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Synthesis and Spectral Studies on Co^{2+}, Ni^{2+} and Fe^{2+} Complexes with *o*-, *p*-, *m*-methoxyphenylimino-1-phenyl-2-hydroxyiminopropane

H.C. RAI and VIBHA KUMARI*
Department of Chemistry
L.S. College, Muzaffarpur-842 001

A series of Co^{2+}, Ni^{2+}, and Fe^{2+} complexes of the type $M(HL^{1,2,3})_2X_2$, where M = Co(II), Ni(II) and Fe(II); HL^1, HL^2, HL^3 = 1-*o*-, *p*-, *m*-methoxyphenylimino-1-phenyl-2-hydroxyiminopropane have been synthesized and characterized by analytical, conductivity, thermal and magnetic, infrared and electronic spectral data. The studies show that the complexes are isostructural and possess octahedral geometry. Semi-quantitative group theoretical study suggests complexes to possess *trans*- structure.

INTRODUCTION

1-*o*-, *p*-, *m*-methoxyphenylimino-1-phenyl-2-hydroxyiminopropanes are imine-oxime type Schiff bases which have received widespread applications as biochemical[1], analytical[2] and antimicrobial[3] reagents. It has been further reported that imine oximes when administered in the form of metal complexes are good anticancer, antitumor, antituberculosis and antipyretic agents. Recently it has been proposed that such imine oxime metal chelates serve as excellent fungicides and plant growth regulators[4,5]. In the present comunication we describe the synthesis and characterization of a series of Co^{2+}, Ni^{2+} and Fe^{2+} complexes of bidentate imine oxime like N-donor Schiff base derived from 1-phenyl-2-hydroxyiminopropan-1-one and *o*-, *p*-, *m*-anisidines.

EXPERIMENTAL

The ligands, 1-*o*-, *p*-, *m*-methoxyphenylimino-1-phenyl-2-hydroxyiminopropane were prepared following literature methods[6]. The ligands were synthesized by the condensation of 1-phenyl-2-hydroxyiminopropan-1-one with *o*-, *p*-, *m*-anisidines in an ethanolic medium in the molar ratio 1:1. Their melting points agreed well with the reported values[7]. All the complexes were prepared by adopting an *'in situ'* method using the corresponding dry alcohols as media. The preparation of one typical complex is described below for each of the series of complexes.

Bis-(1-o-methoxyphenylimino-1-phenyl-2-hydroxyiminopropane) dichlorocobalt(II), $Co(HL^1)_2Cl_2$: An ethanolic solution of $CoCl_2 \cdot 6H_2O$ (1.18 g, 0.005 mol) and 1-phenyl-2-hydroxyiminopropan-1-one (1.63 g, 0.01 mol) was refluxed over a hot water bath for 1 h. A brown colour complex which separated

out on slow evaporation was filtered, washed several times with methanol and finally with ether and then dried in vacuum over fused calcium chloride.

Bis-(1-o-methoxyphenylimino-1-phenyl-2-hydroxyiminopropane) dichloronickel(II), $Ni(HL^1)_2Cl_2$: A solution of $NiCl_2 \cdot 6H_2O$ in ethanol (1.1 g; 0.005 mol) was treated with an ethanolic solution of the ligand (2.46 g, 0.01 mol). The mixture was refluxed over a hot water bath. The red colour complex thus separated out on cooling was filtered, washed, dried in vacuum over $CaCl_2$.

Bis-(1-o-methoxyphenylimino-1-phenyl-2-hydroxyiminopropane) dichloroiron (II), $Fe(HL^1)_2Cl_2$: An alcoholic solution of iron(II) chloride tetrahydrate (1.0 g, 0.005 mol) was treated with an alcoholic solution of the ligand (2.46 g, 0.01 mol) and the resulting solution was refluxed over a hot water bath for 1 h. The brown precipitate thus obtained was filtered, washed with alcohol followed by ether and dried as above.

All the chemicals used were of analytical grade. 1-Phenyl-2-hydroxyiminopropan-1-one was of Loba quality and dry ethanol used of Bengal Chemicals. *o*-, *p*- and *m*- Anisidines were of BDH reagents redistilled before use. The Co(II), Ni(II) and Fe(II) solutions were reagent grade chemicals from S. Merck.

Analytical data (C, H, N and Cl) for the ligands and their metal complexes were obtained from C.D.R.I., Lucknow. Metal contents were determined by using standard procedure[8]. Molar conductivities of the complexes were measured using a Digisun Digital Conductivity Meter, Model DI–909. Thermal data of the complexes were obtained using a Stanton thermobalance. Magnetic measurements in the solid state were made in a Gouy balance using $Hg[Co(CNS)_4]$ as the calibrant. The electronic spectra of the complexes in nujol mull and ethanol were recorded on a Hitachi model 330 spectrophotometer in the 25,000–10,000 cm^{-1} region. Infrared spectra of the complexes were recorded as KBr pellets in the 4000–200 cm^{-1} region on a Beckman IR-20 spectrophotometer.

RESULTS AND DISCUSSION

All the complexes are stable at room temperature, non-hygroscopic and insoluble in water and in many of the common organic solvents but are soluble in the DMF and DMSO. Analytical data of the complexes (Table-1) indicate that the metal-ligand molar ratio is 1 : 2 and all the complexes are also associated with two chloride ions. The conductance measurements in DMF are too low to account for any dissociation of the complexes. Hence, the complexes may be regarded as non-electrolytes[9]. Decomposition temperatures, determined from thermograms (Table-1), indicate that the complexes are thermally stable up to 200°C and no water molecule is present in the complexes. The sharp decomposition associated with the loss of ligands starts above 230°C.

The infrared spectra of 1-*o*-, *p*-, *m*-methoxyphenylimino-1-phenyl-2-hydroxyiminopropane shows two fairly strong and broad bands at 3485 and 3355 cm^{-1} (Table-2) implying hydrogen-bonded structure involving the N—OH group[10]. These bands persist in the spectra of the complexes with reduced breadth and increased intensity indicating ligands to be co-ordinated in their uncharged state. Reduction in breadth indicates absence of hydrogen bonding and supports the *trans*-structure for the complexes.

TABLE-1
THE ANALYTICAL AND PHYSICAL DATA OF THE COMPLEXES OF 1-*o*-, *p*-, *m*-METHOXYPHENYLIMINO-1-PHENYL-2-HYDROXYIMINOPROPANE; (HL^1), (HL^2), (HL^3)

Complexes (Colour)	Decomposition Temperature (°C)[a]	% Analysis, Found (Calcd.)			
		M	C	H	N
$Co(HL^1)_2Cl_2$ (Brown)	322	8.84 (9.02)	64.28 (64.20)	1.77 (1.70)	8.40 (8.31)
$Co(HL^2)_2Cl_2$ (Dark brown)	319	8.88 (9.02)	64.32 (64.20)	1.81 (1.70)	8.41 (8.31)
$Co(HL^3)_2Cl_2$ (Shining brown)	313	8.86 (9.02)	64.38 (64.20)	1.79 (1.70)	8.43 (8.31)
$Ni(HL^1)_2Cl_2$ (Red)	308	8.90 (8.78)	64.31 (64.20)	1.62 (1.71)	8.41 (8.36)
$Ni(HL^2)_2Cl_2$ (Reddish brown)	312	8.87 (8.78)	64.29 (64.20)	1.82 (1.71)	8.27 (8.38)
$Ni(HL^3)_2Cl_2$ (Dark green)	311	8.90 (8.78)	64.25 (64.20)	1.80 (1.71)	8.27 (8.36)
$Fe(HL^1)_2Cl_2$ (brown)	320	9.53 (9.38)	64.33 (64.50)	1.79 (1.60)	9.46 (9.40)
$Fe(HL^2)_2Cl_2$ (Greenish brown)	312	9.28 (9.38)	64.38 (64.50)	1.71 (1.60)	9.51 (9.40)
$Fe(HL^3)_2Cl_2$ (Violet)	318	9.46 (9.38)	64.30 (64.50)	1.69 (1.60)	9.45 (9.40)

[a]All the complexes decompose above the temperature cited.

In the spectra of the ligands there appear two sharp and moderately intense bands in the region 1685–1675 cm^{-1} and another in the region 1530–1500 cm^{-1} which have been attributed to the ν(C—N) stretching vibrations of azomethine and oxime respectively[11]. These bands shift to a lower region ($\Delta\nu = 50\ cm^{-1}$) in all the complexes, indicating the involvement of the azomethine and oxime nitrogen atoms in co-ordination.

The strongest band appearing in the region 1200–1000 cm^{-1} has been assigned to the ν(N—O)[12]. These bands were found unaffected in the spectra of metal complexes, indicating non-involvement of oxygen atom of the N—O group in coordination.

In the electronic spectral data (Table-3), the ligands exhibit strong bands around 34,000 and 31,000 cm^{-1} which may be assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions respectively.

Electronic spectra of Co^{2+} complexes display two important bands in the region 10,000–8,000 and 22,000–17,000 cm^{-1} which may be assigned to the spin allowed transitions $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ (ν_1) and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (ν_3) respectively characteristic of octahedral geometry[13] around Co^{2+}. $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transition band appear as relatively intense double peak band due to spin-orbit coupling of the

$^4T_{1g}(P)$ state. A weak band is found in the region 17,000–11,000 cm^{-1} which being weak is scarcely observed and has been assigned to the transition $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ (ν_2)[14]. One of the important features of the spectra is the appearance of a strong charge transfer band above 20,000 cm^{-1} and has in a few cases impeded clear resolution of the spectra in the vicinity of this region.

TABLE-2
SOME IMPORTANT INFRARED SPECTRAL DATA (cm^{-1}) OF THE COMPLEXES OF 1-*o*-, *p*-, *m*-METHOXYPHENYLIMINO-1-PHENYL-2-HYDROXYIMINOPROPANE; (HL^1), (HL^2), (HL^3)[a]

Complex	ν(O—H)	ν(C⋯N) (azomethine)	ν(C⋯N) (oxime)	ν(N⋯O)
$Co(HL^1)_2Cl_2$	3480 s, 3365 s (3490b, 3370b)	1630 s (1680 s)	1570 b (1525 b)	1110 s
$Co(HL^2)_2Cl_2$	3485 s, 3370 s (3490 b, 3370 b)	1635 s (1685 s)	1565 s (1520 b)	1120 s
$Co(HL^3)_2Cl_2$	3490 s, 3355 s (3490 b, 3360 b)	1630 s (1675 s)	1565 b (1515 m)	1120 s
$Ni(HL^1)_2Cl_2$	3485 s, 3350 s (3480 b, 3355 b)	1625 b (1675 m)	1570 s (1530 s)	1100 s
$Ni(HL^2)_2Cl_2$	3495 s, 3370 s (3495 b, 3367 b)	1630 s (1685 m)	1575 s (1530 s)	1100 s
$Ni(HL^3)_2Cl_2$	3440 s, 3340 s (3442 b, 3336 b)	1625 s (1680 b)	1575 s (1525 s)	1110 s
$Fe(HL^1)_2Cl_2$	3490 s, 3358 s (3487 b, 3360 b)	1630 b (1675 s)	1570 s (1520 s)	1070 s
$Fe(HL^2)_2Cl_2$	3480 s, 3365 s (3480 b, 3367 b)	1630 m (1680 s)	1565 s (1530 s)	1110 s
$Fe(HL^3)_2Cl_2$	3490 s, 3360 s (3485 b, 3355b)	1630 s (1685 s)	1565 s (1530 m)	1100 s

[a]Values in parentheses are free ligand bands
s = strong, b = broad, m = medium

Ni(II) complexes also exhibit three bands, one in the region 15,500–13,000 cm^{-1}, the next one in the vicinity of 20,000 cm^{-1} followed by the strong intense band near 26,000 cm^{-1}. These bands may be assigned to the transitions $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ (ν_1), $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ (ν_2) and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ (ν_3) respectively[15]. The appearance of two bands in the region 20,000–12,000 cm^{-1} suggests the central Ni^{2+} to be present in an octahedral field with certain amount of tetragonal distortion.

During the course of investigation Fe(II) complexes show a broad band in the region 12,000–10,000 cm^{-1} which can be assigned to the transition $^5T_{2g} \rightarrow {}^5E_g$ and suggest an octahedral environment[16, 17] of the ligand atoms around Fe^{2+}. The broad and unsymmetrical band indicates the presence of Jahn-Tellor distortion in excited state.

TABLE-3
MAGNETIC AND ELECTRONIC SPECTRAL DATA OF THE COMPLEXES OF 1-*o*-, *p*-, *m*-METHOXYPHENYLIMINO-1-PHENYL-2-HYROXYIMINOPROPANE; (HL^1), (HL^2), (HL^3)

Complexes	Band positions			Band assignments	Charge transfer bands (cm^{-1})	μ_{eff} (B.M.)
	ν_1 (cm^{-1})	ν_2 (cm^{-1})	ν_3 (cm^{-1})			
$Co(HL^1)_2Cl_2$	8200	17200	21100	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ (ν_1)	23920	5.18
$Co(HL^2)_2Cl_2$	8000	17210	21250	$^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ (ν_2)	23900	5.25
$Co(HL^3)_2Cl_2$	8190	17180	21210	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (ν_3)	23910	5.24
$Ni(HL^1)_2Cl_2$	13700	18840	25750	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ (ν_1)	—	2.90
$Ni(HL^2)_2Cl_2$	13710	18000	25870	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ (ν_2)	—	3.05
$Ni(HL^3)_2Cl_2$	13700	18820	25790	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ (ν_3)	—	2.83
$Fe(HL^1)_2Cl_2$	11980	—	—	$^5T_{2g} \rightarrow {}^5E_g$ (ν_1)	—	5.10
$Fe(HL^2)_2Cl_2$	11700	—	—	$^5T_{2g} \rightarrow {}^5E_g$ (ν_1)	—	5.20
$Fe(HL^3)_2Cl_2$	11990	—	—	$^5T_{2g} \rightarrow {}^5E_g$ (ν_1)	—	5.10

The magnetic moments of the Co(II), Ni(II) and Fe(II) complexes have been found in the range 5.18–5.24 B.M., 2.9–3.1 B.M. and 5.1–5.2 B.M. respectively corresponding to paramagnetic behaviour and octahedral geometry of all the complexes.

On the basis of infrared spectra, electronic spectra, magnetic moment data and conductivity data complexes are expected to possess the *trans* structures as shown in Fig. 1(a) or a *cis*- one as in Fig. 1(b).

The *trans* structure for complexes as suggested in Fig. 1(a) is also supported by semi-empirical group-theoretical study of some of the complexes as detailed in the following paragraphs:

On the basis of semi-quantitative group theoretical analysis[18], the *trans* structure as shown in Fig. 1(a) is preferred.

Γ_R(M—N) is found to be composed of $2A_1$ and $2B_2$. All the four vibrational modes are infrared active as all of them transform according as one of the dipole moment components M_X, M_Y and M_Z. In the case of *trans*- isomer Γ_R(M—N) is found to be composed of $2A_g + 2B_u$ and out of these four vibrational modes, only two ($2B_u$) are infrared active. The spectra of present series of complexes in the far infrared region show only two bands for M—N, one in the region (450–445) cm^{-1} and another in the region (555–550) cm^{-1}. So the structure as shown in Fig. 1(a) is preferred one.

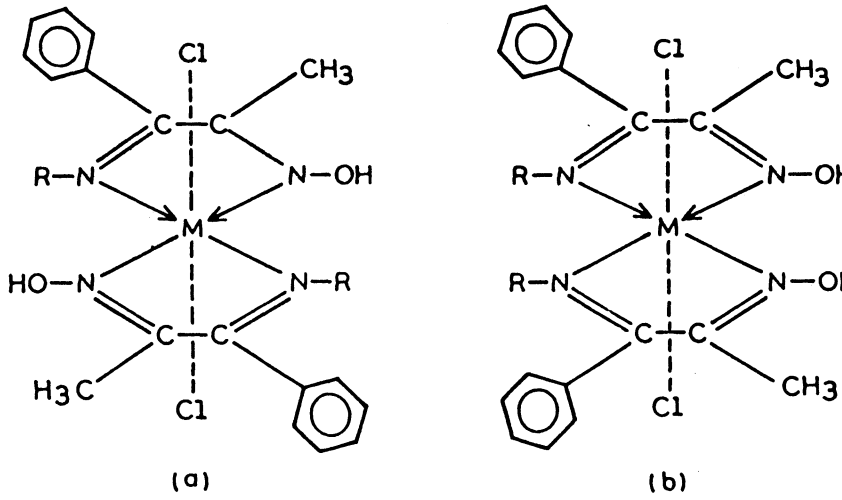

Fig. 1. Structure of (a) *trans*-complex; (b) *cis*-complexes.

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