766 **RESEARCH PAPER** DECEMBER, 766–769 JOURNAL OF CHEMICAL RESEARCH 2009

Synthesis and characterisation of Schiff base macrocyclic Pb(II), Zn(II), Cd(II) and La(III) complexes by template reaction of (±)-*trans*-1,2-diaminocyclohexane with metal nitrates and salicylaldehyde derivatives

Salih Ilhan*

Department of Chemistry, Faculty of Art and Sciences, Siirt University, Siirt, Turkey

Eight macrocyclic complexes have been synthesised by template reaction of (±)-*trans*-1,2-diaminocyclohexane with metal nitrates and 1,10-bis(2-formylphenyl)-1,4,7,10-tetraoxadecane or 1,7-bis(2-formylphenyl)-1,4,7-trioxaheptane, and their structures are proposed on the basis of elemental analysis, FT-IR, UV-Vis, molar conductivity measurements, ^{1}H The complexes NMR and mass spectra. The metal-to-ligand molar ratios are 1 : 1 in the complexes, which are 1 : 2 electrolytes for Pb(II), Cd(II) and Zn(II) and 1 : 3 electrolytes for La(III)

Keywords: macrocyclic Schiff base complexes, 1,7-bis(2-formylphenyl)-1,4,7-trioxaheptane, 1,10-bis(2-formylphenyl)-1,4,7,10-tetraoxadecane, (±)-*trans*-1,2-diaminocyclohexane

Schiff bases have played an important role in the development of coordination chemistry as they readily form stable complexes with most of the transition metals.[1] The preparation of macrocyclic polyamine ligands bearing functional pendant donor groups and their subsequent ligation to various metal ions has been an active area of research in recent years.[2,3] Macrocyclic ligands containing a heteroatom are important complexing agents for cations, anions and molecules and the chemical properties of macrocyclic complexes can be tuned to force metal ions to adopt unusual coordination geometries.[4] Synthesis of Schiff-base complexes can be achieved through template reactions or by transmetallation reactions when transition metal cations are ineffective as templates.[5] The stability of macrocyclic metal complex depends upon a number of factors, including the number and type of donor atoms present in the ligand and their relative positions within the macrocyclic skeleton, as well as the number and size of the chelate rings formed on complexation. For transition metal ions, features such as the nature and magnitude of crystal-field effects play also an important role.[6,7] In the present work, Pb(III), Zn(II) and La(III) complexes have been synthesised by template reaction of (±)-*trans*-1,2-diaminocyclohexane and salicylaldehyde derivatives with $M(NO_3)_n\cdot 6H_2O$ (n = 2 or 3) in methanol.

Experimental

Analytical methods

Elemental analysis was carried out on a Leco CHNS model 932 elemental analyser. ^{1}H NMR spectra were recorded using a Bruker Avance DPX-400 NMR spectrometer. IR spectra were recorded on a Perkin Elmer Spectrum RX1 FTIR spectrometer as KBr discs. Electronic spectra were determined on a Shimadzu model 160 UV-Vis spectrophotometer. Molar conductivity was measured in DMSO solution with a WTW LF model 330 conductivity meter. LC/MS-API-ES mass spectra were recorded using an Agilent model 1100 MSD mass spectrophotometer. All chemicals and solvents were of analytical grade and used as received.

Chemical and starting materials

The salicylaldehyde derivatives used in the synthesis were prepared according to the literature method and are shown in Fig. 1.[8,9]

General synthesis of complexes

To a stirred solution of salicylaldehyde derivatives (2 mmol) and metal nitrate in methanol (50 mL) was added dropwise (±)-*trans*-1,2-diaminocyclohexane (2 mmol) in methanol (30 mL). The reaction was continued for 2 h at 80 °C and 1 h at room temperature. After the reaction was complete, the precipitate was filtered, washed with methanol and dried in air. Yield: 33–14%.

$[PbL^1][NO_3]_2\cdot 2H_2O$: Yield: 0.29 g (19.6%). Anal. Calcd for $PbC_{24}H_{28}N_4O_9\cdot H_2O$: C, 38.87; H, 4.05; N, 7.56. Found: C, 39.01; H, 4.19; N, 7.53%. ^{1}H NMR (DMSO-d_6, δ ppm): δ = 3.86 (H1, t, 4H, J = 4.9), δ = 4.20 (H2, t, 4H, J = 6.1), δ = 3.18 (H3, t, 4H, J = 6.6), δ = 1.90 (H4, p, 4H, J = 7.3), δ = 1.56 (H5, t, 4H, J = 7.6), δ = 3.40 (H_2O), δ = 7.01–8.04 (m, 8H, ArH), δ = 10.35 (s, 2H, HC=N). Selected IR data (KBr, ν cm^{-1}): 3373 $\nu(H_2O)$, 1638 ν(C=N), 1384 ν(ionic NO_3^-), 493 ν(Pb–O), 447 ν(Pb–N). Λ_M = 159 Ω^{-1} mol^{-1} cm^2. UV-Vis (λ_{max}, nm) (DMSO): 279, 327, 381. Mass spectrum (*m/z*): [584, 3.5%, $\{PbL^1\text{-}(CH_2)\}^+$].

$[Zn(H_2O)L^1][NO_3]_2\cdot 2H_2O$: Yield: 0.30 g (23.6%). Anal. Calcd for $ZnC_{24}H_{30}N_4O_{10}\cdot 2H_2O$: C, 45.35; H, 5.35; N, 8.82. Found: C, 45.43; H, 5.51; N, 8.72% ^{1}H NMR (DMSO-d_6, δ ppm): δ = 3.83 (H1, t, 4H, J = 5.8), δ = 4.21 (H2, t, 4H, J = 7.2), δ = 3.17 (H3, t, 4H, J = 6.3), δ = 1.89 (H4, p, 4H, J = 7.6), δ = 1.56 (H5, t, 4H, J = 7.8), δ = 3.41 (H_2O), δ = 7.03–8.06 (m, 8H, ArH), δ = 10.36 (s, 2H, HC=N). Selected IR data (KBr, ν cm^{-1}): 3371 $\nu(H_2O)$, 1644 ν(C=N), 1384 ν(ionic NO_3^-), 517 ν(Zn–O), 471 ν(Zn–N). Λ_M = 171 Ω^{-1} mol^{-1} cm^2. UV-Vis (λ_{max}, nm) (DMSO): 276, 326, 379. Mass spectrum (*m/z*): [537, 2.6%, $\{[Zn(H_2O)L^1][NO_3]\}^+$].

$[CdL^1][NO_3]_2\cdot 4H_2O$: Yield: 0.28 g (20.0%). Anal. Calcd for $CdC_{24}H_{28}N_4O_9\cdot 4H_2O$: C, 41.08; H, 5.14; N, 7.99. Found: C, 40.97; H, 5.11; N, 8.07%. ^{1}H NMR (DMSO-d_6, δ ppm): δ = 3.85 (H1, t, 4H, J = 7.4), δ = 4.20 (H2, t, 4H, J = 5.7), δ = 3.17 (H3, t, 4H, J = 6.4), δ = 1.90 (H4, p, 4H, J = 7.1), δ = 1.54 (H5, t, 4H, J = 5.9), δ = 3.40 (H_2O), δ = 6.98–8.05 (m, 8H, ArH), δ = 10.37 (s, 2H, HC=N). Selected IR data (KBr, ν cm^{-1}): 3369 $\nu(H_2O)$, 1647 ν(C=N), 1384 ν(ionic NO_3^-), 509 ν(Cd–O), 469 ν(Cd–N). Λ_M = 161 Ω^{-1} mol^{-1} cm^2. UV-Vis (λ_{max}, nm) (DMSO): 278, 322, 376. Mass spectrum (*m/z*): [630, 0.9%, $\{[CdL^1][NO_3]_2 + H\}^+$].

$[La(H_2O)L^1][NO_3]_3\cdot H_2O$: Yield: 0.33 g (21.9%). Anal. Calcd for $LaC_{24}H_{30}N_5O_{13}\cdot H_2O$: C, 38.25; H, 4.25; N, 9.30. Found: C, 38.34; H, 4.41; N, 9.23%. ^{1}H NMR (DMSO-d_6, δ ppm): δ = 3.88 (H1, t, 4H, J = 8.1), δ = 4.19 (H2, t, 4H, J = 7.1), δ = 3.20 (H3, t, 4H, J = 4.8), δ = 1.89 (H4, p, 4H, J = 7.4), δ = 1.55 (H5, t, 4H, J = 7.8), δ = 3.41 (H_2O), δ = 7.02–8.04 (m, 8H, ArH), δ = 10.36 (s, 2H, HC=N). Selected IR data (KBr, ν cm^{-1}): 3377 $\nu(H_2O)$, 1639 ν(C=N), 1384 ν(ionic NO_3^-), 494 ν(La–O), 462 ν(La–N). Λ_M = 234 Ω^{-1} mol^{-1} cm^2. UV-Vis (λ_{max}, nm) (DMSO): 276, 327, 378. Mass spectrum (*m/z*): [577, 5.6%, $[LaL^1\text{-}(O)]^+$].

$[PbL^2][NO_3]_2\cdot 3H_2O$: Yield: 0.27 g (16.4%). Anal. Calcd for $PbC_{26}H_{32}N_4O_{10}\cdot 3H_2O$: C, 47.96; H, 4.62; N, 6.81. Found: C, 48.06; H, 4.79; N, 6.73%. ^{1}H NMR (DMSO-d_6, δ ppm): δ = 3.61 (H1, t, 4H, J = 8.3), δ = 3.87 (H2, t, 4H, J = 8.5), δ = 4.23 (H3, t, 4H, J = 7.2), δ = 3.17 (H4, t, 4H, J = 6.2), δ = 1.86 (H5, q, 4H, J = 5.6), δ = 1.56 (H6, t, 4H, J = 7.6), δ = 3.42 (H_2O), δ = 7.02-8.06 (m, 8H, ArH), δ = 10.37 (s, 2H, HC=N). Selected IR data (KBr, ν cm^{-1}): 3368 $\nu(H_2O)$, 1636 ν(C=N), 1384 ν(ionic NO_3^-), 486 ν(Pb–O), 449 ν(Pb–N). Λ_M = 149 Ω^{-1} mol^{-1} cm^2. UV-Vis (λ_{max}, nm) (DMSO): 278, 323, 377. Mass spectrum (*m/z*): [628, 4.1%, $\{PbL^2\text{-}(CH_2)\}^+$].

$[ZnL^2][NO_3]_2\cdot H_2O$: Yield: 0.25 g (19.4%). Anal. Calcd for $ZnC_{26}H_{32}N_4O_{10}\cdot H_2O$: C, 48.52; H, 5.29; N, 8.71. Found: C, 49.06; H, 5.41; N, 8.62%. δ = 3.62 (H1, t, 4H, J = 6.5), δ = 3.88 (H2, t, 4H, J = 5.6), δ = 4.22 (H3, t, 4H, J = 7.7), δ = 3.18 (H4, t, 4H, J = 5.2), δ = 1.88 (H5, q, 4H, J = 8.1), δ = 1.55 (H6, t, 4H, J = 7.3), δ = 3.41 (H_2O), δ = 6.96–8.08 (m, 8H, ArH), δ = 10.38 (s, 2H, HC=N). Selected IR data (KBr, ν cm^{-1}): 3375 $\nu(H_2O)$, 1637 ν(C=N), 1384 ν(ionic NO_3^-), 513 ν(Zn–O), 473 ν(Zn–N). Λ_M = 158 Ω^{-1} mol^{-1} cm^2. UV-Vis (λ_{max}, nm) (DMSO): 279, 326, 380. Mass spectrum (*m/z*): [563, 2.0%, $\{[ZnL^2][NO_3]\}^+$].

---

* Correspondent. E-mail: salihsiirt@gmail.com

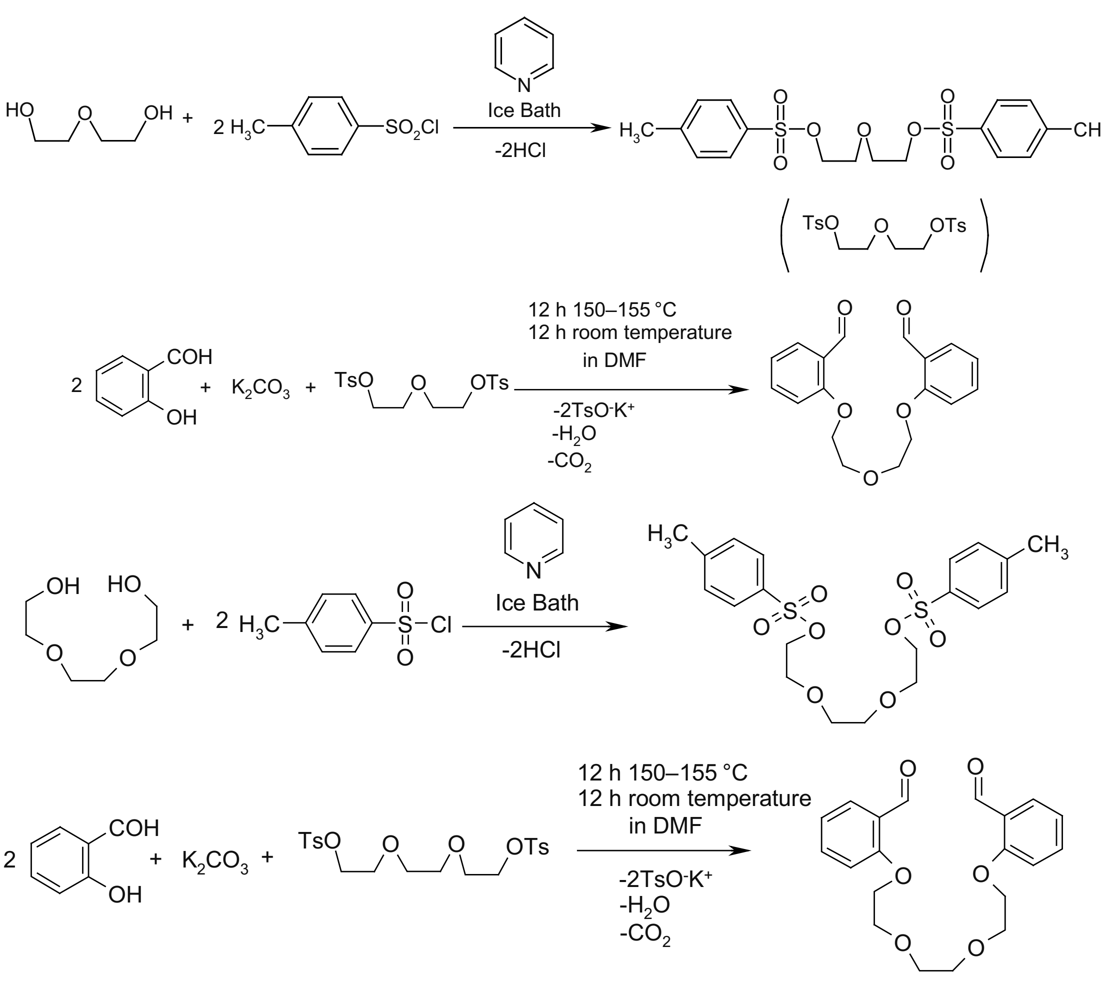

Fig. 1 Synthesis of 1,7-bis(2-formylphenyl)-1,4,7-trioxaheptane and 1,10-bis(2-formylphenyl)-1,4,7,10-tetraoxadecane.

[CdL²][NO₃]₂·2H₂O: Yield: 0.24 g (22.8%). Anal. Calcd for $CdC_{26}H_{32}N_4O_{10}·2H_2O$: C, 44.07; H, 5.08; N, 7.91. Found: C, 44.02; H, 5.01; N, 8.05%. ^1H NMR (DMSO-d_6, δ ppm):): δ = 3.62 (H1, t, 4H, *J* = 6.4), δ = 3.89 (H2, t, 4H, *J* = 5.5), δ = 4.21 (H3, t, 4H, *J* = 7.4), δ = 3.16 (H4, t, 4H, *J* = 6.8), δ = 1.87 (H5, q, 4H, *J* = 6.8), δ = 1.57 (H6, t, 4H, *J* = 8.2), δ = 3.40 (H_2O), δ = 7.00–8.07 (m, 8H, ArH), δ = 10.36 (s, 2H, HC=N). Selected IR data (KBr, ν cm^{-1}): 3369 ν(H_2O), 1639 ν(C=N), 1384 ν(ionic NO_3^-), 504 ν(Cd–O), 461 ν(Cd–N). Λ_M = 155 Ω^{-1} mol^{-1} cm^2. UV-Vis (λ_{max}, nm) (DMSO): 275, 321, 376. Mass spectrum (*m/z*): [671, 4.1%, $\{[CdL^2][NO_3]_2\text{-}H\}^+$].

[LaL²][NO₃]₃·2H₂O: Yield: 0.28 g (17.5%). Anal. Calcd for $LaC_{26}H_{32}N_5O_{13}·2H_2O$: C, 39.10; H, 4.51; N, 8.77. Found: C, 39.21; H, 4.63; N, 8.78%. δ = 3.60 (H1, t, 4H, *J* = 7.6), δ = 3.88 (H2, t, 4H, *J* = 8.3), δ = 4.21 (H3, t, 4H, *J* = 6.8), δ = 3.19 (H4, t, 4H, *J* = 5.3), δ = 1.88 (H5, q, 4H, *J* = 8.6), δ = 1.54 (H6, t, 4H, *J* = 7.9), δ = 3.42 (H_2O), δ = 7.03-8.10 (m, 8H, ArH), δ = 10.38 (s, 2H, HC=N).

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

Compound	Yield Gram (%)	(Calcd) Found %C	%H	%N	Λ_M mol^{-1}) (ohm^1cm^2	Formula weight	MS/EI	Assigment
$[PbL^1][NO_3]_2·2H_2O$	0.29 (19.6)	(38.87) 39.01	(4.05) 4.19	(7.56) 7.53	159	741	584	$\{[PbL^1\text{-}(CH_2)]^+\}$.
$[Zn(H_2O)L^1][NO_3]_2·2H_2O$	0.30 (23.6)	(45.35) 45.43	(5.35) 5.51	(8.82) 8.72	171	635	537	$\{[Zn(H_2O)L^1][NO_3]\}^+$
$[CdL^1][NO_3]_2·4H_2O$	0.28 (20.0)	(41.08) 45.43	(5.14) 5.51	(7.99) 8.72	161	630	701	$\{[CdL^1][NO_3]_2 + H\}^+$
$[La(H_2O)L^1][NO_3]_3·H_2O$	0.33 (21.9)	(38.25) 38.34	(4.25) 4.41	(9.30) 9.23	234	753	577	$[LaL^1\text{-}(O)]^+$
$[PbL^2][NO_3]_2·3H_2O$	0.27 (16.4)	(47.96) 41.46	(4.62) 5.19	(6.81) 6.33	149	822	628	$[PbL^2\text{-}(CH_2)]^+$
$[ZnL^2][NO_3]_2·H_2O$	0.25 (19.4)	(48.52) 49.19	(5.29) 6.11	(8.71) 7.50	158	643	563	$\{[ZnL^2][NO_3]\}^+$
$[CdL^2][NO_3]_2·2H_2O$	0.24 (22.8)	(44.07) 44.02	(5.08) 5.01	(7.91) 8.05	155	708	671	$\{[CdL^1][NO_3]_2\text{-}H\}^+$
[LaL2][NO3]3.2H2O	0.28 (17.5)	(39.10) 39.21	(4.51) 4.63	(8.77) 8.78	241	798	761	{[LaL2][NO3]3}+

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

Compound	ν(H_2O)	ν(C=N)	Ionic ν(NO_3^-)	ν(M–O)	ν(M–N)	Π–π* transition	N–π* transition
$[PbL^1][NO_3]_2{\cdot}2H_2O$	3373 s	1638 m	1384 m	493 w	447 w	279	327, 381
$[Zn(H_2O)L^1][NO_3]_2{\cdot}2H_2O$	3371 s	1644 m	1384 m	517 w	471 w	276	326, 379
$[CdL^1][NO_3]_2{\cdot}4H_2O$	3369 s	1647 m	1384 m	509 w	469 w	278	322, 376
$[La(H_2O)L^1][NO_3]_3{\cdot}H_2O$	3377 s	1639 m	1384 m	494 w	462 w	276	327, 378
$[PbL^2][NO_3]_2{\cdot}3H_2O$	3368 s	1636 m	1384 m	486 w	449 w	278	323, 377
$[ZnL^2][NO_3]_2{\cdot}H_2O$	3375 s	1637 m	1384 m	413 w	473 w	279	327, 380
$[CdL^2][NO_3]_2{\cdot}2H_2O$	3369 s	1639 m	1384 m	504 w	461 w	275	321, 376
$[LaL^2][NO_3]_3{\cdot}2H_2O$	3373 s	1647 m	1384 m	497 w	465 w	274	322, 378

M, medium; s, strong; w, weak.

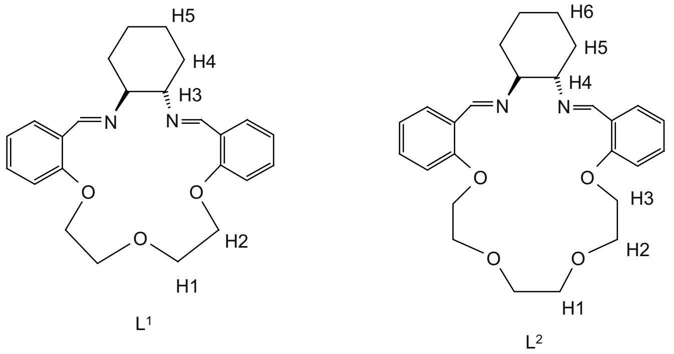

Fig. 2 Structure of the ligands in the complexes.

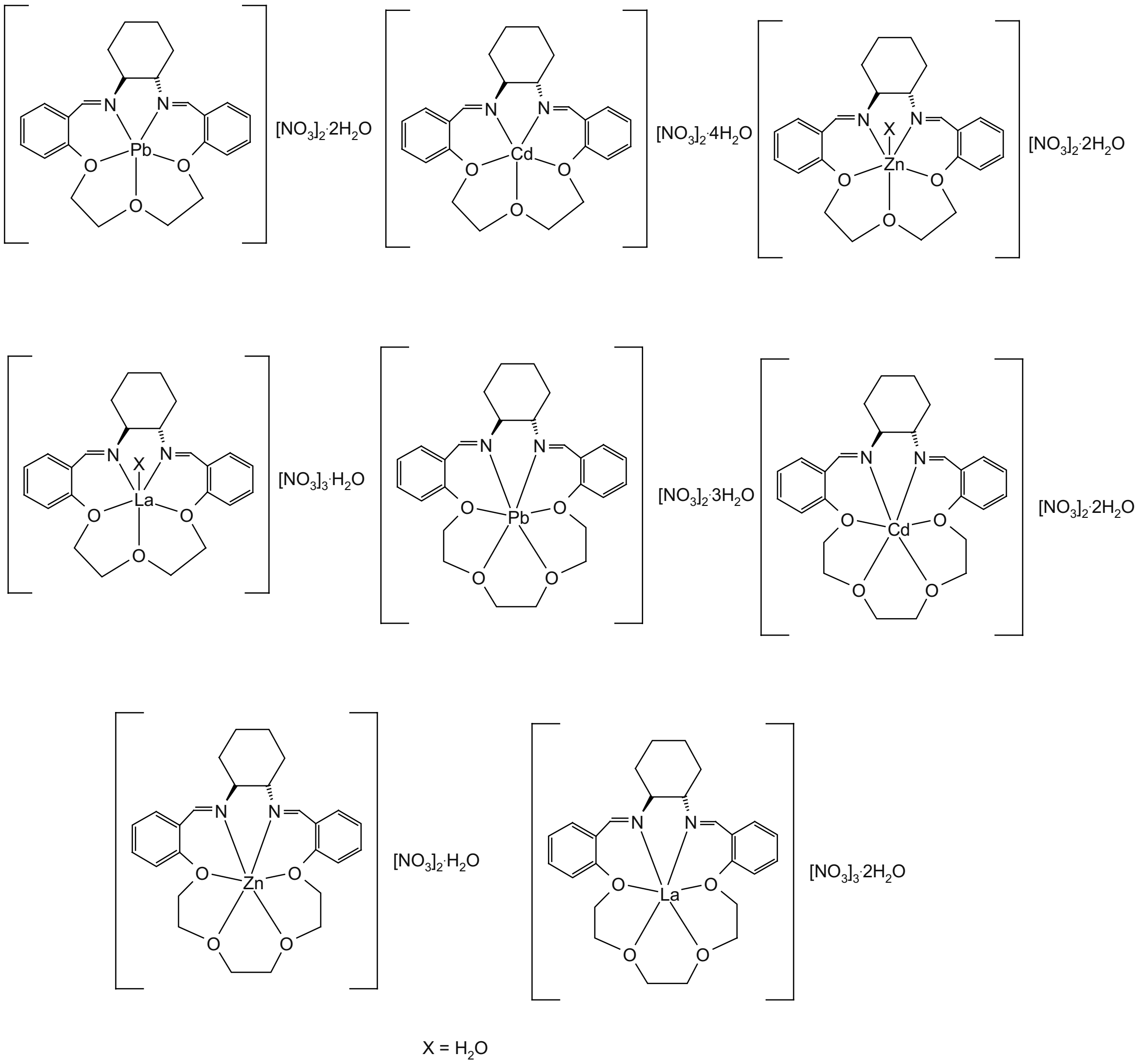

Fig. 3 Suggested structure of the complexes.

Selected IR data (KBr, ν cm^{-1}): 3373 ν(H_2O), 1647 ν(C=N), 1384 ν(ionic NO_3^-), 497 ν(La–O), 465 ν(La–N). Λ_M = 241 Ω^{-1} mol^{-1} cm^2. UV-Vis (λ_{max}, nm) (DMSO): 274, 322, 378. Mass spectrum (*m/z*): [761, 3.8%, {[LaL^2][NO_3]$_3$}$^+$]. (M.W = 798 g mol^{-1})

Results and discussion

Macrocyclic Schiff base complexes

In the reaction between 1,7-bis(2-formylphenyl)-1,4,7-trioxaheptane and 1,10-bis(2-formylphenyl)-1,4,7,10-tetraoxadecane, metal nitrate and (±)-*trans*-1,2-diaminocyclohexane in methanol, [1 + 1] macrocyclic Schiff-base complexes are formed. The macrocyclic complexes have been characterised by elemental analysis, UV-Vis spectra, conductivity measurements, and mass, ^{1}H 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. The crystals were unsuitable for single-crystal X-ray structure determination and are insoluble in most common solvents, including water, ethanol, ethyl acetate, and acetonitrile (Table 1).

FTIR spectra

The characteristic IR spectrum data are given in the experimental section. The broad bands within the range *ca* 3370 cm^{-1} for all complexes can be attributed to stretching vibrations of water molecules, υ(H_2O).[10,11] In the IR spectrum of the complexes absence of a ν(NH_2) peak at around 3300 cm^{-1} and 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* 1645 cm^{-1} region is attributed to υ(C=N) stretch, indicating coordination of the azomethine nitrogen to metal.[12,13] The absorptions at *ca* 1460–1452 (ν_5), 1300 (ν_1) and 1040 (ν_2) cm^{-1}, indicate the presence of nitrate groups: an intense band at *ca* 1384 cm^{-1} attributable to ionic nitrate, is also presen.[14,15] The spectra of all the complexes are dominated by bands between 2965 and2855 cm^{-1} due to ν(aliphatic-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[16,17] (Table 2).

Electronic spectra

Electronic absorption spectral data of complexes in dimethylformamide (DMSO) at room temperature are presented in the experimental section. The spectra show four peaks in the visible-ultraviolet region. The absorption bands below *ca* 300 nm are practically identical and can be attributed to $\pi\rightarrow\pi^*$transitions in the benzene ring and azomethine (–C=N) groups.[18,19] The absorption bands observed in the 300–330 nm range are most probably due to the transitions $n\rightarrow\pi^*$ of imine groups.[20,21]

Molar conductivity

The complexes are 1 : 2 electrolytes for Pb(II) and Zn(II), as shown by their molar conductivities (Λ_M) in DMSO at 10^{-3} M, which are in the range 140–200 Ω^{-1} cm^2 mol^{-1} and 1:3 electrolytes for La(III), as shown by their molar conductivities in the range 200–250 Ω^{-1} cm^2 mol^{-1}.[22,23]

Mass spectra

The mass spectra of the complexes are useful for characterisation of the complexes[24-27] (Table 3, deposited in the Electronic Supplemetary Information).

NMR spectra

The ^{1}H NMR spectra of the complexes are simple, indicating the integrity of the complexes in solution. They show a multiplet in the range 7.0–8.0 ppm due to aromatic protons, and resonances at 3.4 ppm due to H_2O protons, at around 1.5–4.5 ppm due to CH_2, OCH_2 and OCH_2Ph protons and at 10.4 ppm corresponding to the imine protons; but no signals corresponding to the formyl or amine protons are present[13-15] (see Fig. 2).

Conclusion

On the basis of the physical measurements detailed above, the novel eight Schiff base macrocyclic complexes are suggested to have the structures shown in Fig. 3. The La(III), Zn(II) and Pb(II) and Cd(II) (for L^2) complexes probably have octahedral geometry and Pb(II) and Cd(II) (for L^1) complexes probably have square pyramid geometry.[6,24] 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 in $CHCl_3$, CH_2Cl_2 and very poorly soluble in MeOH, EtOH, CH_3CN. Crystals were unsuitable for single-crystal X-ray structure determination. Similar binding modes have been reported in the literature for Pb(II), Cd(II), Zn(II) and La(III) metal ions.[6,24,28,29] The presence of several bands in the region associated with nitrate vibrations clearly identifies these species as containing nitrate groups.

Received 29 July 2009; accepted 20 November 2009
Paper 09/0712 doi: 10.3184/030823409X12596000099172

References

1 H. Khanmohammadi, S. Amani, H. Lang and T. Rueffer, *Inorg. Chim. Acta,* 2007, **360**, 579.
2 A.A. Khandar, S.A. Hosseini-Yazdi and S.A. Zarei, *Inorg. Chim. Acta,* 2007, **360**, 3211.
3 A.A. Khandar, S.A. Hosseini-Yazdi, M. Khatamian, P. McArdle and S.A. Zarei, *Polyhedron*, 2007, **26**, 33.
4 S. Chandra and L.K. Gupta, *Spectrochim. Acta Part A*, 2005, **62**, 307.
5 S. İlhan, *Russian Journal of Coord. Chem.*, 2009, **35**, 347.
6 S. İlhan, H. Temel and S. Pasa, *Chin. Chem. Lett.*, 2009, **20**, 339.
7 S. İlhan and H. Temel, *Indian J. Chem. Sect. A (IJC-A),* 2008, **47A**, March, 378.
8 S. İlhan, *Indian J. Chem. Sec A (IJC-A),* 2008, **47A**, March, 374.
9 S. İlhan, H. Temel and A. Kılıç, *J. Coord. Chem.*, 2008, **61,** 277.
10 S. İlhan, H. Temel, A. Kılıç and E. Taş, *Transition Metal Chem.,* 2007, **32**, 1012.
11 S. İlhan, H. Temel, A. Kılıç and İ. Yılmaz, *Transition Met. Chem.,* 2007, **32,** 344.
12 S. İlhan, H. Temel, A. Kılıç and E. Taş, *Journal of Coord. Chem.*, 2008, **61**, 1143.
13 S. İlhan, H. Temel, R. Ziyadanogullari and M. Sekerci, Trans*ition Metal Chem.* 2007, **32**, 584.
14 S.İlhan, H. Temel, M. Sünkür and İ. Teğin *Indian Journal of Chem. Sec A (IJC-A),* **47A**, 2008, April, 560.
15 S. İlhan and H. Temel, Trans*ition Metal Chem.,* 2007, **32**, 1039.
16 H. Temel, S. İlhan and M. Şekerci, *Synt. React. Inorg. Met-Org. Chem.*, 2002, **32,** 1625.
17 Ü. Çakır, H. Temel, S. İlhan and H.İ. Uğraş, *Spectrosc. Lett.,* 2003, **36,** 429.
18 H. Temel, S. İlhan, M. Şekerci, and R. Ziyadanoğulları, *Spectrosc. Lett.*, 2002, **35**, 219.
19 H. Temel, S. İlhan, M. Aslanoğlu and H. Alp, *Indian J. Chem., Sec A* (IJC-A), 2007, **46A,** 1109.
20 H. Temel and S. İlhan, *Russ. J. Coord. Chem.,* 2007, **33,** 914.
21 S. İlhan and H. Temel, *J. Mol. Struct.*, 2008**, 891,** 157.
22 S. Ilhan, H. Temel, M. Aslanoglu, A. Kılıc and E. Tas, *J. Chin. Chem. Soc.,* 2006, **53,** 1027.
23 H. Temel, H. Alp, S. Ilhan and B. Ziyadanoğulları, *J. Coord. Chem.*, 2008, **61**, 1146.
24 S. İlhan, H. Temel, I. Yilmaz and M. Sekerci, *J. Organomet. Chem.*, 2007, **692**, 3855.
25 H. Temel, H. Alp, S. İlhan, B. Ziyadanoğulları and İ. Yilmaz, *Monatsh. Chem.*, 2007, **138**, 1199.
26 S. İlhan, *Journal of Coord. Chem.*, 2008, **61**, 3634-3641 (2008).
27 H. Temel and S. İlhan, *Spectrochim Acta Part A,* 2008, **69**, 896.
28 A. Freiri, R. Bastida, L. Valencia, Al. Macıas, C.Lodeiro and H. Adams, *Inorg. Chim. Acta*, 2006, **359**, 2383.
29 S. James, D.S. Kumar, and V. Alexander, *J. Chem. Soc., Dalton Trans.*, 1999, 1773.