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Synthesis and Characterization of Transition Metal Complexes of Oxime

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In this study a novel oxime, isonitroso-*p*-methoxyacetophenone was synthesized. A new schiff base have been synthesized by the condensation 1,2-diaminoethane (HL) with isonitroso-*p*-methoxyacetophenone. The complexes of nickel(II), copper(II), cobalt(II), zinc(II), cadmium(II) and mercury(II) with HL were prepared. The ligand and their complexes were charecterized by spectroscopic techniques.

Key Words: Schiff bases, Iminoximes, Metal complexes, Characterization.

INTRODUCTION

Numerous oximes and schiff base and their transition metal complexes have been investigated in past[1,2]. The exceptional stability and interesting electronic properties of these complexes can be attributed to their planar structure[3]. Acyclic ligands containing nitrogen, oxygen and sulphur donor atoms in their structures can act as an effective chelating agents for transition and non-transition metal ions[4].

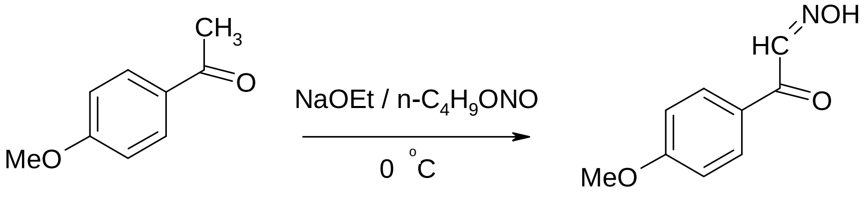
In this study, prepared nitroso compound were reacted with diamino compounds to obtain iminooxime such as ethylimino-*bis*(isonitroso-*p*-methoxyacetophenone) (Fig. 1) and its transition metal complexes were synthesised.

EXPERIMENTAL

$Ni(CH_3COO)_2$, $Cu(CH_3COO)_2$, $Co(CH_3COO)_2$, $Zn(CH_3COO)_2$, $Cd(CH_3COO)_2$ and $HgCI_2$ and *p*-methoxyacetophenone, 1,2-diaminoethane, were obtained from Merck (KGaA, Germany) and all of them were purified according to literature[5].

The carbon, hydrogen and nitrogen analyses were obtained using a Carlo Erba 1106 autoelemental analyser. Jasco FT/IR-300 E Spectrometer was used for charecterisation. The electronic spectra in the 200-800 nm range were recorded in DMF on a Shimadzu UV-160 a spectrophotometer. Conductivities were measured in DMF using a LF 330/SET conductivity meter and were performed at 24ºC. Magnetic moments were measured by the Gouy method by using $Hg[Co(SCN)_4]$ as calibrant. The ^1H NMR spectra of the ligand HL was recorded with a Bruker Avance-500 NMR instrument .

Preperation of Isonitroso-*p*-methoxyacetophenone: The oxime was prepared according to literature. Isonitroso-*p*-methoxyacetophenone was prepared by reacting *p*-methoxyacetophenone with *n*-butylnitrite in presence of sodium ethoxide[6,7].



p-methoxyacetophenone Isonitroso-*p*-methoxyacetophenone

Preperation of schiff base ligand: The ligand were prepared according to literature[8]. Isonitroso-*p*-methoxyacetophenone 0.183 g (1 mmol) dissolved in methanol (20 mL), was added with constant stirring to a solution 1,2-diaminoethane (HL) 0.030 g (0.5 mmol) in methanol (10 mL). The mixture was allowed to stirrer magnetically at 30ºC for 4.5 h. After cooling, the resulting precipitate was filtered and recrystallized by benzene/ methanol(1:1).

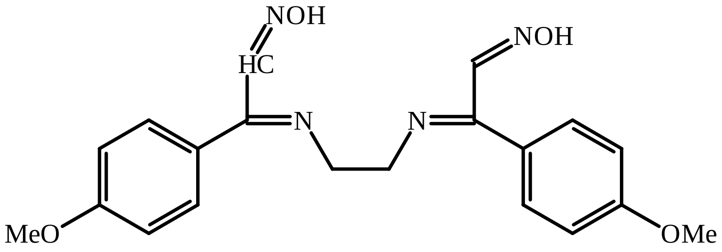


Fig. 1. Structure of the Ligands HL

Preparation of metal complexes: All the metal complexes were synthesized by the reaction of the Schiff base ligand (1 mmol, in 20 mL methanol) with the corresponding metal salts (0.5 mmol, 10 mL methanol) at 50ºC during 4 h. The resulting precipitate was filtered, washed several times with methanol and dried over calcium chloride under vacuum.

RESULTS AND DISCUSSION

The analytical data for the ligand and its metal complexes are listed in Table-1. The result of the elementel analyses show that the metal to ligand ratio is 1:1 in all the metal complexes. The composition of the complexes is [ML]. The schiff base ligand is soluble in common organic solvents. All complexes are soluble in DMF, DMSO and insoluble in the other organic solvents.

The tentative assigment of the most charecteristic infrared bands were observed (Table-2). The vibration of the sterically hindered of oxime groups of the free schiff base ligands oxime and HL are observed 3500-3400 cm^{-1}, respectively[9,10]. When the spectra of the complexes are compared with those of the uncomplexed schiff base ligands the ν(C=N) band are shifted to lower frequency[11,12].

This indicate that the imine nitrogen is coordinated to the metal ion. The spectra of complexes show a few expected absorption bands 560-520 cm^{-1} and 420-380 cm^{-1} ranges assigned to ν(M-N)[9] and ν(M-O)[10,11].

Electonic spectra: The electronic absorbtion spectral data of the free ligand and its metal complexes are given in Table-3. In the spectra of the schiff base ligand bands at 255-278 nm are attribute to the benzene π-π^* transtions[13-15]. The bands at 331-379 nm are assigned to the imine π-π^* transition. Compared to the free ligand, the imine π-π^* transitions of the complexes were shifted to some extent, because the imine nitrogen is involved in coordination with the metal ion.

Conductance measurements: The molar conductance values of the synthesized schiff base ligands and their Ni(II), Co(II), Cu(II), Zn(II), Cd(II) and Hg(II) complexes are in the range 0.1 to 35.9 Ω^{-1} cm^2 mol^{-1} in 10^{-3} M DMF solutions indicating the non-electrolytic nature of these compounds[12].

NMR spectra of the schiff bases: In order to understand the solution structure of the a novel oxime and free schiff base ligands, ^{1}H NMR spectra have been employed. The ^{1}H-NMR assignments are listed in Table-4. The doublet-doublet observed at 7.0-8.0 ppm are assigned to the aromatic ring proton of the oxime and ligand HL. The singlets at 8.2 and 7.8 ppm have been assigned to the protons of CH and the proton of the aldoxime group, respectively. The singlet at 3.90 ppm have been assigned to protons of methoxy group. Futhermore, the triplet at 1.70 ppm in the ligand HL is attributed to the protons of methelene group[9,10,12].

MS studies: In the MS spectra of the ligand a novel oxime m/e 179 [$C_9H_9NO_3$, 20%], (M^{+1} 180, 5%), 161 [$C_9H_7NO_2^+$, 9%], 135 [$C_8H_7O_2^+$, 100%], 107 [$C_7H_7O^+$, 20%], 92 [$C_6H_4O^+$, 25%], 77 [$C_6H_5^+$, 40%]. MS spectra of the ligand HL, m/e 382, 339 [M^+-CH_2NO, 40%], 275 [M^+-C_7H_7O, 5%], 231 [M^+-$C_8H_9NO_6$, 5%], 179 [M^+-$C_{11}H_{11}N_2O_2$, 10%], 178 [M^+-$C_{11}H_{12}N_2O_2$, 100%], 150 [M^+-$C_{11}H_{10}N_3O_3$, 5%].

TABLE-1

SOME ANALYTICAL DATA AND PHYSICAL PROPERTIES OF THE SCHIFF BASE LIGANDS AND COMPLEXES

Compound	Empirical Formula	Formula wt.	Colour	m.p. (°C)	Yield (%)	Analysis found (calcd.) %		
						C	H	N
A novel oxime	$C_9H_9NO_3$	179	White	113	67	66.30 (66.33)	5.00 (5.06)	7.75 (7.81)
HL	$C_{20}H_{21}N_4O_4$	381	Orange	163^d	81	62.85(62.98)	5.50(5.54)	14.50(14.68)
LCo	$C_{20}H_{20}N_4O_4Co$	439	Red	200^d	80	54.55(54.67)	4,56(4.58)	12.73(12.75)
LNi	$C_{20}H_{20}N_4O_4Ni$	439	Green	265^d	86	54.60(54.75)	4.50(4.59)	12.70(12.76)
LCu	$C_{20}H_{20}N_4O_4Cu$	443	Dark-green	240^d	90	54.00 (54.11)	4.45 (4.54)	12.60 (12.62)
LZn	$C_{20}H_{20}N_4O_4Zn$	445	Yellow	164	76	53.75(53.88)	4.45(4.52)	12.50(12.56)
LCd	$C_{20}H_{20}N_4O_4Cd$	492	Yellow	154^d	83	48.70(48.74)	4.02(4.09)	11.25(11.36)
LHg	$C_{20}H_{20}N_4O_4Hg$	580	Orange	135^d	79	41.10(41.34)	3.30(3.46)	9.40(9.64)

d: Decomposition points of corresponding molecules.

TABLE-2

INFRARED SPECTRAL BANDS (cm^{-1}) OF THE FREE LIGANDS AND THEIR COMPLEXES

Compound	ν(NOH)	$\nu(C=N)_{im}$	$\nu(C=N)_{ox}$	$\nu(R\text{-}OCH_3)$	ν(C-N)	ν(M-N)	ν (M-O)
Oxime	3250-3350	-	1650	1275	1100	-	-
HL	3400	1640	1600	1200	1100	-	-
LCo	-	1605	1600	1220	1100	510	420
LNi	-	1603	1600	1215	1100	580	480
LCu	-	1620	1600	1210	1105	500	410
LZn	-	1623	1603	1200	1107	501	470
LCd	-	1633	1603	1178	1097	560	460
LHg	-	1630	1600	1209	1107	551	450

TABLE-3

MAGNETIC MOMENTS (μ_{eff}) AND ELECTRONIC SPECTRAL DATA (λ_{max}) OF THE SCHIFF BASE LIGANDS AND THEIR METAL COMPLEXES

Compound	μ_{eff}	λ_{max} (ε, M^{-1}, cm^{-1})
HL	-	732sh(100), 259(570), 271(2080)
LCo	3.41	401(2950), 379(2500), 360(2800), 261(630)
LNi	2.92	346(1730), 331(1560), 306(1820), 260(660)
LCu	1.68	560(200), 302(880), 259(720)
LZn	Diamag	271(960), 259(630)
LCd	Diamag	710sh(100), 275(1920), 258(600)
LHg	Diamag	740sh(110), 278(2195), 255(550)

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TABLE-4

THE ^1H NMR SPECTRA OF THE SCHIFF BASE LIGANDS

A novel oxime			**HL**		
δ (ppm)	Peak	Assignments	δ (ppm)	Peak	Assignments
3.90	4 (H)	OCH_3 Groups	1.70	4 (H)	CH_2 proton
7-8	4 (H)	Aromatic ring (H)	3.90	4 (H)	OCH_3 Groups
7.20	1 (H)	CH (aldoxime) proton	7-8	8 (H)	Aromatic ring (H)
8.40	2 (H)	OH	8.2	1 (H)	CH (aldoxime) proton
			8.4	2 (H)	OH

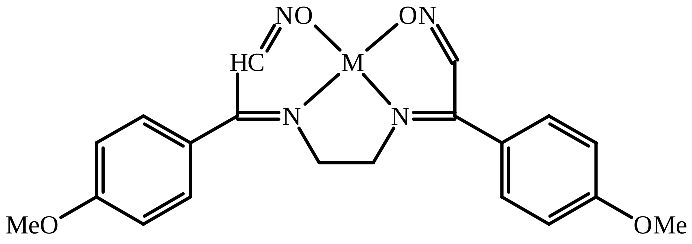

Fig. 2. Structure of the Complexes (M = Ni, Cu,Co, Zn, Cd, Hg)

There are similiar peaks for the cobalt complexes (LCo), m/e 439, 339 [M^+-CH_2NO, 40%], 410 [M^+-OCH_3, 7%], 283 [M^+-$C_{11}H_9O$, 55%], 255 [M^+-$C_{13}H_{16}O$, 100%], 178 [M^+- $C_{12}H_{12}N_3OCo$, 68%], 147 [M^+-$C_{11}H_{11}N_3O_3$, 70%][12].

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