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Synthesis and Characterization of Cu(II), Cd(II) and Hg(II) Complexes with Schiff Bases

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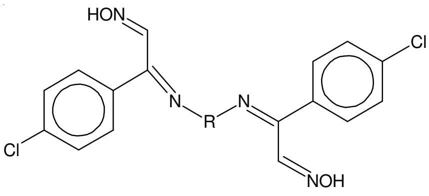
Two new Schiff base have been synthesized by the condensation 1,2-diaminoethane (HL) and 1,4-diamino butane (HL') with isonitroso-*p*-chloroasetafenon. The complexes of copper(II), cadmium(II) and mercury(II) with HL and HL' were prepared. The ligands and their metal complexes were characterized by spectroscopic techniques.

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

INTRODUCTION

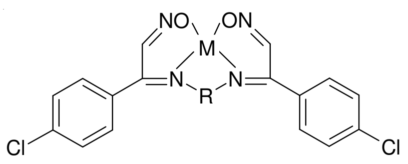
Generally, the chelating ligands are poly functional molecule which can encage the metal in an organic sphere. Many types of the Schiff base ligands are known and properties of their metal chelates have been investigated[1,2]. Acyclic ligands containing nitrogen, oxygen and sulphur donor atoms in their structures can act as an effective chelating agents for transition and non-transition metal ions[3].

In this study, new Schiff base ligands (Fig. 1) and their transition metal complexes (Fig. 2) were synthesised and the type of coordination which takes place to the metal ions were interpreted.



R= $(CH_2)_2$ (HL), $(CH_2)_4$ (HL')

Fig. 1. Structure of 1,2-diaminoethane (HL) and 1,4-diamino butane (HL')



R = $(CH_2)_2$ (HL), $(CH_2)_4$ (HL') (M = Cu, Cd, Hg)

Fig. 2. Structure of the metal complexes

EXPERIMENTAL

$Cu(CH_3COO)_2$, $Cd(CH_3COO)_2$ and $HgCl_2$ and *p*-chloroacetophenone, 1,2-diaminoethane, 1,4-diaminobutane were obtained from Merck (KGaA, Germany) and all of them were purified according to literature[4].

The carbon, hydrogen and nitrogen analyses were obtained using a Carlo Erba 1106 autoelemental analyzer. Jasco FTIR - 300E Spectrometer was used for charecterization. The elektronic 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 metod by using $Hg[Co(SCN)_4]$ as calibrant. The ^1H NMR spectra of the ligands HL and HL' were recorded with a Bruker Avance-500 NMR instrument.

Preperation of Schiff base ligands: The ligands were prepared according to literature[5]. Isonitroso-*p*-chloroasetafenone 0.183 g (1 mmol) dissolved in methanol (20 mL), was added with constant stirring to a solution of 1,2-diaminoethane (HL) 0.030 g (0.5 mmol) or 1,4-diaminobutane (HL') 0.088 g (0.5 mmol) in methanol (10 mL). The mixture was allowed to stirrer magnetically at 50ºC during 4.5 h. After cooling, the resulting precipitate was filtered and recrystallized by hexane:methanol (1:1).

Preparation of complexes: All of the 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 ligands and their metal complexes are listed in Table-1. The result of the elemental analyses show that the metal to ligand ratio is 1:1 in all the complexes. The composition of the complexes is [ML]. The Schiff base ligands are soluble in common organic solvents. All the metal complexes are soluble in DMF and DMSO and insoluble in the other organic solvents.

Infrared spectra: The tentative assigment of the most characteristic IR bands were observed and are given in Table-2. The vibration of the sterically hindered oxime groups of the free schiff base ligands HL and HL' are observed 3500-3400 cm^{-1}, respectively[6,7]. When the spectra of the complexes are compared with those of the uncomplexed Schiff base ligands the $\nu(C=N)$ band are shifted to lower frequency[8,9]. This indicated that the imine nitrogen is coordinated to the metal ion. The spectra of complexes show a few expected absorption bands 560-520 and 420-380 cm^{-1} ranges assigned to $\nu(M–N)$[10] and $\nu(M–O)$[11].

TABLE-1
ANALYTICAL DATA AND PHYSICAL PROPERTIES OF THE SCHIFF BASE LIGANDS AND METAL COMPLEXES

Compd.	m.f. (m.w.)	Colour	m.p. (°C)	Yield (%)	Found (Calcd.) % C	H	N
HL	$C_{18}H_{16}N_4O_2Cl_2$	Orange	151[d]	55	55.10	4.09	14.23
	(391.2)				(55.25)	(4.12)	(14.32)
[CuL]	$C_{18}H_{18}N_4O_4Cl_2Cu$	Green	235	52	47.50	3.90	12.25
	(454.7)				(47.54)	(3.99)	(12.32)
[CdL]	$C_{18}H_{14}N_4O_2Cl_2Cd$	Yellow	300>	50	42.80	3.52	11.05
	(503.6)				(42.92)	(3.60)	(11.12)
[HgL]	$C_{18}H_{14}N_4O_2Cl_2Hg$	Yellow	127	70	36.35	3.00	9.25
	(591.8)				(36.53)	(3.06)	(9.46)
HL'	$C_{20}H_{20}N_4O_2Cl_2$	Orange	110[d]	67	57.51	4.71	13.45
	(419.3)				(57.28)	(4.80)	(13.36)
[CuL']	$C_{20}H_{22}N_4O_4Cl_2Cu$	Green	120[d]	65	49.50	4.05	11.30
	(482.8)				(49.75)	(4.17)	(11.60)
[CdL']	$C_{20}H_{18}N_4O_2Cl_2Cd$	Yellow	150[d]	55	45.02	3.45	10.35
	(531.7)				(45.17)	(3.79)	(10.53)
[HgL']	$C_{20}H_{18}N_4O_2Cl_2Hg$	Yellow	124[d]	60	38.50	3.04	9.00
	(619.8)				(38.75)	(3.25)	(9.03)

[d] Decomposition points of corresponding molecules.

TABLE-2
INFRARED SPECTRAL DATA OF THE LIGANDS AND THEIR METAL COMPLEXES

Compd.	ν(OH)[a]	ν(OH)[b]	$\nu(C{=}N)_{im}$	$\nu(C{=}N)_{ox}$	ν(C–N)	ν(C–Cl)	ν(M–N)	ν(M–O)
HL	-	3500-3400	1633	1603	1107	740	-	-
[CuL]	-	-	1608	1600	1090	750	540	400
[CdL]	-	-	1605	1600	1100	760	560	380
[HgL]	-	-	1610	1603	1100	767	520	390
HL'	-	3500-3400	1653	1605	1137	755	-	-
[CuL']	-	-	1613	1600	1090	750	550	410
[CdL'$_2$]	-	-	1605	1600	1100	760	555	420
[HgL'$_2$]	-	-	1613	1600	1105	767	550	410

[a] = ν(OH) Vibration of the hydrated water molecule.

[b] = ν(OH) Vibration of sterically hindered oxime.

Electonic spectra: The electronic absorption spectral data of the free ligands and their complexes are given in Table-3. In the spectra of the Schiff base ligand bands at 220-280 nm are attribute to the benzene π-π*

TABLE-3
MAGNETIC MOMENTS AND ELECTRONIC SPECTRAL DATA OF SCHIFF BASE AND THEIR METAL COMPLEXES

Compd.	μ_{eff} (BM)	λ_{max} (ε, M^{-1}, cm^{-1})
HL	-	659 (390), 336 (2530), 275 (1300), 221(2070)
[CuL]	1.80	710 (122), 680sh (106), 560 (158), 500 (316), 410 (1601)
[CdL]	Diamag.	580 (540), 500 (710), 420 (111), 400 (137)
[HgL]	Diamag.	740sh (140), 480 (350), 440 (540), 410 (850)
HL'	-	526 (390), 340 (1330), 278 (2150), 217 (130)
[CuL']	1.90	720sh (298), 560 (319), 500 (509), 440 (1054), 420 (1310), 400 (1866)
[CdL']	Diamag.	360 (555), 320 (756), 300 (1615), 280 (2313), 260 (424)
[HgL']	Diamag.	640 (100), 560 (122), 460 (179) 400 (243)

transtions[12-14]. The bands at 338-342 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 Cu(II), Cd(II) and Hg(II) complexes are in the range 0.1 to 12.3 Ω^{-1} cm^2 mol^{-1} in 10^{-3} M DMF solutions indicating the non-electrolytic nature of these compounds[9].

NMR spectra of Schiff bases: In order to understand the solution structure of the free schiff base ligands, ^1H NMR spectra have been employed. The ^1H NMR assignments are listed in Table-4. The doublet-doublet observed at 7.60-7.20 ppm (J 8.75 Hz) are assigned to the aromatic ring proton of the ligand HL. The singlets at 8.40 and 12.60 ppm have been

TABLE-4
^1H NMR SPECTRA OF THE SCHIFF BASE LIGANDS

HL			HL'		
δ (ppm)	Peak	Assignments	δ (ppm)	Peak	Assignments
3.40	4 (H)	CH_2 groups	1.65	4 (H)	CH_2^a proton
7.20-7.60	8 (H)	aromatic ring(H)	3.55	4 (H)	CH_2 proton
8.40	2 (H)	CH (aldoxime) proton	7.30-7.50	8 (H)	aromatic ring(H)
12.60	2 (H)	OH	8.2	2 (H)	CH (aldoxime) proton
			11.40	2 (H)	OH

[a] = proton of the aliphatic -$(CH_2)_2$- group.

assigned to the protons of CH_2 and the proton of the oxime group, respectively. The triplet at 3.40 ppm have been assigned to protons of methylene group. In a like manner, similiar peaks for the ligand HL' were also observed. Futhermore the multiplet at 1.65 ppm in the ligand HL' is attributed to the protons of methylene group.

MS studies: In the MS spectra of the ligand HL, m/e 391[M^+, 5 %], 357 [M^+-2OH, 12 %], 343 [M^+-$(OH)_2N$, 13 %], 191 [M^+-$(OH)_2NC_7H_4Cl$, 11 %], 42.36 [$C_2H_4N^+$, 28 %], 137.5 [$NC_7H_4Cl^+$, 100 %]. There are similiar peaks for the ligand HL', m/e 419 [M^+, 8 %], 385 [M^+-2OH, 15 %], 371 [M^+-$(OH)_2N$, 18 %], 233.5 [M^+-$(OH)_2NC_7H_4Cl$, 23 %], 70.4 [$C_4H_8N^+$, 15%], 123.5 [$C_7H_4Cl^+$, 100 %].

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REFERENCES

1. D.H. Busch, *Helv. Chim. Acta*, **50**, 174 (1967).
2. N.F. Curtis, *Coord. Chem. Rev.*, **3**, 3 (1968).
3. M. Tümer, H. Köksal, S. Serin and S. Patat, *Synth. React. Inorg. Met.-Org. Chem.*, **27**, 59 (1997).
4. M. Casey, J. Leonard, B. Lygo and G. Proccto, Advanced Practical Organic Chemistry, Blackie Academic & Professional, Chp 4. pp. 28-39 (1993).
5. U. Casellato, P.A. Vigato, R. Graziani, M. Vidali, F. Milani and M.M. Musiani, *Inorg. Chim. Acta*, **61**, 121 (1982).
6. A.I. Pekacar, B. Mercimek and E. Özcan, *Synth. React. Inorg. Met.-Org. Chem.*, **27**, 455 (1997).
7. S. Yildirim, A.I. Pekacar and M. Uçan, *Synth. React. Inorg. Met.-Org. Chem.*, **33**, 873 (2003).
8. D.K. Rastogi and C.K. Sharma, *J. Inorg. Nucl. Chem.*, **36**, 2219 (1974).
9. I. Demir, A.I. Pekacar, *Synth. React. Inorg. Met.-Org. Nano-Met. Chem.*, **35**, 825 (2005).
10. E.R. Souaya, W.G. Hanna, E.H. Ismail and N.E. Milad, *Molecules*, **5**, 1121 (2000).
11. M.T.H. Tarafder, T.-J. Khoo, K.A. Crouse, A.M. Ali, B.M. Yamin and H.-K. Fun, *Polyhedron*, **21**, 2691 (2002).
12. L. Casella, M. Gullotti and G. Pacchioni, *J. Am. Chem. Soc.*, **104**, 2386 (1982).
13. V. Deiztsch, P. Strauch and E. Hoyer, *Coord. Chem. Rev.*, **121**, 43 (1992).
14. A.R. Latham, V.C. Hascall and H.B. Gray, *Inorg Chem.*, **6**, 788 (1965).

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