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COBALT (II) AND NICKEL (II) COMPLEXES WITH SCHIFF BASE LIGANDS 1,2-DIPHENYL-2-ALKYLIMINOETHAN-1-ONE OXIME

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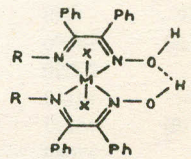
A number of complexes of the type $[M(HL^{1-4})_2X_2]$ where M=Ni(II), Co(II); HL^{1-4}=Schiff base ligands derived by the condensation of 1,2-diphenyl-1-hydroxyiminoethan-2-one with n-butylamine (HL^1), isobutylamine (HL^2), n-propylamine (HL^3) and isopropylamine (HL^4); X = Cl^-, Br^-, I^-, NO^-_3 and ClO^-_4 have been synthesized and characterised on the basis of elemental analysis, magnetic susceptibility, conductivity, infrared and electronic spectral data.

Key words: Metal complexes with imine-oxime ligands.

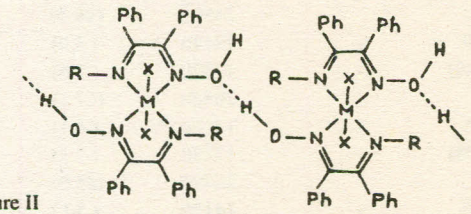
Introduction

Schiff base ligands having azomethine functional group, >C=N- are produced by the union of an active carbonyl group and a primary amine. The metal complexes of Schiff bases have received great attention during recent years due to their paramount biological and industrial importance as evidenced by the bulk of literature [1-5]. This prompted us to prepare metal complexes with Schiff bases derived from 1,2-diphenyl-1-hydroxyiminoethan-2-one and aliphatic amines. These ligands act in a bidentate manner to produce a series of complex having the formula $[M(HL^{1-4})_2X_2]$, (M = Co(II), Ni(II); X = Cl^-, Br^-, I^-, $N0^-_3$, ClO^-_4).



Structure I

R = -(n)C_4H_9, -(ISO)C_4H_9, -(n)C_3H_7, -(ISO)C_3H_7



Structure II

R = -(n)C_4H_9, -(ISO)C_4H_9, -(n)C_3H_7, -(ISO)C_3H_7

Materials and Methods

All the chemicals used were E. Merck reagents except 1,2-diphenylethan-1,2-dione which was of Loba quality. 1,2-diphenyl-1-hydroxyiminoethan-2-one was prepared according to the literature method [6] (m.p. 145°C; lit. 143°C). The ligands (HL^{1-4}) were synthesized by condensing equimolar quantities of 1,2-diphenyl-hydroxyiminoethan-2-one and aliphatic amines in an ethanolic medium. The solid ligands were separated by allowing the solution to stand overnight in a dish.

Preparation of Complexes. The complexes with all the four ligands (HL^{1-4}) were prepared by the method reported earlier [7]. The preparation of one typical complex is described as:

Dichlorobis (1,2-diphenyl-2-isobutyliminoethan-1-one oxime) cobalt (II) $[Co(HL^2)_2Cl_2]$.

An ethanolic solution of 1,2-diphenyl-2 isobutyliminoethan-1-one oxime (0.01 mol) was treated with an alcoholic solution of cobalt (II) chloride hexahydrate (0.005 mol). The mixture was heated under reflux over a hot water bath for three hours when yellowish-red precipitates of cobalt (II) complex were obtained. It was filtered, washed with cold water followed by methanol and ether and dried in vacuo.

The compounds were analysed using standard procedures [8] such as nickel as bis (dimethylglyoximato) nickel (II), cobalt as its oxinate, halides as their respective silver halides and carbon, hydrogen and nitrogen by semimicro combustion methods. The infrared spectra of the ligands and the complexes were recorded on a Beckmann IR-20 spectrophotometer. The conductivity measurements were made on a systronic conductometer Model 303 using dimethyl sulphoxide as a solvent. Magnetic moments were measured by the Guoy method using $Hg[Co(CNS)_4]$ as the calibrant. The absorption spectra of dimethylsulphoxide solution of these complexes were recorded on Cary-2390 spectrophotometer using a pair of 1 cm quartz cuvettes. Analytical, spectral, conductivity and magnetic moment data are recorded in Table 1.

Results and Discussion

The molecular formulae of the complexes have been assigned on the basis of their analytical data (Table1). The

Table 1. Colour, Analytical Data, Electronic Spectra and Magnetic Moment Values of Metal Complexes.

Compounds	Colour	Found (Calc) %					λ_{max} (electronic)		μ_{eff} (B.M.)
		M	C	N	H	Halogen	cm^{-1}	(ε)	
$Ni(HL^1)_2Cl_2$	Red	8.61	62.80	8.04	5.91	10.10	13900	(5.8)	2.90
		(8.52)	(62.71)	(8.14)	(5.87)	(10.17)	17600	(7.2)	
							25850	(14.3)	
$Ni(HL^2)_2Cl_2$	Orange	8.39	62.61	8.25	5.71	10.15	13910	(5.7)	2.92
		(8.52)	(62.71)	(8.14)	(5.82)	(10.17)	17620	(7.1)	
							25870	(14.2)	
$Ni(HL^3)_2Cl_2$	Blue	8.61	62.80	8.40	5.91	10.45	13890	(5.8)	2.88
		(8.88)	(62.71)	(8.49)	(5.82)	(10.61)	17570	(7.3)	
							25840	(14.2)	
$Ni(HL^4)_2Cl_2$	Violet	9.00	61.63	8.62	5.32	10.47	13900	(5.6)	2.90
		(8.88)	(61.74)	(8.49)	(5.25)	(10.61)	17590	(7.3)	
							25860	(14.3)	
$Ni(HL^1)_2Br_2$	Reddish	7.67	55.36	7.05	5.24	20.71	14000	(6.1)	3.00
	Brown	(7.53)	(55.40)	(7.20)	(5.15)	(20.55)	17900	(7.4)	
							26000	(17.1)	
$Ni(HL^2)_2Br_2$	Orange	7.69	55.39	7.05	5.00	20.41	14010	(6.2)	3.02
		(7.53)	(55.47)	(7.20)	(5.15)	(20.55)	17920	(7.3)	
							26010	(16.8)	
$Ni(HL^3)_2Br_2$	Light green	7.92	54.21	7.63	4.93	21.17	13990	(6.1)	3.05
		(7.81)	(54.34)	(7.47)	(4.81)	(21.32)	17880	(7.4)	
							25980	(17.2)	
$Ni(HL^4)_2Br_2$	Green	7.65	54.22	7.56	4.69	21.41	14000	(6.2)	3.00
		(7.81)	(54.34)	(7.47)	(4.81)	(21.32)	17910	(7.3)	
							26000	(16.8)	
$Ni(HL^1)_2I_2$	Red Brown	6.79	49.62	6.57	4.44	29.00	14100	(5.9)	3.10
		(6.71)	(49.50)	(6.43)	(4.59)	(29.11)	18100	(7.1)	
							27050	(16.7)	
$Ni(HL^2)_2I_2$	Bluish	6.83	49.42	6.32	4.51	29.31	14120	(6.0)	3.12
	violet	(6.71)	(49.50)	(6.43)	(4.59)	(29.11)	18130	(7.5)	
							27070	(17.2)	
$Ni(HL^3)_2I_2$	Violet	7.00	48.42	6.52	4.35	31.70	14090	(5.7)	3.08
		(6.95)	(48.30)	(6.64)	(4.28)	(30.20)	18090	(7.5)	
							27020	(14.3)	
$Ni(HL^4)_2I_2$	Green	7.00	48:21	6.75	4.19	29.10	14110	(5.5)	3.12
		(6.95)	(48.30)	(6.64)	(4.28)	(30.10)	18110	(7.2)	
							27040	(14.1)	
$Ni(HL^1)_2(NO_3)_2$	Yellowish	8.00	58.00	7.69	5.31	-	14120	(5.8)	2.80
	green	(7.85)	(58.16)	(7.55)	(5.40)	-	17800	(7.5)	
							26500	(16.3)	
$Ni(HL^2)_2(NO_3)_2$	Deep red	7.68	58.31	7.45	5.29	-	14140	(5.9)	2.83
		(7.85)	(58.16)	(7.55)	(5.40)	-	17820	(7.6)	
							26520	(17.1)	
$Ni(HL^3)_2(NO_3)_2$	Dark blue	8.02	57.21	8.05	4.95	-	14100	(6.1)	2.81
		(8.21)	(57.08)	(7.85)	(5.05)	-	17790	(7.3)	
							26490	(15.9)	
$Ni(HL^4)_2(NO_3)_2$	Violet	7.99	57.21	8.00	5.00	-	14120	(5.8)	2.85
		(8.21)	(57.08)	(7.85)	(5.05)	-	17810	(7.2)	
							26510	(17.3)	
$Ni(HL^1)_2(ClO_4)_2$	Reddish	7.31	52.75	6.99	5.00	-	13800	(6.1)	2.90
	brown	(7.18)	(52.89)	(6.87)	(4.91)	-	18000	(7.1)	
							26470	(16.7)	
$Ni(HL^2)_2(ClO_2)_2$	Dark green	7.00	52.75	6.97	4.79	-	13820	(5.9)	2.92
		(7.18)	(52.89)	(6.87)	(4.91)	-	18030	(7.21)	
							26490	(17.1)	
$Ni(HL^3)_2(ClO_4)_2$	Violet	7.32	51.59	7.21	5.00	-	13810	(6.1)	2.90
		(7.43)	(51.73)	(7.11)	(5.08)	-	18090	(7.3)	
							26460	(16.8)	

(Continue.....)

(Table continued)

$Ni(HL^4)_2(ClO_4)_2$	Dark violet	7.28 (7.43)	51.61 (51.73)	7.00 (7.11)	4.95 (5.08)	- -	13820 18010 26480	(5.9) (7.2) (17.2)	2.95
$Co(HL^1)_2Cl_2$	Yellowish red	8.60 (8.56)	62.75 (62.69)	8.00 (8.12)	5.85 (5.80)	10.00 (10.15)	16900	(9.2)	5.15
$Co(HL^2)_2Cl_2$	Yellowish red	8.50 (8.56)	62.50 (62.69)	8.20 (8.12)	5.75 (5.80)	9.50 (10.15)	16910	(9.0)	5.17
$Co(HL^3)_2Cl_2$	Brown	8.82 (8.92)	61.55 (61.72)	8.55 (8.47)	5.35 (5.44)	10.50 (10.59)	16890	(9.1)	5.15
$Co(HL^4)_2Cl_2$	Bluish green	9.00 (8.92)	61.65 (61.72)	8.40 (8.47)	5.50 (5.44)	10.50 (10.59)	16900	(10.3)	5.17
$Co(HL^1)_2Br_2$	Yellowish green	7.50 (7.57)	55.55 (55.45)	7.10 (7.18)	5.25 (5.13)	20.60 (20.53)	16800	(9.8)	5.20
$Co(HL^2)_2Br_2$	Green	7.45 (7.57)	55.30 (55.45)	7.10 (7.18)	5.00 (5.13)	20.45 (20.53)	16810	(9.5)	5.24
$Co(HL^3)_2Br_2$	Greenish brown	7.65 (7.85)	54.40 (54.72)	7.30 (7.45)	4.90 (4.79)	21.45 (21.30)	16810	(9.6)	5.20
$Co(HL^4)_2Br_2$	Brown	8.00 (7.85)	54.21 (54.32)	7.34 (7.45)	4.65 (4.79)	21.15 (21.30)	16820	(0.2)	5.25
$Co(HL^1)_2I_2$	Dark brown	6.87 (6.75)	49.60 (49.48)	6.29 (6.41)	4.55 (4.57)	29.21 (29.09)	17200	(8.9)	5.10
$Co(HL^2)_2I_2$	Yellowish brown	6.67 (6.75)	49.35 (49.48)	6.33 (6.41)	4.69 (4.51)	29.00 (29.09)	17210	(9.5)	5.12
$Co(HL^3)_2I_2$	Orange	7.15 (6.99)	48.35 (48.28)	6.53 (6.62)	4.37 (4.26)	30.89 (30.50)	17200	(10.7)	5.10
$Co(HL^4)_2I_2$	Reddish orange	6.85 (6.99)	48.21 (48.28)	6.48 (6.62)	4.15 (4.26)	30.00 (30.50)	17210	(10.1)	5.12
$Co(HL^1)_2(NO_3)_2$	Dark brown	8.05 (7.89)	58.23 (58.14)	7.42 (7.53)	5.47 (5.38)		17400	(10.3)	5.30
$Co(HL^2)_2(NO_3)_2$	Yellowish brown	7.75 (7.89)	58.05 (58.14)	7.65 (7.53)	5.27 (5.38)		17410	(9.7)	5.32
$Co(HL^3)_2(NO_3)_2$	Greenish brown	8.10 (8.25)	57.00 (57.86)	8.00 (7.83)	5.15 (5.03)		17390	(9.8)	5.30
$Co(HL^4)_2(NO_3)_2$	Brown	8.39 (8.25)	57.15 (57.06)	7.13 (7.83)	5.10 (5.03)		17410	(9.5)	5.32
$Co(HL^1)_2(ClO_4)_2$	Pink	7.31 (7.22)	53.05 (52.87)	7.00 (6.85)	4.78 (4.89)		17600	(10.2)	5.15
$Co(HL^2)_2(ClO_4)_2$	Yellowish red	7.05 (7.22)	53.10 (52.87)	6.74 (6.85)	4.75 (4.89)		17610	(10.5)	5.18
$Co(HL^3)_2(ClO_4)_2$	Dark red	7.57 (7.47)	51.85 (51.71)	7.00 (7.09)	5.15 (5.06)		17600	(10.3)	5.15
$Co(HL^4)_2(ClO_4)_2$	Red	7.59 (7.47)	51.60 (51.71)	6.97 (7.09)	5.00 (5.06)		17610	(9.5)	5.18

cobalt (II) and nickel (II) complexes are thus assigned the formulae, $M(HL^{1-4})_2X_2$.

The vibrational spectra (Table 2) of the complexes have been recorded in the frequency range, 4000-400 cm^{-1} and structurally important vibrational bands for O-H stretch, C=N stretch (oxime and azomethine) and N-O stretch provide unequivocal evidence relating to the structure of the complexes.

The infrared spectra of all the metal complexes of the type $[M(HL^{1-4})_2X_2]$ shows a broad and strong band at 3400-3420 cm^{-1} which is assigned to υ_{O-H} of the N-O-H groups. The width of this band manifests intramolecular as well as intermolecular hydrogen bonding. It also exhibits two sharp and strong bands at 1615-1625 cm^{-1} and 1465-1480 cm^{-1} which have been attributed to C=N stretching vibrations of azomethine and oxime groups respectively. The characteristic behaviour of these bands, that is, the shift of the azomethine and oxime C=N bands respectively towards red and blue region of the spectra as compared with the free ligands (HL^{1-4}) can be attributed to the variation in electronic environment due to coordination with metal ions. The next group of bands appear in the region 1200-1000 cm^{-1} and one of them is the strongest which has been assigned to the υ_{N-O}. It suggests that oxygen atoms of the N-O group is not involved in coordination.

The appearance of few additional sharp and intense bands in comparison to ligands in the vicinity of 700 cm^{-1} indicate the presence of metal-halogen or metal oxygen bonds.

Table 2. Important IR Bands (cm^{-1}) of the Ligands and Metal Complexes.

Compounds	υ_{O-H}	υ_{C-N} (azomethine)	υ_{C-N} (oxime)	υ_{N-O}
HL^1	3420 mb	1630 s	1455 s	1090 s
HL^2	3425 mb	1635 s	1450 s	1095 s
HL^3	3415 mb	1630 s	1445 s	1090 s
HL^4	3420 mb	1635 s	1450 s	1085 s
$Ni(HL^1)_2Cl_2$	3410 mb	1620 s	1475 s	1090 s
$Ni(HL^2)_2Cl_2$	3415 mb	1620 s	1475 s	1090 s
$Ni(HL^3)_2Cl_2$	3425 mb	1615 s	1465 s	1075 s
$Ni(HL^4)_2Cl_2$	3430 mb	1620 s	1470 s	1080 s
$Ni(HL^1)_2Br_2$	3415 mb	1615 s	1475 s	1070 s
$Ni(HL^2)_2Br_2$	3420 mb	1620 s	1480 s	1075 s
$Ni(HL^3)_2Br_2$	3410 mb	1615 s	1470 s	1075 s
$Ni(HL^4)_2Br_2$	3415 mb	1620 s	1475 s	1080 s
$Ni(HL^1)_2I_2$	3400 mb	1610 s	1475 s	1085 s
$Ni(HL^2)_2I_2$	3405 mb	1620 s	1480 s	1090 s
$Ni(HL^3)_2I_2$	3405 mb	1615 s	1480 s	1080 s
$Ni(HL^4)_2I_2$	3410 mb	1620 s	1485 s	1085 s
$Ni(HL^1)_2(NO_3)_2$	3415 mb	1610 s	1470 s	1075 s
$Ni(HL^2)_2(NO_3)_2$	3420 mb	1615 s	1475 s	1080 s
$Ni(HL^3)_2(NO_3)_2$	3410 mb	1615 s	1475 s	1080 s
$Ni(HL^4)_2(NO_3)_2$	3415 mb	1620 s	1480 s	1085 s
$Ni(HL^1)_2(ClO_4)_2$	3420 mb	1615 s	1465 s	1075 s
$Ni(HL^2)_2(ClO_4)_2$	3425 mb	1610 s	1470 s	1080 s
$Ni(HL^3)_2(ClO_4)_2$	3415 mb	1620 s	1470 s	1080 s
$Ni(HL^4)_2(ClO_4)_2$	3420 mb	1605 s	1475 s	1085 s
$Co(HL^1)_2Cl_2$	3405 mb	1615 s	1465 s	1075 s
$Co(HL^2)_2Cl_2$	3400 mb	1620 s	1470 s	1070 s
$Co(HL^3)_2Cl_2$	3400 mb	1610 s	1465 s	1070 s
$Co(HL^4)_2Cl_2$	3395 mb	1615 s	1460 s	1065 s
$Co(HL^1)_2Br_2$	3410 mb	1610 m	1465 s	1075 s
$Co(HL^2)_2Br_2$	3408 mb	1605 m	1470 s	1065 s
$Co(HL^3)_2Br_2$	3405 mb	1615 m	1465 s	1060 s
$Co(HL^4)_2Br_2$	3410 mb	1610 m	1470 s	1070 s
$Co(HL^1)_2I_2$	3415 mb	1610 m	1480 s	1080 s
$Co(HL^2)_2I_2$	3420 mb	1615 m	1475 s	1075 s
$Co(HL^3)_2I_2$	3410 mb	1615 m	1465 s	1065 s
$Co(HL^4)_2I_2$	3415 mb	1610 m	1470 s	1070 s
$Co(HL^1)_2(NO_3)_2$	3410 mb	1615 m	1475 s	1080 s
$Co(HL^2)_2(NO_3)_2$	3415 mb	1620 m	1480 s	1075 s
$Co(HL^3)_2(NO_3)_2$	3415 mb	1610 m	1470 s	1075 s
$Co(HL^4)_2(NO_3)_2$	3420 mb	1615 m	1475 s	1070 s
$Co(HL^1)_2(ClO_4)_2$	3415 mb	1610 m	1470 s	1075 s
$Co(HL^2)_2(ClO_4)_2$	3420 mb	1610 m	1475 s	1075 s
$Co(HL^3)_2(ClO_4)_2$	3410 mb	1615 m	1470 s	1080 s
$Co(HL^4)_2(ClO_4)_2$	3415 mb	1615 m	1465 s	1075 s

m = medium. b = broad. s = strong.

Besides these, one more band at 1485 cm^{-1} has been observed which is characteristic of the phenyl ring system. The remaining expected bands due to presence of phenyl groups might have been superimposed by the oxime and azomethine bands.

On the basis of above discussion, complexes of the type $M(HL^{1-4})_2X_2$ may be assigned structure I or II.

These structures are supported by magnetic moment and electronic spectral studies as discussed in the following paragraphs.

The nickel (II) complexes of the type $[Ni(HL^{1-4})_2X_2]$ have magnetic moment values in the region 2.7-3.1 B.M. at room temperature which suggest octahedral arrangement of the ligand atoms around it. The electronic spectra of these complexes consists of three bands, in the region, 13500-14500 cm^{-1} (13810-14140 cm^{-1}), the next one in the vicinity of 18000 cm^{-1} (17570-18310 cm^{-1}) followed by a strong intense band near 26000 cm^{-1} (25850-27070 cm^{-1}). These bands may be assigned to the transitions, $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ in an octahedral field. The cobalt (II) complexes of the type, $[Co(HL^{1-4})_2X_2]$ possess magnetic moment values in the range 5.15 - 5.32 B.M. at 25°C and exhibit a multiple band structure in the region 16000-18000 cm^{-1} (16800-17610 cm^{-1}), the nature and width of which spreading over 3000 cm^{-1} suggest octahedral environment around cobalt (II) ion in these complexes. The molar extinction co-efficients lie in the range 20-30 and the band may be assigned to the combination of two transitions, $^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ and $^4A_{2g}(F) \rightarrow {}^4T_{1g}(P)$. Symmetry of complexes of the type, $[M(HL^{1-4})_2X_2]$ is lowered from octahedral to C_{2v} as the ligands, HL^{1-4} and X are not equivalent. It corresponds to the strengthening of the ligand field along C_2 axis and splitting of T_{1g}, T_{2g} and E_g into non-degenerate levels.

Molar conductance values for the complexes are found in the range 15-22 $ohm^{-1}cm^2$ mol^{-1} which support non electronic nature of the complexes.

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