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Synthesis and Spectral Studies of New Macrocyclic Schiff Base Cu(II), Ni(II), Cd(II), Zn(II), Pb(II), and La(III) Complexes Containing Pyridine Head Unit[1]

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Abstract—1,6-Bis(2-formylphenyl)hexane (I) was derived from 1,6-dibromohexane with salicylaldehyde and K_2CO_3 and the ligand (L) was derived from compound I and 2,6-diaminopyridine. Then, the Cu(II), Ni(II), Pb(II), Zn(II), Cd(II), and La(III) complexes with L were synthesized by the reaction of this ligand and $Cu(NO_3)_2 \cdot 3H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $Pb(NO_3)_2$, $Zn(NO_3)_2 \cdot 6H_2O$, $Cd(NO_3)_2 \cdot 6H_2O$, and $La(NO_3)_3 \cdot 6H_2O$, respectively. The ligand and its metal complexes were characterized by elemental analysis, IR, ^1H and ^{13}C NMR, UV-Vis spectra, magnetic susceptibility, conductivity measurements, and mass spectra. All complexes are diamagnetic and the Cu(II) complex is binuclear.

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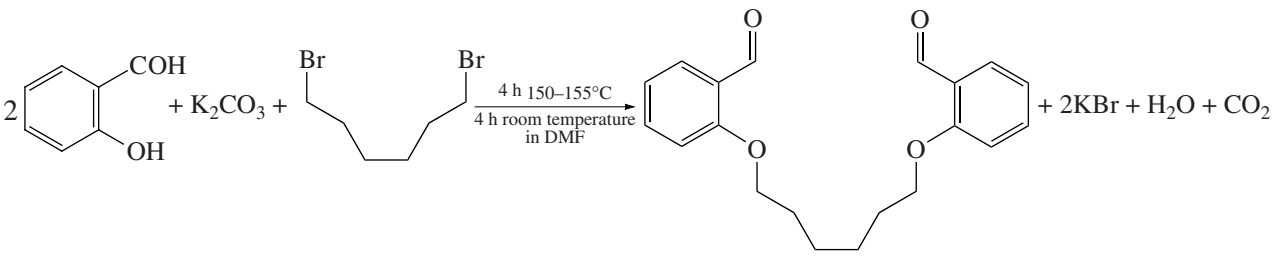
INTRODUCTION

The coordination chemistry of macrocyclic ligands is a fascinating area of study for inorganic chemists [1]. Schiff base macrocycles have been of great importance in macrocyclic chemistry [2]. There is a continued interest in synthesizing macrocyclic complexes [3–5] because of their potential applications in fundamental and applied sciences [5–7] and importance in the area of coordination chemistry [8, 9]. The development of the field of bioinorganic chemistry has been another important factor in spurring the growth in interest in macrocyclic compounds [10]. In the present work, the Cu(II), Ni(II), Pb(II), Zn(II), Cd(II), and La(III) complexes with the ligand L (prepared from 1,6-*bis*(2-formylphenyl)hexane (**I**) with 2,6-diaminopyridine (**II**) and K_2CO_3) were synthesized by the reaction of this ligand and $Cu(NO_3)_2 \cdot 3H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $Pb(NO_3)_2$, $Zn(NO_3)_2 \cdot 6H_2O$, $Cd(NO_3)_2 \cdot 6H_2O$, and $La(NO_3)_3 \cdot 6H_2O$, respectively. Spectral and magnetic properties of the new compounds were studied in detail.

EXPERIMENTAL

Elemental analysis was carried out on a LECO CHNS model 932 elemental analyzer. ^1H NMR spectra were recorded using a model BRUKER AVANCE DPX-400 NMR spectrometer. IR spectra were recorded on a Midac 1700 FTIR spectrometer on KBr discs in a wavenumber range of 4000–400 cm^{-1}. Electronic spectral studies were conducted on a SHIMADZU model 160 UV Visible spectrophotometer in the wavelength region 200–800 nm in DMSO solutions of the complex (10^{-3} M). Molar conductivity was measured with a WTW LF model 330 conductivity meter, using a prepared solution of the complex (10^{-3} M in DMSO). Electrospray ionization mass spectrometric analyses (ESI–MS) were obtained on a AGILENT 1100 MSD spectrometer. Compounds **I** and L were prepared in the same way as in the literature [1, 2] according Eqs. (1) and (2), respectively:



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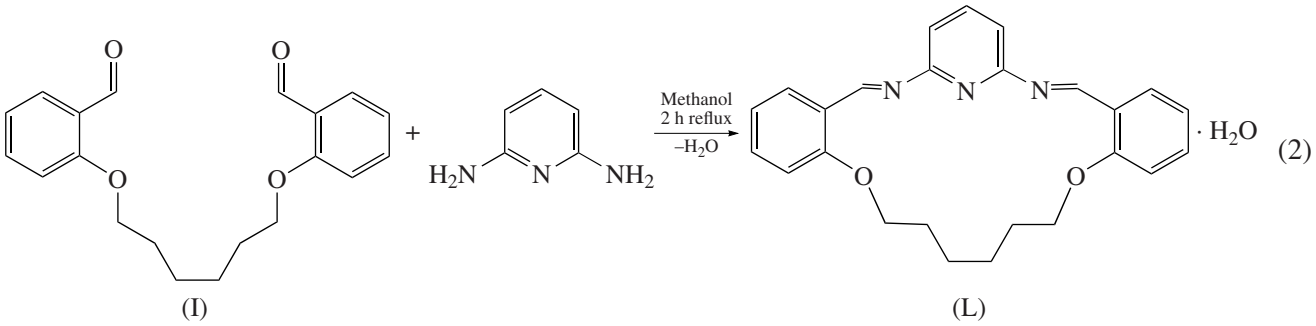


(I) (L) (2)

All the chemicals and solvents were of analytical grade and used as received.

Synthesis of complexes. To a stirred solution of the ligand in chloroform (60 ml) was added dropwise $M(NO_3)_2 \cdot nH_2O$ (2 mmol and 4 mmol if M = Cu) in methanol (40 ml). After the addition was completed, the stirring was continued for 2 h. Then the precipitate was filtered and washed with $CHCl_3$, methanol, respectively and dried in air.

Physical characterization, analytical, molar conductance, and mass spectra data of the complexes are given in the Table 1, FT-IR and electronic spectra are listed in the Table 2.

RESULTS AND DISCUSSION

The IR spectrum of the ligand (L) shows a ν(C=N) peak at 1689 cm^{-1}; the absence of a ν(C=O) peak at around 1700 cm^{-1}, and the absence of a ν(NH_2) peak at around 3300 cm^{-1} indicate Schiff's base condensation. The IR spectra of all complexes show ν(C=N) bands at ~1645 cm^{-1} and it is found that the ν(C=N) bands in the complexes are shifted by about 40 cm^{-1} to lower energy regions compared to that for the free ligand. This phenomenon appears to be due to the coordination of azomethine nitrogen to the metal ion [11, 12]. A broad band in the region at 3328–3383 cm^{-1} appears due to H_2O groups [13, 14]. The absorptions of the nitrate ions, at ~1460–1452 (ν_5), 1300 (ν_1), and 1040 (ν_2) cm^{-1} suggest the presence of bidentate nitrate groups: an intense band at ~1384 cm^{-1} attributable to ionic nitrate is also present [15, 16]. The IR spectra of the complexes clearly demonstrate that the COC and CCO stretching vibrations are altered compared to the ligands due to conformational changes. The fact that the C–O–C absorptions of the complexes are shifted to lower wavenumbers compared to that of the ligand also confirms the complex formation [17, 18]. In the spectra of all the complexes, bands between 2955–2828 cm^{-1} due to ν(α-CH) groups predominate, and a strong band appearing

Table 1. Physical characterization, analytical, molar conductance, mass spectra and magnetic susceptibility data of the complexes

Compound	Contents (calcd/found), %			Λ_M, $Ohm^{-1} cm^2 mol^{-1}$	Formula weight	MS/EI	Assignment	Color	Yield, g (%)
	C	H	N						
$[Cu_2(L)(NO_3)_2][NO_3]_2 \cdot \cdot H_2O$	37.88/ 38.03	3.41/ 3.51	12.37/ 12.13	167	792	793	$[[Cu_2(L)(NO_3)_2][NO_3]_2 + + H]^+$	Brown	0.54 (34.1)
$(C_{25}H_{25}Cu_2N_7O_{14} \cdot H_2O)$									
$[Ni(L)(NO_3)_2] \cdot 2H_2O$	48.54/ 48.66	4.53/ 4.72	11.13/ 11.53	38	618	583	$[Ni(L)(NO_3)_2+H]^+$	Yellow	0.34 (27.5)
$(C_{25}H_{25}NiN_5O_8 \cdot 2H_2O)$									
$[Pb(L)(NO_3)][NO_3] \cdot \cdot 2H_2O$	39.16/ 39.32	3.79/ 3.91	9.14/ 9.29	82	766	668	$[Pb(L)(NO_3)]^+$	Yellow	0.45 (29.4)
$(C_{25}H_{25}PbN_5O_8 \cdot 2H_2O)$									
$[Cd(L)](NO_3)_2 \cdot 3H_2O$	43.92/ 44.17	4.54/ 4. 65	10.25/ 10.07	188	683	635	$[Cd(L)](NO_3)_2]^+$	Yellow	0.53 (38.8)
$(C_{25}H_{25}CdN_5O_8 \cdot 3H_2O)$									
$[La(L)(NO_3)_3(H_2O)] \cdot \cdot 2H_2O$	38.81/ 39.16	4.01/ 4.21	10.8/ 10.99	43	773	661	$[La(L)(NO_3)_2–H]^+$	Yellow	0.61 (39.4)
$(C_{25}H_{27}LaN_6O_{12} \cdot 2H_2O)$									
$[Zn(L)(NO_3)_2] \cdot H_2O$	49.50/ 49.59	4.46/ 4.61	11.55/ 11.84	51	606	586	$[Zn(L)(NO_3)_2–2H]^+$	Yellow	0.35 (28.9)
$(C_{25}H_{25}ZnN_5O_8 \cdot H_2O)$									

Table 2. IR (cm^{-1}) and UV–Vis (nm) spectral data for the ligand and its complexes

Compound	ν(C=N)	$\nu(C=N)_{Py}$	$\nu(H_2O)$	$\nu(NO_3^-)$	π–π* transition	*n*–π* transition
$[Cu_2(L)(NO_3)_2][NO_3]_2 \cdot H_2O$	1649	1598	3349	1384	274	326, 375
$[Ni(L)(NO_3)_2] \cdot 2H_2O$	1644	1598	3381		276	328, 377
$[Pb(L)(NO_3)][NO_3] \cdot 2H_2O$	1639	1598	3367	1384	274	326, 377
$[Cd(L)](NO_3)_2 \cdot 3H_2O$	1646	1598	3369	1384	275	325, 376
$[La(L)(NO_3)_3(H_2O)] \cdot 2H_2O$	1652	1598	3363		274	326, 376
$[Zn(L)(NO_3)_2] \cdot H_2O$	1645	1598	3366		277	327, 378

in the 1598 cm^{-1} region was assigned to the $\nu(C=N)_{Py}$ mode [19, 20].

^1H NMR of the complexes in a DMSO-d_6 solution show that they are NMR-active. The ^1H NMR spectrum of the complexes showed a singlet at 10.40 ppm due to the imine protons, a multiplet in the range approximately 6.90–7.90 ppm due to the aromatic protons, 1.55 ppm due to $CH_2\underline{CH_2}CH_2$ protons, 1.85 ppm due to $\underline{CH_2}CH_2O$ protons, 4.20 ppm due to $CH_2\underline{CH_2}O$ protons. The ^1H NMR spectra of the complexes exhibited almost the same values as those of the ligand. Although we expected a shift of the position of the CH=N signal in the NMR spectra of the complexes, no significant shift was observed. The CH=N signal is observed with intensity compared to the ligand [21, 22].

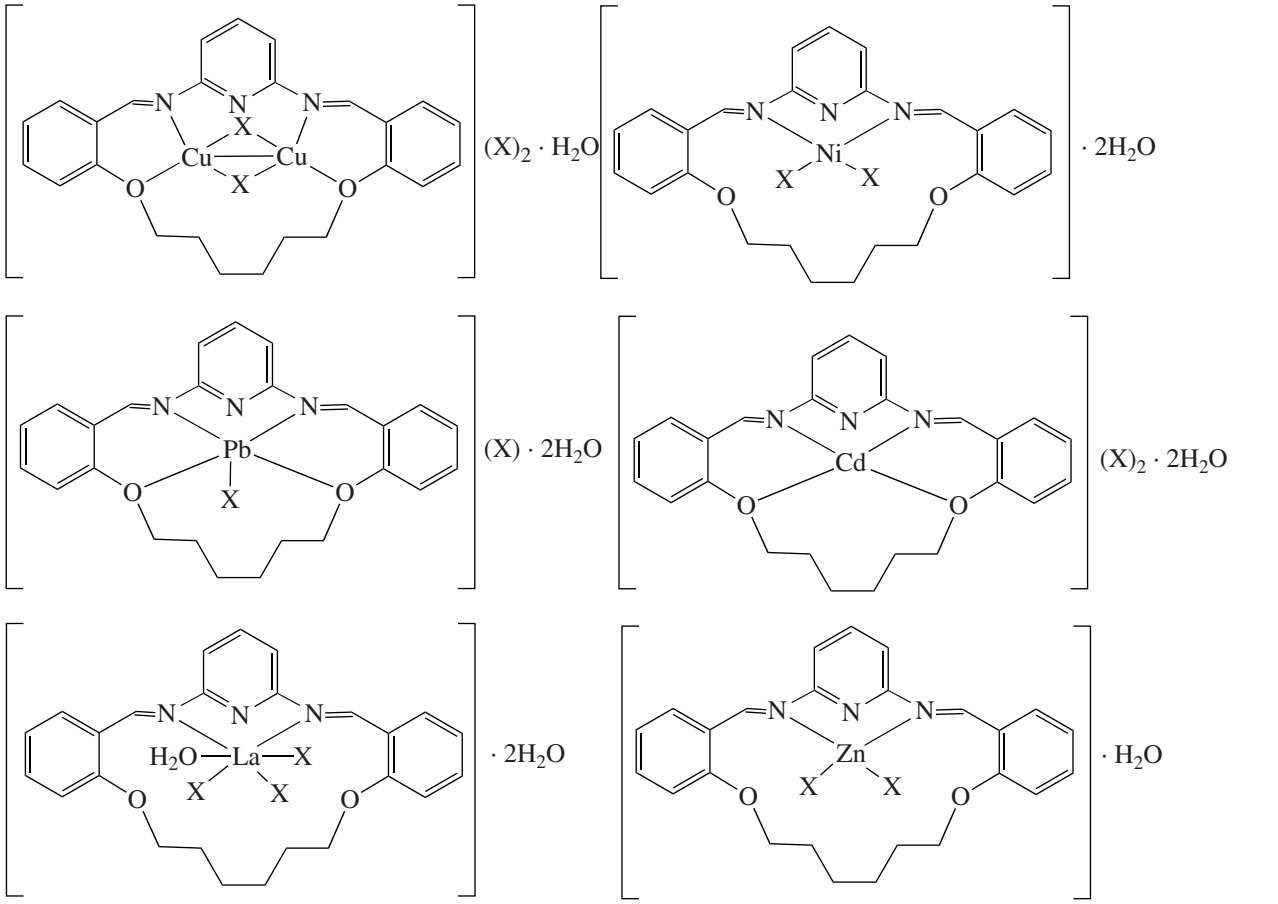
The electronic spectrum of the ligand (L) in DMSO shows absorption bands at ~280, 320, and 370 nm (Table 2). The bands are indicative of benzene and other chromofore moieties present in L. The absorption bands of the complexes are shifted to longer wavenumbers compared to that of the ligand as expected. No *d–d* transitions for the complexes were observed probably due to the low solubility of the complexes. A moderately intensive band observed in a range of 320–380 nm is due to π–π* [23] transition, and the strong band observed in a range of 270–280 nm is due to *n*–π* for these complexes [24].

The room-temperature magnetic moment was observed for the binuclear Cu(II) complex, and the other mononuclear complexes are found to be diamagnetic. The diamagnetic behavior of the binuclear complex may be explained by a very strong antiferromagnetic interaction in the Cu–Cu pair [21, 22].

The conductivity data (in DMSO, 10^{-3} M) are reported in a range of 2 : 2 and 1 : 1 electrolytes in these solvents. The complexes $[Cu_2(L)(NO_3)_2][NO_3]_2 \cdot H_2O$, $[Cd(L)][NO_3]_2 \cdot 3H_2O$, and $[Pb(L)(NO_3)][NO_3] \cdot 2H_2O$ have values of 167, 169, and 82 $Ohm^{-1}\ cm^2\ mol^{-1}$. It indicates 1 : 2 and 1 : 1 electrolytes, respectively. The other complexes are nonelectrolytes [25, 26].

The mass spectra of the complexes with the ligand play an important role in conforming the monomeric [1 + 1] (dicarbonyl and diamine) nature of the complexes. The mass spectra of the complexes peaks nan be attributed to the molecular ions 793 $[[Cu_2(L)(NO_3)_2][NO_3]_2 + H]^+$, 583 $[Ni(L)(NO_3)_2 + H]^+$, 668 $[Pb(L)(NO_3)]^+$, 635 $[Cd(L)](NO_3)_2]^+$, 661 $[La(L)(NO_3)_2 - H]^+$, and 586 $[Zn(L)(NO_3)_2 - 2H]^+$ [26–28].

The complexes have no clearly defined melting point and begin to decompose in the temperature range 250–350°C. The ligand is soluble in DMSO, DMF, $CHCl_3$, CH_2Cl_2, and CH_3CN but insoluble in H_2O, EtOH, and MeOH. The complexes are air stable, partly soluble in DMF and DMSO, and insoluble in $CHCl_3$, CH_2Cl_2, and CH_3CN. The crystals were unsuitable for single-crystal X-ray structure determination. It is seen that the complex formation reaction between the ligand and relatively large Cd^{2+} and Pb^{2+} ions results in the Cd(II) and Pb(II) complexes. The binding mode of the ligand for the Pb(II), Cd(II), and Cu(II) complexes are different from that of the other complexes. In the first case, the ligand behaves as a tetradentate ligand with the lone electron pairs of the azomethine nitrogen atoms and the lone electron pairs of two oxygen in ether groups. In the second case, the ligand behaves as a bidentate ligand with the lone electron pairs of the azomethine nitrogen atoms. The long-distance binding process can be favored for too large Cd^{2+}, Pb^{2+} ions but not other metal ions due to a smaller ion size than of the Pb^{2+} and Cd^{2+} ions. So, its coordination is satisfied with two or three NO_3^- and one H_2O for the La(III) complex in the second case. Similar binding mode was observed in literature for Pb^{2+} and Cd^{2+} ions [21, 22]. These results clearly verify different binding modes of the ligand in the case of the Cd^{2+} and Pb^{2+} ions. As expected, in the case of the relatively small (Ni^{2+} and Zn^{2+}) ions, the ligand behaves as a bidentate ligand with the lone electron pairs of azomethine nitrogen atoms and the inner coordination sphere is donated with the NO_3^- ligands. Similar cases can be found in the literature [29–31]. Suggested structures of the complexes were shown below:



The La(III) complexes probably have octahedral geometry, the Zn(II) and Cd(II) complexes probably have tetrahedral geometry, the Ni(II) complex probably has square planar geometry, the Pb(II) complex probably has square pyramid geometry and the binuclear Cu(II) complex probably is a bipyramid around the central metal ions [20–22].

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