have non-equivalent axial and equatorial ligands which suggests that the compounds possess an octahedral geometry with some amount of tetragonal distortion.

The nickel(II) compounds of the type $[NiL_2^{1-7}]$ are diamagnetic indicating square planar environment around nickel(II) ion. The electronic spectrum consists of a broad band centred at 18,600 cm^{-1} which suggests a planar environment around nickel(II) with the chromophore, NiN_4.

The band is assigned to the transition $^1A_{1g} \rightarrow {}^1B_{1g}$ for $a_{1g}^2e_g^4b_{2g}^2 \rightarrow a_{1g}^2e_g^4b_{2g}^1b_{1g}^1$. The cobalt(II) complexes of the type $[CoL_2^{1-7}]$ have magnetic moment in the range 2.0–2.2 B.M. with a broad band centred at 2100 cm^{-1} indicating the planar environment around cobalt(II) with the chromophore CoN_4.

The copper(II) compounds of the type [CuL^{1-7}] have magnetic moment in the range 1.8 to 2.0 B.M. and a single broad band at 14,000 cm^{-1} suggesting a planar environment around copper(II) with the chromophore CuN_4. The broad band which shows considerable structure represents at least two superimposed absorptions assignable to the transitions $^2B_{1g} \rightarrow {}^2B_{2g}$ for $a_{1g}^2e_g^4b_{2g}^2b_{1g}^1 \rightarrow a_{1g}^2e_g^4b_{2g}^1b_{1g}^2$ and $^2B_{1g} \rightarrow {}^2E_g$ for $a_{1g}^2e_g^4b_{2g}^2b_{1g}^1 \rightarrow a_{1g}^2e_g^3b_{2g}^2b_{1g}^2$

The copper(II) compounds of the type [$CuL^{1-7}Cl$] show two broad ligand field bands in the region 12,000–11,000 cm^{-1} and 18,500–17,500 cm^{-1} and have magnetic moments in the region 1.5–1.7 B.M.

Both the electronic spectral bands seem to be due to the same d–d transition differing in energy due to presence of different ligand fields[8] as shown in Fig. (IIIa). The high frequency band may be due to chromophore, CuN_4 in D_{4h} symmetry while the low frequency band may be due to the chromophore, CuO_2Cl_2 and a lower symmetry[9] such as C_2. Alternatively, the two bands might also be due to difference in coordination numbers of copper(II) ions and possibility of complexes having a polymeric structure (IIIb) cannot be ruled out[10,11].

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