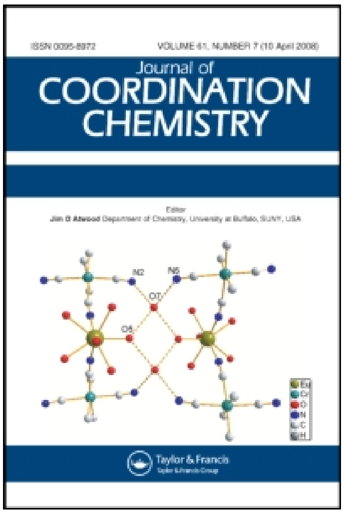

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# Synthesis and spectroscopic characterization of a new macrocyclic Schiff base formed by the reaction of 1,5- <i>bis</i> (2-formylphenyl)pentane and 2,6-diaminopyridine, and a study of its metal complexes

Salih İlhan[a]; Hamdi Temel[b]
[a] Faculty of Arts and Sciences, Chemistry Department, Siirt University, Siirt, Turkey [b] Faculty of Education, Chemistry Department, Dicle University, Diyarbakir, Turkey

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# Synthesis and spectroscopic characterization of a new macrocyclic Schiff base formed by the reaction of 1,5-*bis*(2-formylphenyl)pentane and 2,6-diaminopyridine, and a study of its metal complexes

SALIH İLHAN*† and HAMDI TEMEL‡

†Faculty of Arts and Sciences, Chemistry Department, Siirt University, Siirt, Turkey
‡Faculty of Education, Chemistry Department, Dicle University, Diyarbakir, Turkey

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A new dialdehyde 1,5-*bis*(2-formylphenyl)pentane was synthesized from 1,5-dibromopentane with salicylaldehyde and $K_2CO_3$; macrocyclic ligand was synthesized by reaction of 2,6-diaminopyridine and 1,5-*bis*(2-formylphenyl)pentane. Cu(II), Ni(II), Pb(II), Zn(II), Cd(II) and La(III) complexes were synthesized by reaction of the ligand and $Cu(ClO_4)_2 \cdot 6H_2O$, $Ni(ClO_4)_2 \cdot 6H_2O$, $Pb(ClO_4)_2 \cdot 6H_2O$, $Zn(ClO_4)_2 \cdot 6H_2O$, $Cd(ClO_4)_2 \cdot 6H_2O$ and $La(ClO_4)_3 \cdot 6H_2O$, respectively. The ligand and its metal complexes have been 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 Cu(II) complex is binuclear.

*Keywords*: 1,5-*Bis*(2-formylphenyl)pentane; 2,6-Diaminopyridine; Macrocyclic Schiff base; Macrocyclic Schiff-base complexes

## 1. Introduction

Schiff bases and their metal complexes play a key role in coordination chemistry of transition metal ions [1], widely studied because of their industrial, antifungal and biological applications [2]. Schiff-base macrocycles have been of great importance in macrocyclic chemistry [3]. The chemistry of macrocyclic complexes has received attention for various applications in bioinorganic chemistry [4]. Macrocyclic ligands with additional donor atoms appended to the ring have interest because of their capacity to bind and transport metal ions, to study their mixed-valence forms, and as models for metalloproteins [5]. There is continued interest in synthesizing macrocyclic complexes [6–10] because of their potential applications in fundamental and applied sciences [10–12] and importance in coordination chemistry [13, 14]. Coordination chemistry of macrocyclic ligands is an area of intense study for inorganic chemists [15].

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*Corresponding author. Email: salihsiirt@gmail.com; salihilhan@dicle.edu.tr

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Transition metal macrocyclic complexes have received attention as active sites in metalloenzymes (biomimic model compounds) due to their resemblance with natural proteins like hemerythrin and enzymes [16, 17].

In the present work, we have synthesized a new dialdehyde 1,5-*bis*(2-formylphenyl)pentane derived from 1,5-dibromopentane with salicylaldehyde and $K_2CO_3$. Then a new macrocyclic Schiff base was formed by reaction of 2,6-diaminopyridine and 1,5-*bis*(2-formylphenyl)pentane. Complexes were synthesized by reaction of ligand and $Cu(ClO_4)_2 \cdot 6H_2O$, $Ni(ClO_4)_2 \cdot 6H_2O$, $Pb(ClO_4)_2 \cdot 6H_2O$, $Zn(ClO_4)_2 \cdot 6H_2O$, $Cd(ClO_4)_2 \cdot 6H_2O$ and $La(ClO_4)_3 \cdot 6H_2O$. Spectral and magnetic properties of the new compounds are reported.

## 2. Experimental

1,5-*Bis*(2-formylphenyl)pentane used in the synthesis was prepared from 1,5-dibromopentane with salicylaldehyde and $K_2CO_3$ [18, 19]. All other chemicals and solvents were of analytical grade and used as received. Elemental analysis was carried out on a LECO CHNS model 932 elemental analyzer. $^1H$ NMR and $^{13}C$ NMR spectra were recorded using a BRUKER AVANCE DPX-400 NMR spectrometer. IR spectra were recorded on a Midac 1700 FTIR spectrometer as KBr discs in the wavenumber range of 4000–400 $cm^{-1}$. Electronic spectral studies were conducted on a SHIMADZU model 160 UV–Visible spectrophotometer from 200–800 nm. Molar conductivity was measured with a WTW LF model 330 conductivity meter using 1.00 mmolar solutions of the complexes in DMSO. Electrospray ionization mass spectrometric analyses (ESI–MS) were obtained on an AGILENT 1100 MSD spectrometer. Magnetic susceptibilities were determined on a Sherwood Scientific Magnetic Susceptibility Balance (Model MK1) at room temperature (20°C) using $Hg[Co(SCN)_4]$ as calibrant; diamagnetic corrections were calculated from Pascal's constants [20].

### 2.1. *Synthesis of 1,5-bis(2-formylphenyl)pentane*

To a stirred solution of salicylaldehyde (24.4 g, 0.2 mol) and $K_2CO_3$ (13.8 g, 0.1 mol) in DMF (80 mL) was added dropwise 1,5-dibromopentane (23.0 g, 0.1 mol) in DMF (20 mL). The reaction was continued for 4 h at 150–155°C and 4 h at room temperature (figure 1). After the reaction was complete, 200 mL of distilled water was added and the solution placed in a refrigerator; 1 h later the precipitate was filtered and washed with 500 mL water, dried in air, recrystallized from EtOH and filtered under vacuum. Yield: 24.3 g (78%), m.p.: 66–67°C, color: White Anal. Calcd for $C_{19}H_{20}O_4$ : C, 73.1; H, 6.5.

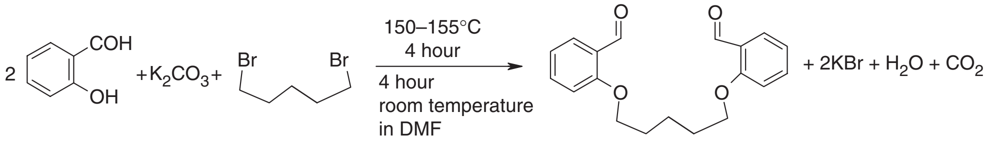


Figure 1. Synthesis of 1,5-*bis*(2-formylphenyl)pentane.

Found: C, 73.3; H, 6.6. $^{13}$C NMR (DMSO-d$_6$, $\delta$ ppm): $CH_2\mathbf{CH_2}CH_2$: 22.57, $\mathbf{CH_2}CH_2O$: 28.66, $CH_2\mathbf{CH_2}O$: 68.67, HC=O: 189.55, Aromatic: 113.98, 120.98, 124.71, 128.03, 136.86, 161.53. $^1$H NMR (DMSO-d$_6$, $\delta$ ppm): 1.66 (q, 2H, $J = 8.4$ Hz, $CH_2\mathbf{CH_2}CH_2$), 1.87 (p, 4H, $J = 7.6$ Hz, $\mathbf{CH_2}CH_2O$), 4.16 (t, 4H, $J = 6.4$ Hz, $CH_2\mathbf{CH_2}O$), 7.03–7.70 (m, 8H, Ar–H), 10.39 (s, 2H, HC=N). Selected IR data (KBr, $\nu$ cm$^{-1}$): 3074, 3039 $\nu$(Ar–CH), 2947, 2873 $\nu$(Alf.–CH), 1682 $\nu$(C=O), 1485, 1458 $\nu$(Ar–C=C), 1284, 1242 $\nu$(Ar–O), 1188, 1052 $\nu$(R–O), 752 $\nu$(substituted benzene). Mass spectrum ($m/z$): 312 [M]$^+$.

## 2.2. *Synthesis of macrocyclic Schiff base (L)*

The macrocyclic ligand (L) was prepared by dropwise addition of a solution of 2,6-diaminopyridine (0.22 g, 2 mmol) in methanol (40 mL) to a stirred solution of 1,5-*bis*(2-formylphenyl)pentane (0.63 g, 2 mmol) in methanol (60 mL). After the addition was complete, stirring was continued for 2 h. A yellow precipitate was filtered, washed with methanol and dried (figure 2). Yield: 0.31 g (38.5%). Anal. Calcd for $C_{24}H_{23}N_3O_2 \cdot H_2O$: C, 74.8; H, 6.0; N, 10.9. Found: C, 75.0; H, 6.1; N, 10.8. $^{13}$C NMR (DMSO-d$_6$, $\delta$ ppm): $CH_2\mathbf{CH_2}CH_2$: 22.59, $\mathbf{CH_2}CH_2O$: 28.66, $CH_2\mathbf{CH_2}O$: 68.65, HC=N: 189.60, Aromatic: 112.68, 113.95, 120.99, 124.68, 128.06, 136.90, 155.60, 159.71, 161.53. $^1$H NMR (DMSO-d$_6$, $\delta$ ppm): 1.66 (2H, $CH_2\mathbf{CH_2}CH_2$), 1.86 (4H, $\mathbf{CH_2}CH_2O$), 4.16 (4H, $CH_2\mathbf{CH_2}O$), 7.05–7.68 (m, 11H, Ar–H), 10.40 (s, 2H, HC=N). Selected IR data (KBr, $\nu$ cm$^{-1}$): 3383 ($H_2O$), 3066, 3039 $\nu$(Ar–CH), 2935, 2866 $\nu$(Alf.–CH), 1683 $\nu$(C=N), 1597 (C=N(pyridine)), 1489, 1454 $\nu$(Ar–C=C), 1284, 1242 $\nu$(Ar–O), 1160, 1053 $\nu$(R–O), 752 $\nu$(substituted benzene). UV–Vis ($\lambda_{max}$, nm) (DMSO): 265, 321, 373. Mass spectrum ($m/z$): 385 [L]$^+$.

## 2.3. *Synthesis of complexes*

To a stirred solution of L in chloroform (60 mL) was added dropwise $M(ClO_4)_n \cdot 6H_2O$ (2 mmol, if M=Cu 4 mmol) in methanol (40 mL). After the addition was complete, stirring was continued for 2 h. The precipitate was filtered, washed with $CHCl_3$ and methanol, respectively, and dried in air (figure 3).

## 2.4. *Characterization of $[Cu_2(L)(ClO_4)_2][ClO_4]_2 \cdot 2H_2O$*

Color: Brown. Yield: 0.40 g (21.1%). Anal. Calcd for $Cu_2C_{24}H_{23}N_3Cl_4O_{18} \cdot 2H_2O$: C, 30.4; H, 2.8; N, 4.4. Found: C, 30.6; H, 3.0; N, 4.3. $^1$H NMR (DMSO-d$_6$, $\delta$ ppm): 1.66 ($CH_2\mathbf{CH_2}CH_2$), 1.88 ($\mathbf{CH_2}CH_2O$), 4.18 ($CH_2\mathbf{CH_2}O$), 7.06–7.68 (Ar–H), 10.40 (HC=N). Selected IR data (KBr, $\nu$ cm$^{-1}$): 3348 ($H_2O$), 3066 $\nu$(Ar–CH), 2931, 2866 $\nu$(Alf.–CH),

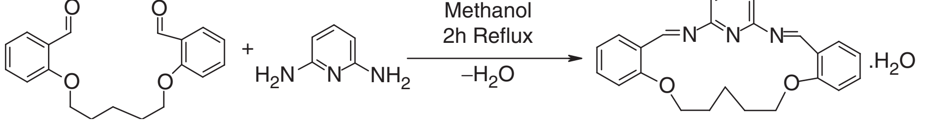


Figure 2. Synthesis of the ligand.

$$\text{Ligand} + 2Cu(ClO_4)_2\cdot 6H_2O \rightarrow [Cu_2(L)(ClO_4)_2][ClO_4]_2\cdot 2H_2O + 11H_2O$$

$$\text{Ligand} + Ni(ClO_4)_2\cdot 6H_2O \rightarrow [Ni(L)(ClO_4)_2]\cdot 3H_2O + 4H_2O$$

$$\text{Ligand} + Pb(ClO_4)_2\cdot 6H_2O \rightarrow [Pb(L)(ClO_4)][ClO_4]\cdot 2H_2O + 5H_2O$$

$$\text{Ligand} + Cd(ClO_4)_2\cdot 6H_2O \rightarrow [Cd(L)][ClO_4]_2\cdot 4H_2O + 3H_2O$$

$$\text{Ligand} + La(ClO_4)_3\cdot 6H_2O \rightarrow [La(L)(ClO_4)_3(H_2O)]\cdot H_2O + 5H_2O$$

$$\text{Ligand} + Zn(ClO_4)_2\cdot 6H_2O \rightarrow [Zn(L)(ClO_4)_2]\cdot 2H_2O + 5H_2O$$

Figure 3. Synthesis of the complexes.

1651 ν(C=N), 1597 (C=N(pyridine)), 1489, 1454 ν(Ar–C=C), 1242 ν(Ar–O), 1103 ν(R–O), 756 ν(substituted benzene), 1112, 629 $\nu(ClO_4^-)$. $\Lambda_M = 201\text{–}\Omega^{-1}\cdot mol^{-1}\cdot cm^2$. UV–Vis ($\lambda_{max}$, nm) (DMSO): 274, 324, 374. Mass spectrum (*m*/*z*): 807 $[[Cu_2(L)(ClO_4)_2][ClO_4] - 3H]^+$.

## 2.5. *Characterization of [Ni(L)(ClO₄)₂] • 3H₂O*

Color: Yellow. Yield: 0.14 g (10.1%). Anal. Calcd for $NiC_{24}H_{23}N_3Cl_2O_{10}\cdot 3H_2O$: C, 41.4; H, 4.2; N, 6.0. Found: C, 41.5; H, 4.3; N, 5.9. $^1$H NMR (DMSO-$d_6$, δ ppm): 1.67 ($CH_2\mathbf{CH_2}CH_2$), 1.91 ($\mathbf{CH_2}CH_2O$), 4.18 ($CH_2\mathbf{CH_2}O$), 7.07–7.70 (Ar–H), 10.40 (HC=N). Selected IR data (KBr, ν cm$^{-1}$): 3367 ($H_2O$), 3067 ν(Ar–CH), 2927, 2866 ν(Alf.–CH), 1651 ν(C=N), 1597 (C=N(pyridine)), 1489, 1454 ν(Ar–C=C), 1288, 1246 ν(Ar–O), 1103, 1049 ν(R–O), 752 ν(substituted benzene), 1109, 627 $\nu(ClO_4^-)$. $\Lambda_M = 29\,\Omega^{-1}\cdot mol^{-1}\cdot cm^2$. UV–Vis ($\lambda_{max}$, nm) (in DMSO): 274, 325, 375. Mass spectrum (*m*/*z*): 641 $[Ni(L)(ClO_4)_2 - H]^+$.

## 2.6. *Characterization of [Pb(L)(ClO₄)][ClO₄] • 2H₂O*

Color: Yellow. Yield: 0.43 g (26.0%). Anal. Calcd for $PbC_{24}H_{23}N_3Cl_2O_{10}\cdot 2H_2O$: C, 34.8; H, 3.3; N, 5.1. Found: C, 35.1; H, 3.4; N, 5.1. $^1$H NMR could not be taken because of the low solubility. Selected IR data (KBr, ν cm$^{-1}$): 3425 ($H_2O$), 3066 ν(Ar–CH), 2931, 2877 ν(Alf.–CH), 1636 ν(C=N), 1598 (C=N(pyridine)), 1488, 1462 ν(Ar–C=C), 1246 ν(Ar–O), 1105 ν(R–O), 751 ν(substituted benzene), 1108, 623 $\nu(ClO_4^-)$. $\Lambda_M = 93\,\Omega^{-1}\cdot mol^{-1}\cdot cm^2$. UV–Vis ($\lambda_{max}$, nm) (in DMSO): 276, 326, 378. Mass spectrum (*m*/*z*): 594 $[Pb(L)] + 2H]^+$.

## 2.7. *Characterization of [Cd(L)][ClO₄]₂ • 4H₂O*

Color: Yellow. Yield: 0.63 g (44.5%). Anal. Calcd for $CdC_{24}H_{23}N_3Cl_2O_{10}\cdot 4H_2O$: C, 40.7; H, 4.4; N, 5.9. Found: C, 40.5; H, 4.2; N, 6.0. $^1$H NMR (DMSO-$d_6$, δ ppm): 1.67 ($CH_2\mathbf{CH_2}CH_2$), 1.91 ($\mathbf{CH_2}CH_2O$), 4.17 ($CH_2\mathbf{CH_2}O$), 7.07–7.68 (Ar–H), 10.40 (HC=N). Selected IR data (KBr, ν cm$^{-1}$): 3379 ($H_2O$), 3070 ν(Ar–CH), 2931, 2873 ν(Alf.–CH), 1637 ν(C=N), 1598 (C=N(pyridine)), 1488, 1454 ν(Ar–C=C), 1242 ν(Ar–O), 1091 ν(R–O), 756 ν(substituted benzene), 1111, 626 $\nu(ClO_4^-)$. $\Lambda_M = 176\,\Omega^{-1}\cdot mol^{-1}\cdot cm^2$. UV–Vis ($\lambda_{max}$, nm) (DMSO): 276, 324, 378. Mass spectrum (*m*/*z*): 697 $[[Cd(L)](ClO_4)_2 + H]^+$.

### 2.8. *Characterization of [La(L)(ClO$_4$)$_3$(H$_2$O)]•H$_2$O*

Color: Yellow. Yield: 0.24 g (14%). Anal Calcd for $LaC_{24}H_{25}N_3Cl_3O_{15}\cdot H_2O$: C, 33.4; H, 3.2; N, 4.9. Found: C, 35.1; H, 3.2; N, 6.8. $^1$H NMR (DMSO-d$_6$, $\delta$ ppm): 1.68 ($CH_2\mathbf{CH_2}CH_2$), 1.92 ($\mathbf{CH_2}CH_2O$), 4.18 ($CH_2\mathbf{CH_2O}$), 7.07–7.70 (Ar–H), 10.40 (HC=N). Selected IR data (KBr, $\nu\,cm^{-1}$): 3352 ($H_2O$), 3067 $\nu$(Ar–CH), 2931, 2862 $\nu$(Alf.–CH), 1651 $\nu$(C=N), 1597 (C=N(pyridine)), 1489, 1454 $\nu$(Ar–C=C), 1288, 1246 $\nu$(Ar–O), 1099, 1049 $\nu$(R–O), 756 $\nu$(substituted benzene), 1113, 624 $\nu(ClO_4^-)$. $\Lambda_M = 34\,\Omega^{-1}\,mol^{-1}\,cm^2$. UV–Vis ($\lambda_{max}$, nm) (in DMSO): 273, 323, 377. Mass spectrum (*m*/*z*): 721 $[La(L)(ClO_4)_2-2H]^+$.

### 2.9. *Characterization of [Zn(L)(ClO$_4$)$_2$]•2H$_2$O*

Color: Yellow. Yield: 0.63 g (45.9%). Anal. Calcd for $ZnC_{24}H_{23}N_3Cl_2O_{10}\cdot 2H_2O$: C, 42.0; H, 3.9; N, 6.3. Found: C, 42.3; H, 6.1; N, 6.2. $^1$H NMR (DMSO-d$_6$, $\delta$ ppm): 1.67 ($CH_2\mathbf{CH_2}CH_2$), 2.01 ($\mathbf{CH_2}CH_2O$), 4.17 ($CH_2\mathbf{CH_2O}$), 6.91–7.69 (Ar–H), 10.42 (HC=N). Selected IR data (KBr, $\nu\,cm^{-1}$): 3371 ($H_2O$), 3066 $\nu$(Ar–CH), 2939, 2873 $\nu$(Alf.–CH), 1643 $\nu$(C=N), 1598 (C=N(pyridine)), 1489, 1454 $\nu$(Ar–C=C), 1292, 1242 $\nu$(Ar–O), 1103, 1049 $\nu$(R–O), 756 $\nu$(substituted benzene), 1107, 627 $\nu(ClO_4^-)$. $\Lambda_M = 24\,\Omega^{-1}\cdot mol^{-1}\cdot cm^2$. UV–Vis ($\lambda_{max}$, nm) (in DMSO): 276, 323, 374. Mass spectrum (*m*/*z*): 650 $[Zn(L)(ClO_4)_2+H]^+$.

## 3. Results and discussion

The ligand and complexes have been synthesized and characterized by elemental analysis, IR, $^1$H and $^{13}$C NMR data, electronic spectra, magnetic susceptibility measurements, molar conductivity and mass spectra. The complexes have no clearly defined m.p. 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, DMSO and insoluble in $CHCl_3$, $CH_2Cl_2$ and $CH_3CN$; the crystals were unsuitable for single-crystal X-ray structure determination. The complex formation reactions between ligand and relatively large Cd(II) and Pb(II) metal ions result in the Cd(II) and Pb(II) complexes. The binding mode of the ligand for Pb(II), Cd(II) and Cu(II) complexes are different than that of the other complexes. In the first case, the ligand is tetradentate with the lone electron pairs of azomethine nitrogens and the lone electron pairs of two oxygens in ether groups. In the second case, the ligand is bidentate with the lone electron pairs of azomethine nitrogens. The long distance binding can be favored for large Cd(II) and Pb(II) metal ions but not other smaller metal ions [29–32]. Coordination is satisfied with two or three $\nu(ClO_4^-)$ and one $H_2O$ for La(III) complex in the second case. Similar binding has been reported for Pb(II) and Cd(II) [21]. Infrared spectra of the metal complexes exhibit an intense band at approximately 1110 $cm^{-1}$ along with a weak band at ca. 620 $cm^{-1}$ assigned to $\nu$(Cl–O) of perchlorate [22]. As expected, in the case of the relatively small [Ni(II) and Zn(II)] metal ions, the ligand is bidentate with the lone electron pairs of azomethine nitrogen atoms and the inner coordination sphere

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

| Compound | $\nu$(C=N) | $\nu$(C=N)pyridine | $\nu$($H_2O$) | $\nu(ClO_4^-)$ | $\pi$–$\pi$* transition | $n$–$\pi$* transition |
|---|---|---|---|---|---|---|
| $C_{19}H_{20}O_4$ | – | – | – | – | – | – |
| $C_{24}H_{23}N_3O_2 \cdot H_2O$ | 1683 | 1597 | 3383 | – | 271 | 321, 373 |
| $[Cu_2(L)(ClO_4)_2][ClO_4]_2 \cdot 2H_2O$ | 1651 | 1597 | 3348 | 1112, 629 | 274 | 324, 374 |
| $[Ni(L)(ClO_4)_2] \cdot 3H_2O$ | 1651 | 1597 | 3367 | 1109, 627 | 274 | 325, 375 |
| $[Pb(L)(ClO_4)][ClO_4] \cdot 2H_2O$ | 1636 | 1598 | 3381 | 1108, 623 | 276 | 326, 378 |
| $[Cd(L)](ClO_4)_2 \cdot 4H_2O$ | 1637 | 1598 | 3379 | 1111, 626 | 276 | 324, 378 |
| $[La(L)(ClO_4)_3(H_2O)] \cdot H_2O$ | 1651 | 1597 | 3352 | 1113, 626 | 273 | 323, 377 |
| $[Zn(L)(ClO_4)_2] \cdot 2H_2O$ | 1643 | 1598 | 3371 | 1107, 627 | 276 | 323, 374 |

completed by $(ClO_4^-)$. However, the diamagnetic behavior of the binuclear complex can be explained by a very strong anti-ferromagnetic interaction for the Cu–Cu pair [23–26].

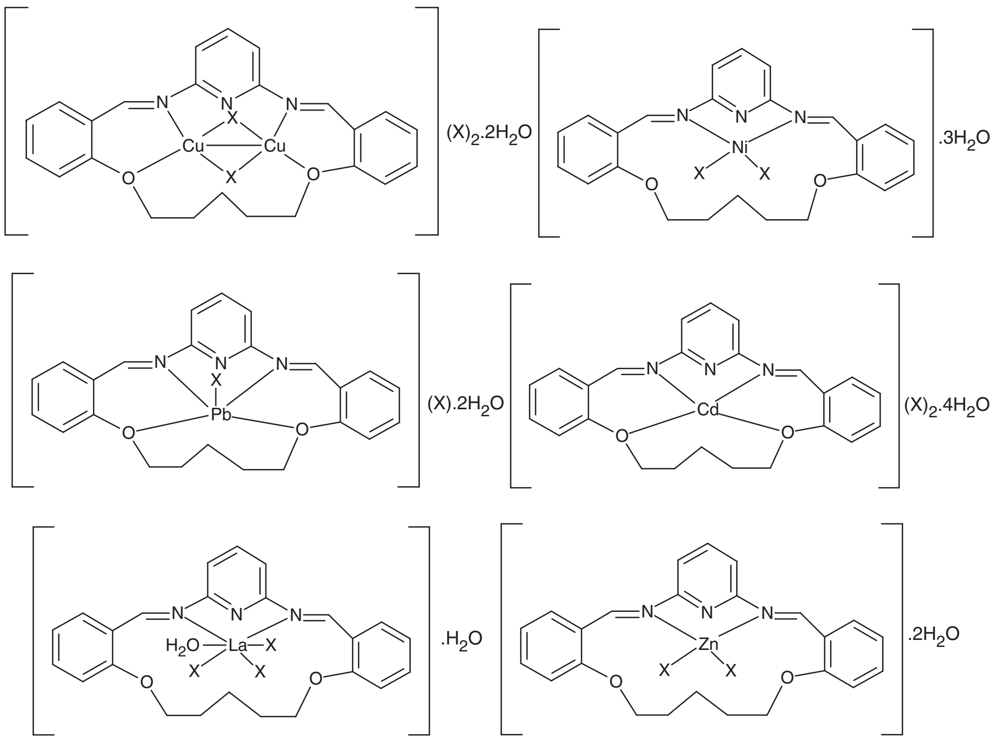
The IR spectrum of L shows (C=N) at 1683 $cm^{-1}$ and the absence of $\nu$(C=O) at 1700 $cm^{-1}$, and $\nu$($NH_2$) peak at 3300 $cm^{-1}$ indicate Schiff-base condensation. The IR spectra of all complexes shows $\nu$(C=N) bands at 1636–1651 $cm^{-1}$ [27]; $\nu$(C=N) bands in the complexes are shifted by 47–29 $cm^{-1}$ to lower energy than in the free ligand, due to coordination of azomethine nitrogen to the metal [28]. Also, a strong $\nu$($H_2O$) band at 3380 $cm^{-1}$ is observed [29] and perchlorate is present [30]. The IR spectra of the complexes clearly demonstrated that COC and CCO stretching vibrations are altered compared to L due to conformational changes. The fact that the C–O–C absorptions of the complexes are shifted to lower wave numbers compared to that of the ligand also confirms complex formation [31]. Spectra of all the metal complexes are dominated by bands between 2955–2828 $cm^{-1}$ due to $\nu$(Alph.–CH) groups. A band at 1598 $cm^{-1}$ was assigned to $\nu(C{=}N)_{(pyridine)}$ [32], which did not change in the complexes; azomethine in the pyridine does not bind the metal ions (table 1) [23–25].

The $^1H$ NMR spectrum of the 1,5-*bis*(2-formylphenyl)pentane showed a singlet at 10.39 ppm due to aldehyde protons, a multiplet in the range 7.03–7.70 ppm due to the aromatic protons, 1.66 ppm due to $CH_2\mathbf{CH_2}CH_2$ protons, 1.87 ppm due to $\mathbf{CH_2}CH_2O$ protons, 4.16 ppm due to $CH_2\mathbf{CH_2}O$ protons. $^{13}C$ NMR spectrum of the 1,5-*bis* (2-formylphenyl)pentane showed 189.55 ppm due to the imine carbon, 22.57 ppm due to $CH_2\mathbf{CH_2}CH_2$ carbon, 28.66 ppm due to $\mathbf{CH_2}CH_2O$ carbon, 68.67 ppm due to $CH_2\mathbf{CH_2}O$ carbon and 133.98–161.53 ppm due to aromatic carbon. The $^1H$ NMR spectrum of the ligand showed a singlet at 10.40 ppm due to imine protons, a multiplet in the range 7.05–7.68 ppm due to the aromatic protons, 1.66 ppm due to $CH_2\mathbf{CH_2}CH_2$ protons, 1.86 ppm due to $\mathbf{CH_2}CH_2O$ protons, 4.16 ppm due to $CH_2\mathbf{CH_2}O$ protons. $^{13}C$ NMR spectrum of the ligand showed 189.60 ppm due to the imine carbon, 22.59 ppm due to $CH_2\mathbf{CH_2}CH_2$ carbon, 28.66 ppm due to $\mathbf{CH_2}CH_2O$ carbon, 68.65 ppm due to $CH_2\mathbf{CH_2}O$ carbon and 112.68–161.53 ppm due to aromatic carbon. The $^1H$ NMR spectra of the complexes exhibited almost the same values as the ligand. Although we expected a shift on the position of CH=N signal for the NMR spectra of the complexes, no significant shift could be observed. However, the CH=N signal is observed in low intensity compared to that of the ligand [23–25].

The electronic spectrum of L in DMSO shows absorptions at ca. 280, 320 and 370 nm, indicative of benzene and other chromophores present in the ligand.

Table 2. Physical characterization, analytical, molar conductance, mass spectra and magnetic susceptibility data of the complexes.

| Compound | (Calcd) Found%C | %H | %N | $\lambda_M$ Ohm$^{-1}$ cm$^2$ mol$^{-1}$ | Formula weight | MS/EI | Assignment |
|---|---|---|---|---|---|---|---|
| $C_{19}H_{20}O_4$ | (73.1) 73.3 | (6.5) 6.6 | – | – | 312 | 312 | $[M]^+$ |
| $C_{24}H_{23}N_3O_2 \cdot H_2O$ | (74.8) 75.0 | (6.0) 6.1 | (10.9) 10.8 | – | 385 | 385 | $[L]^+$ |
| $[Cu_2(L)(ClO_4)_2][ClO_4]_2 \cdot 2H_2O$ | (30.4) 30.6 | (2.8) 3.0 | (4.4) 4.3 | 201 | 946 | 807 | $[[Cu_2(L)(ClO_4)_2][ClO_4] - 3H]^+$ |
| $[Ni(L)(ClO_4)_2] \cdot 3H_2O$ | (41.4) 41.5 | (4.2) 4.3 | (6.0) 5.9 | 29 | 696 | 641 | $[Ni(L)(ClO_4)_2 - H]^+$ |
| $[Pb(L)(ClO_4)][ClO_4] \cdot 2H_2O$ | (34.8) 35.1 | (3.3) 3.4 | (5.1) 5.1 | 93 | 827 | 594 | $[Pb(L) + 2H]^+$ |
| $[Cd(L)](ClO_4)_2 \cdot 4H_2O$ | (40.7) 40.5 | (4.4) 4. 2 | (5.9) 6.0 | 176 | 708 | 697 | $[Cd(L)(ClO_4)_2 + H]^+$ |
| $[La(L)(ClO_4)_3(H_2O)] \cdot H_2O$ | (35. 0) 35.1 | (3.2) 3.2 | (4.9) 4.9 | 34 | 858 | 721 | $[La(L)(ClO_4)_2 - 2H]^+$ |
| $[Zn(L)(ClO_4)_2] \cdot 2H_2O$ | (43.2) 43.3 | (3.8) 3.9 | (6.3) 6.2 | 24 | 686 | 650 | $[Zn(L)(ClO_4)_2]^+$ |



(X: ClO$_4$)

Figure 4. Suggested structures of the complexes.

The absorption bands of the complexes shift to longer wavenumbers compared to the ligand as expected [32, 33]. No d–d transitions for the complexes were observed probably due to the low solubility. A moderately intense band observed in the range of 320–380 nm is due to *n*–$\pi^*$ transition, and the strong band observed in the range of 270–280 nm is due to $\pi$–$\pi^*$ [34] for these complexes.

The observed room-temperature magnetic moment for the binuclear Cu(II) and the mononuclear complexes indicate diamagnetic complexes; the diamagnetic behavior of the binuclear complex may be explained by a very strong anti-ferromagnetic interaction in the Cu–Cu pair [23–25].

The mass spectrum of complexes with ligand play an important role in confirming the monomeric [1 + 1] (dicarbonyl and diamine) nature of the complexes. The mass spectra of the complexes peaks attributable to the molecular ions 312 $[M]^+$, 385 $[L]^+$, 807 $[[Cu_2(L)(ClO_4)_2][ClO_4] - 3H]^+$, 641 $[Ni(L)(ClO_4)_2 - H]^+$, 594 $[Pb(L)] + 2H]^+$, 637 $[[Cd(L)](ClO_4)_2 + H]^+$, 721 $[La(L)(ClO_4)_2 - 2H]^+$, 650 $[Zn(L)(ClO_4)_2]^+$ [35–37] (Supplemental Material).

The conductivity measurements of the Pb(II), Cd(II) and Cu(II) complexes in DMSO resulted in $\Lambda_M$ value 93 mol$^{-1}$cm$^2$, 176 mol$^{-1}$cm$^2$, 201 mol$^{-1}$cm$^2$, indicating 1 : 1, 1 : 2 and 1 : 2 electrolytes, respectively. The other complexes are not electrolytes [38–40] (table 2 and figure 2).

## 4. Conclusion

A Schiff-base macrocycle and six complexes were prepared and characterized by elemental analyses, FTIR, UV–Vis, $^{13}C$ and $^{1}H$ NMR spectra, conductivity measurements, magnetic susceptibilities and mass spectra. General structures of the complexes are shown in figure 4. The La(III) complexes probably have octahedral geometry, Zn(II) and Cd(II) complexes probably are tetrahedral, Ni(II) complex is square planar, Pb(II) complex probably is square pyramidal and binuclear Cu(II) complex probably is bipyramidal.

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