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COORDINATION COMPOUNDS

Synthesis and Spectral Studies of Macrocyclic Pb(II), Zn(II), Cd(II) and La(III) Complexes by Template Reaction of 1,2-Bis(2-formylphenyl)ethane with Metal Nitrate and Various Diamine[1]

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Abstract—Eight new macrocyclic complexes were synthesized by template reaction of 1,4-bis(3-aminopropoxy)butane or (±)-trans-1,2-diaminocyclohexane with metal nitrate and 1,2-bis(2-formylphenyl)ethane and their structures were proposed on the basis of elemental analysis, FT-IR, UV-Vis, molar conductivity measurements, ^{1}H NMR and mass spectra. The metals to ligand molar ratios of the complexes were found to be 1 : 1. The complexes are 1 : 2 electrolytes for Cd(II), Pb(II) and Zn(II) complexes and 1 : 3 electrolytes for La(III) as shown by their molar conductivities (Λ_m) in DMSO at 10^{-3} mol L^{-1}. Due to the existence of free ions in these complexes, such complexes are electrically conductive. The configurations of Cd(II) and Zn(II) complexes were proposed to probably tetrahedral, La(III) complexes are octahedral and Pb(II) complexes are octahedral geometry in the L^1 complex and tetrahedral geometry in the L^2 complex.

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The coordination chemistry of lanthanide(III) ions is rapidly increasing, owing to the relevance of these compounds in basic and applied researches in different scientific areas ranging from chemistry to material science, life science, etc. [1]. The coordination chemistry of macrocyclic ligands is a fascinating area of study for inorganic chemists [2]. Transition metal macrocyclic complexes have received much attention as active part of metalloenzymes as biomimic model compounds due to their resemblance with natural proteins like hemerythrin and enzymes [3, 4]. Schiff base macrocycles have been of great importance in macrocyclic chemistry [5]. There is a continued interest in synthesizing macrocyclic complexes [6, 7] because of their potential applications in fundamental and applied sciences [8–10] and importance in the area of coordination chemistry [11, 12]. The development of the field of bioinorganic chemistry has been another important factor in spurring the growth in interest in macrocyclic compounds [13]. Studies on complexes of Schiff-base macrocyclic ligands with different ring size, and number and nature of donor atoms for coordination with a variety of metal centers have been published [14–17]. In the present work we have synthesized Pb(II), Zn(II), Cd(II) and La(III) complexes by template reaction of (±)-1,4-bis(3-aminopropoxy)butane or (±)-trans-1,2-diaminocyclohexane with metal nitrate and 1,2-bis(2-formylphenyl)ethane in methanol. Then, spectral properties of the new compounds were studied in detail.

EXPERIMENTAL

Elemental analysis was carried out on a LECO CHNS model 932 elemental analyzer. ^{1}H NMR spectra were recorded using a model Bruker Avance DPX-400 NMR spectrometer. IR spectra were recorded on a Perkin Elmer Spectrum RX1 FTIR spectrometer on KBr discs in the wave number range of 4000–400 cm^{-1}. Electronic spectral studies were conducted on a Shimadzu model 160 UV Visible spectrophotometer in the wavelength 200–800 nm. Molar conductivity was measured with a WTW LF model 330 conductivity meters, using prepared solution of the complex in DMSO. LC/MS-API-ES mass spectra were recorded using an Agilent model 1100 MSD mass spectrophotometer. All the other chemicals and solvents were of analytical grade and used as received.

The 1,2-bis(2-formylphenyl)ethane used in the synthesis were prepared as shown in Fig. 1 [18, 19]. All the chemicals and solvents were of analytical grade and used as received.

To a stirred solution of 1,2-bis(2-formylphenyl)ethane (2 mmol) and metal nitrate in methanol (50 mL) was added dropwise diamine (2 mmol) in methanol (30 mL). The reaction was continued for 2 h

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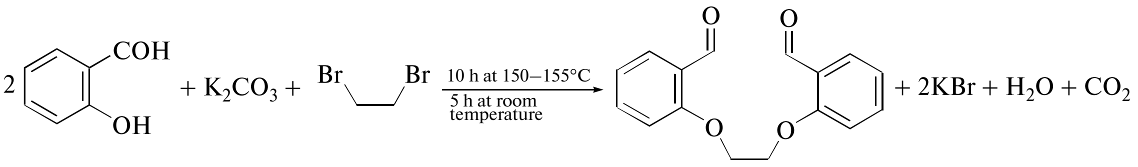


Fig. 1. Synthesis of 1,2-bis(2-formylphenyl)ethane.

at 80°C and 1 h at room temperature. After the reaction was completed, coloured the precipitate was filtered and washed with methanol and, dried in air. Yield: 39–14%.

Characterization of [PbL^1] [NO$_3$]$_2$ · H$_2$O

Yield: 0.24 g (15.3%). Anal. Calcd. for $PbC_{26}H_{34}N_4O_{10} \cdot H_2O$: C, 39.64, H, 4.57, N, 7.11. Found: C, 40.11, H, 4.73, N, 6.93. ^{1}H NMR (DMSO-d$_6$, δ ppm): δ = 4.52 (H1, s, 4H), δ = 3.48 (H2, t, 4H, J = 5.9), δ = 1.89 (H6, p, 4H, J = 6.4), δ = 3.52 (H5, t, 4H, J = 7.1), δ = 3.59 (H4, t, 4H, J = 7.2), δ = 1.34 (H3, t, 4H, J = 5.8), δ = 3.42 (H$_2$O), δ = 6.97–8.04 (m, 8H, Ar-H), δ = 10.39 (s, 2H, HC=N). Selected IR data (KBr, ν cm^{-1}): 3349 ν(H$_2$O), 1645 ν(C=N), 1384 ν(ionic NO_3^-), 489 ν(Pb–O), 442 ν(Pb–N). $\Lambda_M = 194\ \Omega^{-1}\ \mathrm{mol}^{-1}\ \mathrm{cm}^2$. UV-vis ($\lambda_{max}$, nm) (DMSO): 277, 326, 381. Mass spectrum (*m/z*): [569, 7.1%, [PbL^1-(OCH$_2$CH$_2$OCH$_2$)-H]$^+$].

Characterization of [ZnL^1] [NO$_3$]$_2$ · 2H$_2$O

Yield: 0.19 g (14.3%). Anal. Calcd. for $ZnC_{26}H_{34}N_4O_{10} \cdot 2H_2O$: C, 46.92, H, 5.11, N, 8.42. Found: C, 47.07, H, 5.22, N, 8.58. ^{1}H NMR (DMSO-d$_6$, δ ppm): δ = 4.46 (H1, s, 4H), δ = 3.45 (H2, t, 4H, J = 6.2), δ = 1.91 (H6, p, 4H, J = 5.8), δ = 3.53 (H5, t, 4H, J = 7.4), δ = 3.61 (H4, t, 4H, J = 6.3), δ = 1.34 (H3, t, 4H, J = 4.8), δ = 3.41 (H$_2$O), δ = 6.99–8.08 (m, 8H, Ar-H), δ = 10.39 (s, 2H, HC=N). Selected IR data (KBr, ν cm^{-1}): 3347 ν(H$_2$O), 1644 ν(C=N), 1384 ν(ionic NO_3^-), 522 ν(Zn–O), 482 ν(Zn–N). $\Lambda_M = 181\ \Omega^{-1}\ \mathrm{mol}^{-1}\ \mathrm{cm}^2$. UV-vis ($\lambda_{max}$, nm) (DMSO): 278, 322, 378. Mass spectrum (*m/z*): [627, 1.3%, ([ZnL^1][NO$_3$]$_2$)$^+$.

Characterization of [La(H$_2$O)$_2$L^1] [NO$_3$]$_3$ · H$_2$O

Yield: 0.45 g (27.6%). Anal. Calcd. for $LaC_{26}H_{38}N_5O_{15} \cdot H_2O$: C, 38.19, H, 4.90, N, 8.57. Found: C, 38.31, H, 5.11, N, 8.49. ^{1}H NMR (DMSO-d$_6$, δ ppm): δ = 4.39 (H1, s, 4H), δ = 3.47 (H2, t, 4H, J = 4.9), δ = 1.93 (H6, p, 4H, J = 7.4), δ = 3.52 (H5, t, 4H, J = 5.3), δ = 3.58 (H4, t, 4H, J = 6.2), δ = 1.38 (H3, t, 4H, J = 6.4), δ = 3.42 (H$_2$O), δ = 7.01–8.06 (m, 8H, Ar-H), δ = 10.40 (s, 2H, HC=N). Selected IR data (KBr, ν cm^{-1}): 3353 ν(H$_2$O), 1642 ν(C=N), 1384 ν(ionic NO_3^-), 491 ν(La–O), 453 ν(La–N). $\Lambda_M = 259\ \Omega^{-1}\ \mathrm{mol}^{-1}\ \mathrm{cm}^2$. UV-vis ($\lambda_{max}$, nm) (DMSO): 277, 326, 378. Mass spectrum (*m/z*): [801, 7.8%, [La(H$_2$O)$_2$L^1][NO$_3$]$_3$]$^+$].

Characterization of [CdL^1] [NO$_3$]$_2$ · H$_2$O

Yield: 0.21 g (14.8%). Anal. Calcd. for $CdC_{26}H_{34}N_4O_{10} \cdot H_2O$: C, 45.09, H, 5.20, N, 8.09. Found: C, 45.27, H, 5.25, N, 8.02. ^{1}H NMR (DMSO-d$_6$, δ ppm): δ = 4.36 (H1, s, 4H), δ = 3.44 (H2, t, 4H, J = 5.9), δ = 1.94 (H6, p, 4H, J = 5.4), δ = 3.53 (H5, t, 4H, J = 7.6), δ = 3.55 (H4, t, 4H, J = 6.2), δ = 1.39 (H3, t, 4H, J = 7.8), δ = 3.41 (H$_2$O), δ = 6.97–8.02 (m, 8H, Ar-H), δ = 10.38 (s, 2H, HC=N). Selected IR data (KBr, ν cm^{-1}): 3362 ν(H$_2$O), 1639 ν(C=N), 1384 ν(ionic NO_3^-), 509 ν(Cd–O), 467 ν(Cd–N). $\Lambda_M = 152\ \Omega^{-1}\ \mathrm{mol}^{-1}\ \mathrm{cm}^2$. UV-vis ($\lambda_{max}$, nm) (DMSO): 276, 324, 376. Mass spectrum *m/z*): [674, 10.3%, [Cd(L^1][NO$_3$]$_2$]$^+$].

Characterization of [PbL^2][NO$_3$]$_2$ · 2H$_2$O

Yield: 0.31 g (15.4%). Anal. Calcd. for $PbC_{22}H_{24}N_4O_8 \cdot 2H_2O$: C, 36.92, H, 3.92, N, 7.83. Found: C, 36.86, H, 3.83, N, 7.95. ^{1}H NMR (DMSO-d$_6$, δ ppm): δ = 4.39 (H1, s, 4H), δ = 3.21 (H2, t, 2H, J = 7.1), δ = 1.82 (H3, q, 4H, J = 6.6), δ = 1.48 (H4, t, 4H, J = 8.4), δ = 3.41 (H$_2$O), δ = 7.00–8.13 (m, 8H, Ar-H), δ = 10.41 (s, 2H, HC=N). Selected IR data (KBr, ν cm^{-1}): 3356 ν(H$_2$O), 1638 ν(C=N), 1384 ν(ionic NO_3^-), 486 ν(Pb–O), 439 ν(Pb–N). $\Lambda_M = 186\ \Omega^{-1}\ \mathrm{mol}^{-1}\ \mathrm{cm}^2$. UV-vis ($\lambda_{max}$, nm) (DMSO): 277, 326, 378. Mass spectrum (*m/z*): [569, 1.3%, [[PbL^2] · H$_2$O + 2H]$^+$.

Characterization of [ZnL^2] [NO$_3$]$_2$ · 2H$_2$O

Yield: 0.26 g (22.6%). Anal. Calcd. for $ZnC_{22}H_{24}N_4O_8 \cdot 2H_2O$: C, 46.07, H, 4.89, N, 9.77. Found: C, 46.19, H, 5.08, N, 9.65. ^{1}H NMR (DMSO-d$_6$, δ ppm): δ = 4.41 (H1, s, 4H), δ = 3.24 (H2, t, 2H, J = 6.3), δ = 1.83 (H3, q, 4H, J = 5.9), δ = 1.47 (H4, t, 4H, J = 6.7), δ = 3.42 (H_2O), δ = 6.930–8.09 (m, 8H, Ar-H), δ = 10.38 (s, 2H, HC=N). Selected IR data (KBr, ν cm^{-1}): 3351 ν(H_2O), 1646 ν(C=N), 1384 ν(ionic NO_3^-), 526 ν(Zn–O), 484 ν(Zn–N). $\Lambda_M = 171\ \Omega^{-1}\ mol^{-1}\ cm^2$. UV-vis ($\lambda_{max}$, nm) (DMSO): 278, 325, 377. Mass spectrum (*m/z*): [542, 5.8%, $[ZnL^2][NO_3]_2 + 3H]^+$].

Characterization of $[LaL^2(H_2O)_2]\,[NO_3]_3 \cdot H_2O$

Yield: 0.29 g (20.0%). Anal. Calcd. for $LaC_{22}H_{28}N_5O_{13} \cdot H_2O$: C, 36.31, H, 3.85, N, 9.63. Found: C, 36.42, H, 4.01, N, 9.52. ^1H NMR (DMSO-d_6, δ ppm): δ = 4.34 (H1, s, 4H), δ = 3.21 (H2, t, 2H, J = 6.3), δ = 1.79 (H3, q, 4H, J = 6.7), δ = 1.43 (H4, t, 4H, J = 8.1), δ = 3.40 (H_2O), δ = 6.95–8.04 (m, 8H, Ar-H), δ = 10.37 (s, 2H, HC=N). Selected IR data (KBr, ν cm^{-1}): 3348 ν(H_2O), 1644 ν(C=N), 1384 ν(ionic NO_3^-), 491 ν(La–O), 457 ν(La–N). $\Lambda_M = 272\ \Omega^{-1}\ mol^{-1}\ cm^2$. UV-vis ($\lambda_{max}$, nm) (DMSO): 278, 326, 378. Mass spectrum (*m/z*): [579, 1.7%, $[LaL^2\text{-}(OCH_2)][NO_3]\text{-}2H]^+$].

Characterization of $[CdL^2]\,[NO_3]_2 \cdot 2H_2O$

Yield: 0.49 g (39.5%). Anal. Calcd. for $CdC_{22}H_{24}N_4O_8 \cdot 2H_2O$: C, 42.58, H, 4.56, N, 9.03. Found: C, 42.72, H, 4.71, N, 8.92. ^1H NMR (DMSO-d_6, δ ppm): δ = 4.33 (H1, s, 4H), δ = 3.23 (H2, t, 2H, J = 6.1), δ = 1.81 (H3, q, 4H, J = 7.6), δ = 1.44 (H4, t, 4H, J = 7.4), δ = 3.41 (H_2O), δ = 6.97–8.04 (m, 8H, Ar-H), δ = 10.38 (s, 2H, HC=N). Selected IR data (KBr, ν cm^{-1}): 3354 ν(H_2O), 1646 ν(C=N), 1384 ν(ionic NO_3^-), 513 ν(Cd–O), 469 ν(Cd–N). $\Lambda_M = 148\ \Omega^{-1}\ mol^{-1}\ cm^2$. UV-vis ($\lambda_{max}$, nm) (DMSO): 278, 325, 378. Mass spectrum (m/z): [619, 1.1%, [CdL (*m/z*): [619, 1.1%, $[CdL^2][NO_3]_2\text{-}H]^+$].

RESULTS AND DISCUSSION

In the present work, we have synthesized Pb(II), Zn(II), Cd(II) and La(III) complexes by template reaction of 1,4-bis(3-aminopropoxy)butane or (±)-trans-1,2-diaminocyclohexane with metal nitrate and 1,2-bis(2-formylphenyl)ethane in methanol, the [1 + 1] macrocyclic Schiff-base complexes are formed as the product. The macrocyclic complexes were characterized by elemental analysis, UV-vis spectra, conductivity measurements, mass, ^1H NMR and IR spectra. The mass spectrum of complexes plays an important role in confirming the monomeric [1 + 1] (dicarbonyl and diamine) nature of complexes. As the crystals were unsuitable for single-crystal X-ray structure determination and are insoluble in most common solvents, including water, ethanol, methanol, ethyl acetate, and acetonitrile (Table 1).

The characteristic infrared spectrum data are given in the experimental section. Infrared spectra of complexes were recorded in KBr pellet from 4000 to 400 cm^{-1}. The broad bands within the range *ca.* 3370 cm^{-1} for all complexes can be attributed to stretching vibrations of water molecule ν(H_2O) [20,21]. The IR spectrum of the complexes shows a ν(C=N) peak at *ca.* 1650 cm^{-1} and the absence of a ν(C=O) peak at around 1700 cm^{-1} is indicative of Schiff's base condensation. A medium band observed in the IR spectra of the complexes at *ca.*1650 cm^{-1} region which is attributed to the ν(C=N) stretch, indicating of the azomethine nitrogen [22, 23]. The presence of several bands in the region associated with nitrate vibrations clearly identifies these species as containing nitrate groups. The absorptions of the nitrate counterions, at *ca.* 1460–1452 (ν_5), 1300 (ν_1) and 1040 (ν_2) cm^{-1}, suggest the presence of nitrate groups: a intense band at *ca.* 1384 cm^{-1} attributable to ionic nitrate, is also present [24, 25]. In the spectra of all the complexes are dominated by bands between 2965–2855 cm^{-1} due to ν(Alph.-CH) groups. Conclusive evidence of the bonding is also shown by the observation that new bands in the IR spectra of the complexes appear at 525–485 cm^{-1} and 481–435 cm^{-1} assigned to ν(M–O) and ν(M–N) stretching vibrations (Table 2).

Electronic absorption spectral data of complexes in dimethyl sulfoxide (DMSO) at room temperature that are presented in experimental section. The absorption bands below *ca.* 300 nm are practically identical and can be attributed to $\pi \longrightarrow \pi^*$ transitions in the benzene ring and azomethine (–C=N) groups. The absorption bands observed *ca.* the 300–380 nm range are most probably due to the transitions of $n \longrightarrow \pi^*$ of imine groups [28, 29].

The complexes are 1 : 2 electrolytes for Pb(II), Cd(II) and Zn(II) complexes as shown by their molar conductivities (Λ_M) in DMSO at 10^{-3} M, which are in the range 140–210 $\Omega^{-1}\,cm^2\,mol^{-1}$ and 1 : 3 electrolytes for La(III) complexes as shown by their molar conductivities (Λ_M) in DMSO at 10^{-3} M, which are in the range 210–300 $\Omega^{-1}\,cm^2\,mol^{-1}$ [30, 31].

The ^1H NMR spectra were run in DMSO-d_6 and gave the expected simple spectrum, indicating the integrity of the complex in that solvent. The ^1H NMR spectrum of the complexes show a multiplet in the range 6.90–8.15 ppm due to aromatic protons, 3.4 ppm due to H_2O protons, around 1.99–4.32 ppm due to CH_2, OCH_2 and OCH_2Ph protons and 10.40 ppm corresponding to the imine protons, but no signals corresponding to the formyl or amine protons are present [31–33]. Also ^1H NMR spectral data of the complexes were given in experimental section (Fig. 2).

The mass spectra of the complexes play an important role in conforming the monomeric [1 + 1] (dicarbonyl and diamine) nature of the complexes. The fragments observed in the mass spectrum of the complexes

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

Compound	(Calcd.)Found			Λ_M (ohm^1 cm^2 mol$^{-1)}$	Formula Weight	MS/EI	Assigment
	C, %	H, %	N, %				
$[PbL^1][NO_3]_2 \cdot H_2O$	(39.64)	(4.57)	(7.11)	194	787	569	$[PbL^1\text{-}(OCH_2CH_2OCH_2)\text{-}H]^+$
	40.11	4.73	6.93				
$[ZnL^1][NO_3]_2 \cdot 2H_2O$	(46.92)	(5.11)	(8.42)	181	665	627	$[[ZnL^1][NO_3]_2]^+$
	47.07	5.22	8.58				
$[La(H_2O)_2L^1][NO_3]_3 \cdot H_2O$	(38.19)	(4.90)	(8.57)	259	817	801	$[[La(H_2O)_2L^1][NO_3]_3]^+$
	38.31	5.11	8.49				
$[CdL^1][NO_3]_2 \cdot H_2O$	(45.09)	(5.20)	(8.09)	152	692	674	$[[CdL^1][NO_3]_2]^+$
	45.27	5.25	8.02				
$[PbL^2][NO_3]_2 \cdot 2H_2O$	(36.92)	(3.92)	(7.83)	186	715	569	$[[PbL^2] \cdot H_2O + 2H]^+$
	36.86	3.83	7.95				
$[ZnL^2][NO_3]_2 \cdot 2H_2O$	(46.07)	(4.89)	(9.77)	171	573	542	$[[ZnL^2][NO_3]_2 + 3H]^+$
	46.19	5.08	9.65				
$[LaL^2(H_2O)_2][NO_3]_3 \cdot H_2O$	(36.31)	(3.85)	(9.63)	272	727	579	$[LaL^2\text{-}(OCH_2)][NO_3]\text{-}2H]^+$
	36.42	4.01	9.52				
$[CdL^2][NO_3]_2 \cdot 2H_2O$	(42.58)	(4.56)	(9.03)	148	620	619	$[[CdL^2][NO_3]_2\text{-}H]^+$
	45.72	4.71	8.92				

Table 2. IR (cm^{-1}) spectral data for the complexes

Compound	ν(H_2O)	ν(C=N)	Ionic ν(NO_3^-)	ν(M–O)	ν(M–N)
$[PbL^1][NO_3]_2 \cdot H_2O$	3349 s	1645 m	1384 m	489 w	442 w
$[ZnL^1][NO_3]_2 \cdot 2H_2O$	3347 s	1644 m	1384 m	522 w	482 w
$[La(H_2O)_2L^1][NO_3]_3 \cdot H_2O$	3353 s	1642 m	1384 m	491 w	453 w
$[CdL^1][NO_3]_2 \cdot H_2O$	3362 s	1639 m	1384 m	509 w	467 w
$[PbL^2][NO_3]_2 \cdot 2H_2O$	3356 s	1638 m	1383 m	486 w	439 w
$[ZnL^2][NO_3]_2 \cdot 2H_2O$	3351 s	1635 m	1384 m	526 w	484 w
$[LaL^2(H_2O)_2][NO_3]_3 \cdot H_2O$	3348 s	1634 m	1383 m	491 w	457 w
$[CdL^2][NO_3]_2 \cdot 2H_2O$	3354 s	1635 m	1384 m	513 w	469 w

m: medium, s: strong, w: weak.

are useful for characterization of the complexes [32–34].The fragmentation mass spectra of the complexes are described below:

$[PbL^1][NO_3]_2 \cdot H_2O$ – [569, 7.1%, $[PbL^1\text{-}(OCH_2CH_2OCH_2)\text{-}H]^+$], [505, 11.6%, $[PbL^1\text{-}(CH_2CH_2OCH_2CH_2CH_2CH_2OCH_2CH_2)]$, [426, $[L^1\text{-}(CH_2) + H]^+$, 1.8%], [439, 100.0%, $[L^1 + H]$, [426, $[L^1\text{-}(CH_2) + H]^+$, 1.8%], [383, $[L^1\text{-}(CH_2CH_2CH_2CH_2)\text{-}H]^+$, 5.1%], [356, $[L^1\text{-}(OCH_2CH_2CH_2CH_2CH_2) + H]^+$, 2.2%], 183 ($C_{12}N_2H_{11}^+$, 5.0%), 182 ($C_{12}N_2H_{10}^+$, 37.0%), 181 ($C_{12}N_2H_{10}^+$, 20.5%), 103 ($C_7NH_5^+$, 1.7%), 79 ($[C_6H_6]^+$).

$[ZnL^1][NO_3]_2 \cdot 2H_2O$ see Fig. 3.

$[La(H_2O)_2L^1][NO_3]_3 \cdot H_2O$ – [801, 7.8%, $[La(H_2O)_2L^1][NO_3]_3]^+$], [755, 2.3%, $[La(H_2O)L^1\text{-}(CH_2CH_2)][NO_3]_3]^+$], [554, 2.9%, $[LaL^1(CH_2CH_2CH_2) + 2H]^+$], [553, 9.0%, $[LaL^1(CH_2CH_2CH_2) + H]^+$], [505, 5.5%, $[LaL^1(OCH_2CH_2CH_2CH_2O)]^+$], [504, 28.5%, $[LaL^1(OCH_2CH_2CH_2CH_2O)\text{-}H]^+$], [503, 77.1%, $[LaL^1(OCH_2CH_2CH_2CH_2O)\text{-}H]^+$], [440, 23.6%, $[L^1 + 2H]$, [439, 81.6%, $[L^1 + H]$, (206, 11.0%, $[C_{10}H_{24}N_2O_2] + 2H]^+$), (205, 100.0%, $[C_{10}H_{24}N_2O_2] + H]^+$), 103 ($C_7NH_5^+$, 39.2%), (79, 21.0%, $[C_6H_6 + H]^+$).

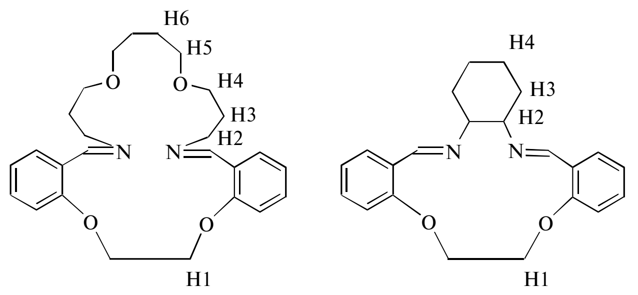


Fig. 2. Structure of the ligands.

$CdL^1][NO_3]_2 \cdot H_2O$ – [674, 10.3%, $[Cd(L^1][NO_3]_2]^+]$, [613, 9.3%, $[Cd(L^1][NO_3] + H]^+]$, [612, 21.7%, $[Cd(L^1][NO_3]]^+]$, [552, 3.7%, $[Cd(L^1) + 2H]^+]$, [551, 10.7%, $[Cd(L^1) + H]^+]$, [550, 37.3%, $[Cd(L^1)]^+]$, [522, 7.3%, $[Cd(L^1)\text{-}(CH_2CH_2)]^+]$, [498, 4.1%, $[Cd(L^1)\text{-}(CH_2CH_2CH_2CH_2)]^+]$, [467, 12.1%, $[Cd(L^1)\text{-}(OCH_2CH_2CH_2CH_2O) + H]^+]$, [440, 17.6%, $[L^1 + 2H]$, [439, 100.0%, $[L^1 + H]$, (206, 14.9%, $[C_{10}H_{24}N_2O_2] + 2H]^+)$, (205, 45.3%, $[C_{10}H_{24}N_2O_2] + H]^+)$, 103 ($C_7NH_5^+$, 9.2%), (79, 11.2%, $[C_6H_6 + H]^+$.

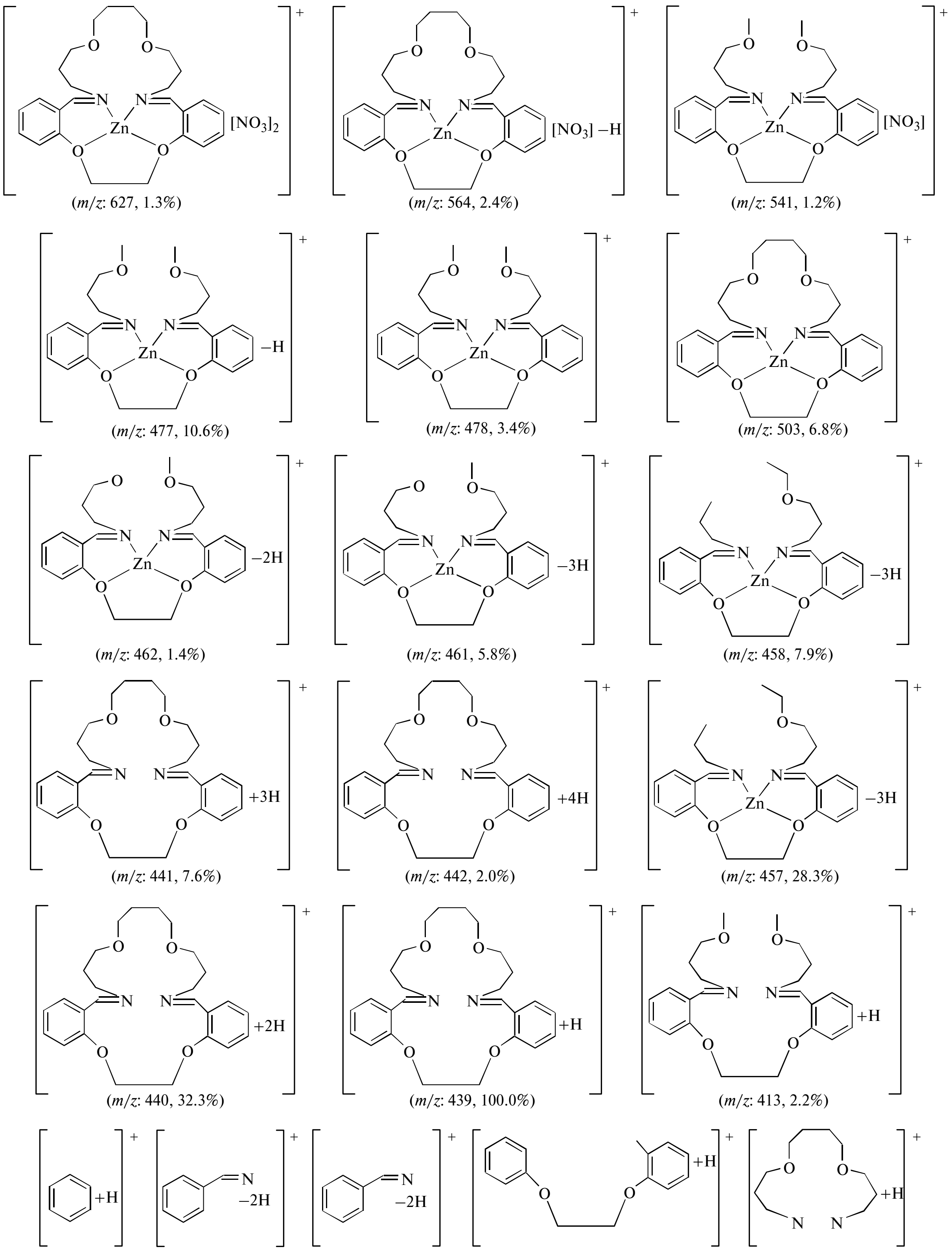
$[PbL^2][NO_3]_2 \cdot 2H_2O$ – [569, 1.3%, $[[PbL^2]. H_2O + 2H]^+]$, [523, 4.8%, $[[PbL^2\text{-}(OCH_2)]\text{-}2H]^+]$, [426, 2.2%, $C_{14}H_7N_2OPb]^+]$, [350, 7.6%, $[[L^2] + 2H]^+]$, [349, 31.9%, $[[L^2] + H]^+]$, [348, 44.0%, $[[L^2]]^+]$, [347, 18.6%, $[[L^2]\text{-}H]^+]$, [346, 21.6%, $[[L^2]\text{-}2H]^+]$, [332, 7.0%, $[[L^2\text{-}(O)]]^+]$, [331, 100.0%, $[[L^2\text{-}(O)]\text{-}H]^+]$, [330, 40.0%, $[[L^2\text{-}(O)]\text{-}2H]^+]$, [329, 45.6%, $[[L^2\text{-}(O)]\text{-}3H]^+]$, [287, 10.2%, $[[L^2\text{-}(OCH_2CH_2)]\text{-}H]^+]$, [286, 12.5%, $[[L^2\text{-}(OCH_2CH_2)]\text{-}2H]^+]$, [285, 10.9%, $[[L^2\text{-}(OCH_2CH_2)]\text{-}3H]^+]$, [284, 6.5%, $[[L^2\text{-}(OCH_2CH_2)]\text{-}4H]^+]$, [182, 97.6%, $[[C_{10}H_{16}NO_2]^+]$, [181, 39.9%, $[[C_{10}H_{15}NO_2]^+]$, [180, 2.6%, $[[C_{10}H_{14}NO_2]^+]$, (78, 4.3%, $[C_6H_6]^+)$.

$[[ZnL^2][NO_3]_2 \cdot 2H_2O$ – [542, 5.8%, $[ZnL^2][NO_3]_2 + 3H]^+]$, [514, 6.2%, $[ZnL^2\text{-}(CH_2CH_2)][NO_3]_2 + 3H]^+]$, [513, 3.9%, $[ZnL^2\text{-}(CH_2CH_2)][NO_3]_2 + 2H]^+]$, [513, 13.4%, $[ZnL^2\text{-}(CH_2CH_2)][NO_3]_2 + H]^+]$, [511, 4.8%, $[ZnL^2\text{-}(CH_2CH_2)][NO_3]_2]^+]$, [510, 15.8%, $[ZnL^2\text{-}(CH_2CH_2)][NO_3]_2\text{-}2H]^+]$, [497, 9.6%, $[ZnL^2\text{-}(OCH_2CH_2)][NO_3]_2 + H]^+]$, [496, 6.1%, $[ZnL^2\text{-}(OCH_2CH_2)][NO_3]_2]^+]$, [495, 24.2%, $[ZnL^2\text{-}(OCH_2CH_2)][NO_3]_2\text{-}H]^+]$, [494, 8.1%, $[ZnL^2\text{-}(OCH_2CH_2)][NO_3]_2\text{-}2H]^+]$, [493, 24.1%, $[ZnL^2\text{-}(OCH_2CH_2)][NO_3]_2\text{-}3H]^+]$, [492, 5.1%, $[ZnL^2\text{-}(OCH_2CH_2)][NO_3]_2\text{-}4H]^+]$, [491, 18.5%, $[ZnL^2\text{-}(OCH_2CH_2)][NO_3]_2\text{-}5H]^+]$, [477, 2.0%, $[ZnL^2\text{-}][NO_3]_2]^+]$, [475, 1.6%, $[ZnL^2]\text{-}[NO_3]_2]^+]$, [413, 6.7%, $[ZnL^2]\text{-}2H]^+]$, [368, 8.6%, $[ZnL^2\text{-}(OCH_2CH_2)]\text{-}2H]^+]$, [367, 32.8%, $[ZnL^2\text{-}(OCH_2CH_2)]\text{-}2H]^+]$, [367, 32.8%, $[ZnL^2\text{-}(OCH_2CH_2)]\text{-}2H]^+]$, [358, 32.8%, $[ZnL^2\text{-}(OCH_2CH_2O)] + 2H]^+]$, [357, 3.5%, $[ZnL^2\text{-}(OCH_2CH_2O)] + H]^+]$, [356, 12.9%, $[ZnL^2\text{-}(OCH_2CH_2O)]]^+]$, [355, 3.3%, $[ZnL^2\text{-}(OCH_2CH_2O)]\text{-}H]^+]$, [350, 8.8%, $[L^2] + 2H]^+]$, [349, 38.6%, $[L^2] + 2H]^+]$, [337, 11.0%, $[L^2\text{-}(CH_2)] + 3H]^+]$, [318, 1.9%, $[L^2\text{-}(OCH_2)]]^+]$, [304, 1.3%, $[L^2\text{-}(O\ CH_2CH_2)]]^+]$, [303, 4.3%, $[L^2\text{-}(OCH_2CH_2)]\text{-}H]^+]$, [302, 1.0%, $[L^2\text{-}(OCH_2CH_2)]\text{-}2H]^+]$, [301, 7.4%, $[L^2\text{-}(OCH_2CH_2)]\text{-}3H]^+]$, [270, 2.4%, $[[C_{16}H_{18}N_2O_2]^+]$, [269, 10.0%, $[[C_{16}H_{17}N_2O_2]^+]$, [268, 1.6%, $[[C_{16}H_{16}N_2O_2]^+]$, [267, 9.3%, $[[C_{16}H_{15}N_2O_2]^+]$, [265, 19.8%, $[[C_{16}H_{14}N_2O_2]^+]$, [191, 7.6%, $[[C_{13}H_{21}N]^+]$, [189, 12.0%, $[[C_{13}H_{19}N]^+]$, [187, 20.0%, $[[C_{13}H_{17}N]^+]$, [116, 5.8%, $[[C_6H_{165}N_2]^+]$, [115, 100.0%, $[[C_6H_{15}N_2]^+]$, [98, 45.2%, $[[C_6H_{12}N]^+]$.

$[LaL^2(H_2O)_2][NO_3]_3 \cdot H_2O$ – [579, 1.7%, $[LaL^2\text{-}(OCH_2)][NO_3]_2\text{-}2H]^+]$, [533, 1.9%, $[LaL^2\text{-}(CH_2)][NO_3]\text{-}2H]^+]$, [351, 2.0%, $[L^2]{+}3H]^+]$, [350, 15.2%, $[L^2] + 2H]^+]$, [349, 61.6%, $[L^2] + H]^+]$, [218, 15.3%, $[[C_{14}H_{18}O_2]^+]$, [217, 100.0%, $[[C_{14}H_{17}O_2]^+]$, [150, 37.4%, $[[C_9H_{14}N_2]^+]$, [115, 31.5%, $[[C_6H_{15}N_2]^+]$, [101, $C_7NH_3^+$, 1.0%), [98, 12.4%, $[[C_6H_{12}N]^+]$, (81, 2.1%, $[C_6H_6 + 3H]^+)$, (79, 27.4%, $[C_6H_6 + H]^+)$.

$[CdL^2][NO_3]_2 \cdot 2H_2O$ – [619, 1.1%, $[CdL^2][NO_3]_2\text{-}H]^+]$, [457, 0.6%, $[CdL^2]\text{-}3H]^+]$, [439, 0.6%, $[CdL^2\text{-}(CH_2CH_2)] + 3H]^+]$, [406, 3.6%, $[CdL^2\text{-}(OCH_2CH_2O)] + 2H]^+]$, [405, 5.2%, $[CdL^2\text{-}(OCH_2CH_2O)] + H]^+]$, [404, 9.5%, $[CdL^2\text{-}(OCH_2CH_2O)]^+]$, [377, 5.4%, $[[CdC_{16}H_{13}N_2O_2]^+]$, [368, 25.6%, $[[CdC_{15}H_{15}N_2O_2]^+]$, [367, 100.0%, $[[CdC_{15}H_{15}N_2O_2]^+]$, [351, 3.2%, $[L^2] + 3H]^+]$, [350, 23.3%, $[L^2] + 2H]^+]$, [349, 90.4%, $[L^2] + H]^+]$, [318, 4.1%, $[L^2\text{-}(OCH_2)]\text{-}3H]^+]$, [115, 7.2%, $[[C_6H_{15}N_2]^+]$, [98, 2.7%, $[[C_6H_{12}N]^+]$.

The novel 6 Schiff base macrocyclic complexes were prepared and characterized by elemental analyses, FTIR and UV-vis spectra, conductivity measurements, ^1H NMR and mass spectra. Suggested structures of the complexes were shown in Fig. 4. The complexes have no clearly defined melting point and begin to decompose in the temperature range 250–350°C. The complexes are air stable, soluble in DMF, DMSO and insoluble $CHCl_3$, CH_2Cl_2 and less soluble MeOH, EtOH, CH_3CN and the crystals were unsuitable for single-crystal X-ray structure determination. The binding mode of the ligand for the Pb(II) complexes behaves as hexadentate or tetradentate ligand with the lone electron pairs of azomethine nitrogen atoms and the lone electron pairs of four or two oxygen in ether groups. The binding mode of the ligand for the La(III), Cd(II) and Zn(II) complexes behaves as a tetradentate ligand with the lone electron pairs of azomethine nitrogen atoms and two atoms in ether groups. The long distance binding process can be favored for too large Pb(II) metal ions but not other metal ions due to having smaller ion size than Pb(II) metal ion. So its coordination is satisfied two H_2O for La(III) complex in the complexes of L^1. Similar binding mode was observed in literature for Pb(II), Zn(II) and La(III) metal ion [31]. These results are clearly verify different binding mode of ligand in the case of the



(m/z: 627, 1.3%) (m/z: 564, 2.4%) (m/z: 541, 1.2%)

(m/z: 477, 10.6%) (m/z: 478, 3.4%) (m/z: 503, 6.8%)

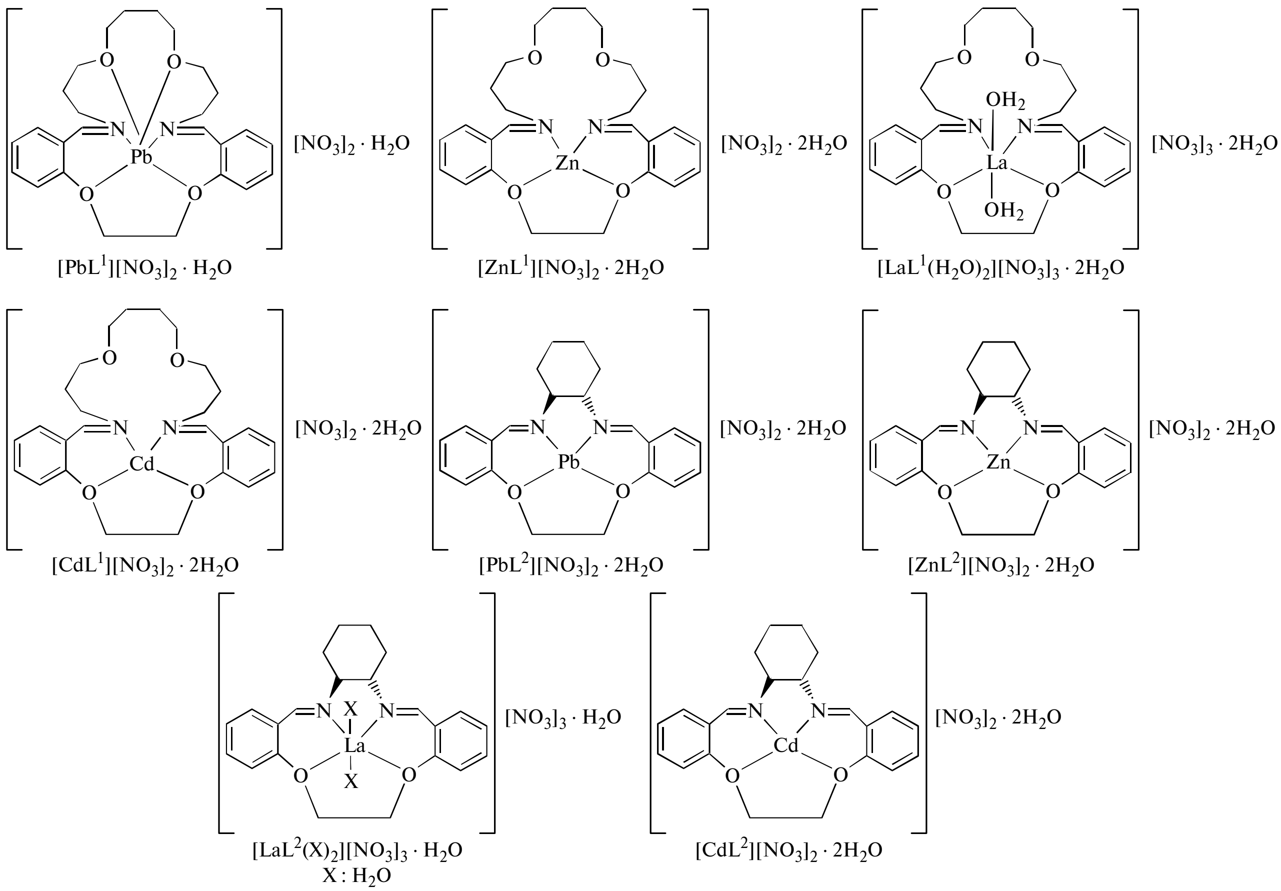
(m/z: 462, 1.4%) (m/z: 461, 5.8%) (m/z: 458, 7.9%)

(m/z: 441, 7.6%) (m/z: 442, 2.0%) (m/z: 457, 28.3%)

(m/z: 440, 32.3%) (m/z: 439, 100.0%) (m/z: 413, 2.2%)

(m/z: 79, 26.5%) (m/z: 101, 6.2%) (m/z: 103, 22.6%) (m/z: 229, 51.4%) (m/z: 205, 100.0%)

Fig. 3. The fragments observed in the mass spectrum of the $[ZnL^1]$ $[NO_3]_2 \cdot 2H_2O$.



$[PbL^1][NO_3]_2 \cdot H_2O$

$[ZnL^1][NO_3]_2 \cdot 2H_2O$

$[LaL^1(H_2O)_2][NO_3]_3 \cdot 2H_2O$

$[CdL^1][NO_3]_2 \cdot 2H_2O$

$[PbL^2][NO_3]_2 \cdot 2H_2O$

$[ZnL^2][NO_3]_2 \cdot 2H_2O$

$[LaL^2(X)_2][NO_3]_3 \cdot H_2O$
X : H_2O

$[CdL^2][NO_3]_2 \cdot 2H_2O$

Fig. 4. Suggested structure of the complexes.

Pb(II) metal ion [32]. Therefore, structure of the Pb(II) complexes are different from structure of the Zn(II) and La(III) complexes. Similar cases can be seen in the literatures [31–34]. As a result Pb(II) metal ion can bind six or four atoms and Zn(II) and Cd(II) ions can bind four atoms and La(III) ions can bind six atoms in the complexes. The Cd(II) and Zn(II) complexes probability show tetrahedral geometry and La(III) complexes probability show octahedral geometry all the complexes, Pb(II) ions probability show octahedral geometry in the L^1 complex and tetrahedral geometry in the L^2 complex [31–33]. Absolute structure of the complexes can be determined using X-ray diffraction method. In this paper only suggested structure of the complexes were given.

REFERENCES

1. S. Tamburini, P. A. Vigato, M. Gatos, et al., Inorg. Chim. Acta **359**, 183 (2006).
2. A. A. Khandar, S. A. Hosseini-Yazdi, M. Khatamian, et al., Polyhedron, **26**, 33 (2007).
3. S. Chandra and L. K. Gupta, Spectrochim. Acta, Pt. A **62**, 307 (2005).
4. W. Radecka-Paryzek, V. Patroniak, and J. Lisowski, Coord. Chem. Rev. **249**, 2156 (2005).
5. S. Tamburini, P. A. Vigato, M. Gatos, et al., Inorg. Chim. Acta **359**, 183 (2006).
6. P. Guerrierro, P. A. Vigato, D. E. Fenton, and P. C. Hellier, Acta Chem. Scand. **46**, 1025 (1992).
7. H. Khanmohammadi, S. Amani, H. Lang, and T. Rueffer, Inorg. Chim. Acta **360**, 579(2007).
8. D. S. Kumar and V. Alexander, Polyhedron **18**, 1561 (1999).
9. S. Tamburini, V. Vigato, M. Gatos, et al., Inorg. Chim. Acta **359**, 183 (2006).
10. M. E. S. Khalıl and K. A. Bashır, J. Coord. Chem. **55** (6), 681 (2002).
11. A. Chaudhary, N. Bansal, A. Gajraj, and R.V. Singh, J. Inorg. Biochem. **96**, 393(2003).
12. R. M. Izan, J. S. Brandshaw, S. A. Neilsen, et al., Chem. Rev. **85**, 271 (1985).
13. S. Chandra and L. K. Gupta, Spectrochim. Acta Pt. A **62**, 307 (2005).
14. S. İlhan, Ind. J. Chem., Sect. A (in press).
15. G. A. Melson, *Coordination Chemistry of Macrocyclic Compounds* (Plenum, New York, 1979).
16. K. K. Nanda, K. Venkatsubramanian, D. Majumdar, and K. Nag, Inorg. Chem. **33**, 1581(1994).

17. V. Alexander, Chem. Rev. **95**, 273(1995).
18. K. R. Adam, A. J. Leong, L. F. Lindoy, et al., J. Am. Chem. Soc. **105**, 4645 (1983).
19. L. F. Lindoy and L. G. Armstrong, Inorg. Chem. **14** (6), 1322 (1975).
20. S. İlhan and H. Temel, Ind. J. Chem., Sect. A **47**, 374 (2008).
21. S. İlhan, H. Temel, and A. Kılıç, Chin. J. Chem. **61**, (2) 277 (2008).
22. S. İlhan, H. Temel, and A. Kılıç, J. Coord. Chem., **25**, (10) 1547 (2007).
23. S. İlhan, H. Temel, A. Kılıç, and İ. Yımaz, Trans. Met. Chem. **32**, 344 (2007).
24. H. Temel, B. Ziyadanoğulları, H. Alp, et al., Russ. J. Coord. Chem. **32** (4), 282 (2006).
25. S. İlhan, H. Temel, A. Kılıç, and E. Tas, Trans. Met. Chem. **32**, 1012 (2007).
26. H. Temel, H. Hosgoren, and M. Boybay, Spectrosc. Lett. **34** (5), 1 (2001).
27. S. İlhan, H. Temel, İ. Yımaz, and M. Sekerci, Polyhedron **26**, 2795 (2007).
28. S. İlhan, H. Temel, İ. Yımaz, and M. Sekerci, J. Org. Met. Chem. **692**, 3855 (2007).
29. S. Ilhan, H. Temel, R. Ziyadanoğulları, and M. Sekerci, Trans. Met. Chem. **32**, 584 (2007).
30. C. Lodeiro, R. Bastda, E. Bertolo, and A. Rodriguez, Can. J. Chem. **82**, 437 (2004).
31. S. İlhan and H. Temel, Trans. Met. Chem. **32**, 1039 (2007).
32. H. Temel, H. Alp, S. İlhan, et al., Monats. Chem., **138**, 1199(2007).
33. A. Freiri and R. Bastida, L. Valencia Macias, et al., Inorg. Chim. Acta **359**, 2383 (2006).
34. S. James, D. S. Kumar, and V. Alexander, J. Chem. Soc. Dalton Trans. 1773(1999).