

Synthesis, structural characterization and electrochemical studies of new macrocyclic Schiff base containing pyridine head and its metal complexes

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Abstract

A new macrocyclic ligand, 1,3,5-triaza-2,4:7,8:13,14-tribenzo-9,12-dioxa-cyclopentadeca-1,5-diene was synthesized by reaction of 2,6-diaminopyridine and 1,2-bis(2-carboxyaldehyde phenoxy)ethane. Then, its Cu(II), Ni(II), Pb(II), Co(III) and La(III) complexes were synthesized by the template effect by the reaction of 2,6-diaminopyridine and 1,2-bis(2-carboxyaldehyde phenoxy)ethane and Cu(NO₃)₂ · 3H₂O, Ni(NO₃)₂ · 6H₂O, Pb(NO₃)₂, Co(NO₃)₂ · 6H₂O, La(NO₃)₃ · 6H₂O, respectively. The ligand and its metal complexes have been characterized by elemental analysis, IR, ¹H and ¹³C NMR, UV–Vis spectra, magnetic susceptibility, thermal gravimetric analysis, conductivity measurements, mass spectra, and cyclic voltammetry. All complexes are diamagnetic and Cu(II) complex is binuclear. The Co(II) was oxidized to Co(III). The comparative electrochemical studies show that the nickel complex exhibited a quasi-reversible one-electron reduction process, while copper and cobalt complexes gave irreversible reduction processes in DMSO solution.

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1. Introduction

Macrocyclic ligands with additional donor atoms appended to ring have attracted considerable interest because of their capacity to bind and transport metal ions, for the potential to prepare and study their mixed-valence forms, and as models for metalloproteins [1,2]. There is a continued interest in synthesizing macrocyclic complexes [3–7] because of their potential applications in fundamental and applied sciences [7–9] and importance in the area of coordination chemistry [10,11]. The development of the field of bioinorganic chemistry has been another important

factor in spurring the growth in interest in macrocyclic compounds [12]. An effective way to use the molecular recognition capability of macrocycles for metal ion separation is to incorporate such ligands into solvent extraction and liquid membrane systems [13]. During the past years, the separation of heavy metals and organic substances have become more important in water purification applications owing to the drastic strengthening of environmental protection laws. In this field, various separation techniques, such as precipitation, extraction, distillation and electro-dialysis, have all been employed. Membrane processes such as liquid-membrane transport systems are potentially quite important in this area [14]. In practical applications, three main types of liquid membranes containing a mobile carrier have been studied: liquid surfactant, supported liquid and dissolvent polymeric membranes [14–18]. In the present work, we have synthesized a new macrocyclic Schiff

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base by reaction of 2,6-diaminopyridine and 1,2-bis(2-carboxyaldehyde phenoxy)ethane. Then, its Cu(II), Ni(II), Pb(II), Co(III) and La(III) complexes were synthesized by template effect by reaction of 2,6-diaminopyridine and 1,2-bis(2-carboxyaldehyde phenoxy)ethane and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Pb}(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, respectively. Spectral, magnetic, and electrochemical properties of the new compounds were studied in detail.

2. Experimental

2.1. Physical measurements

Elemental analysis was carried out on a LECO CHNS model 932 elemental analyzer. ^1H NMR and ^{13}C 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 200–600 nm. Molar conductivity was measured with a WTW LF model 330 conductivity meter, using prepared solution of the complex in DMF–DMSO (1:1). Thermal gravimetric analysis was carried out on a TGA SHIMADZU model 50 thermal gravimetric analyzer. LC/MS-API-ES mass spectra were recorded using a AGILENT model 1100 MSD mass spectrophotometer. An EcoChemie Autolab-12 potentiostat with the electrochemical software package GPES 4.9 (Utrecht, The Netherlands) was used for voltammetric measurements. A three electrode system was used: a platinum wire counter electrode, an Ag/AgCl reference electrode, and a 2 mm sized platinum disc electrode as working electrode. The working electrode was polished with 0.05 μm alumina prior to each experiment. Throughout the experiment, oxygen-free nitrogen was bubbled through the solution for 10 min. Voltammetric experiments were performed at room temperature. Electrochemical grade tetraethylammonium perchlorate (TEAP) (0.1 mol dm^{-3}) was employed as the supporting electrolyte.

2.2. Materials

Ethylene glycol bis(*p*-toluenesulfonate) and 1,2-bis(2-carboxyaldehyde phenoxy)ethane were prepared as mentioned in the literature [19,20]. All the other chemicals and solvents were of analytical grade and used as received.

2.3. Synthesis of 1,3,5-triaza-2,4:7,8:13,14-tribenzo-9,12-dioxo-cyclopentadeca-1,5-diene macrocyclic Schiff base (L)

The macrocyclic ligand (L) was prepared by the dropwise addition of a solution of the 2,6-diaminopyridine (0.22 g, 2 mmol) in methanol (40 mL) to a stirred solution of 1,2-bis(2-carboxyaldehyde phenoxy)ethane (0.54 g,

2 mmol) in methanol (60 mL). After the addition was completed, stirring was continued for 2 h. A yellow coloured precipitate was filtered, then it was dissolved in CH_2Cl_2 . The solution was filtered and *n*-hexane added to the filtered solution to precipitate the desired compound. It was then filtered and obtained as a yellow compound. Yield: 0.45 g (62%). Anal. Calc. for $\text{C}_{21}\text{H}_{17}\text{N}_3\text{O}_2 \cdot \text{H}_2\text{O}$: C, 69.80; H, 5.26; N, 11.63. Found: C, 70.07; H, 5.34; N, 12.06%. ^{13}C NMR (DMSO- d_6 , δ ppm): OCH_2 : 65.6, $\text{HC}=\text{N}$: 161.3, Aromatic: 95.7, 114.0, 121.2, 124.8, 128.2, 136.9, 138.7, 159.2, 189.8. ^1H NMR (DMSO- d_6 , δ ppm): 3.41 (H_2O), 4.58 (s, 4H, $-\text{OCH}_2$), 7.01–8.0 (m, 11H, Ar-H), 10.33 (s, 2H, $\text{HC}=\text{N}$). Selected IR data (KBr, $\nu \text{ cm}^{-1}$): 3381 (H_2O), 1685 ($\text{C}=\text{N}$), 1598 ($\text{C}=\text{N}(\text{py})$). UV–Vis (λ_{max} , nm) (DMF–DMSO (1:1)): 265, 321, 379. Mass spectra: 339 $[\text{M}-4\text{H}]^+$ (Scheme 1).

2.4. Synthesis of complexes

2.4.1. Synthesis of the $[\text{Cu}_2(\text{L})(\text{NO}_3)_2][\text{NO}_3]_2 \cdot 2\text{H}_2\text{O}$

To a stirred solution of 1,2-bis(2-carboxyaldehyde phenoxy)ethane (0.54 g, 2 mmol) and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in methanol (60 mL) was added dropwise 2,6-diaminopyridine (0.22 g, 2 mmol) in methanol (40 mL). After the addition was completed, stirring was continued for 2 h. A brown coloured precipitate was filtered and washed with ethanol, CHCl_3 and diethyl ether, respectively. It was then dried in air. Yield: 0.65 g (45%). Anal. Calc. for $\text{Cu}_2\text{C}_{21}\text{H}_{17}\text{N}_7\text{O}_{14} \cdot 2\text{H}_2\text{O}$: C, 33.42; H, 2.79; N, 13.00. Found: C, 33.24; H, 2.58; N, 13.25%. ^1H NMR (DMSO- d_6 , δ ppm): $\delta = 3.41$ (H_2O), $\delta = 4.30$ (OCH_2), $\delta = 7.06$ – 7.96 (Ar-H), $\delta = 10.38$ ($\text{HC}=\text{N}$). Selected IR data (KBr, $\nu \text{ cm}^{-1}$): 3328 ($\nu(\text{H}_2\text{O})$), 1615 ($\nu(\text{C}=\text{N})$), 1598 ($\text{C}=\text{N}(\text{py})$). $A_{\text{M}} = 146 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$. UV–Vis (λ_{max} , nm) (DMF–DMSO (1:1)): 274, 322. Mass spectra: 719 $[[\text{Cu}_2(\text{L})(\text{NO}_3)_2][\text{NO}_3]_2 + \text{H}]^+$.

2.4.2. Synthesis of the $[\text{Ni}(\text{L})(\text{NO}_3)_2] \cdot \text{H}_2\text{O}$

To a stirred solution of 1,2-bis(2-carboxyaldehyde phenoxy)ethane (0.54 g, 2 mmol) and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.58 g, 2 in methanol (60 mL) was added dropwise 2,6-diaminopyridine (0.22 g 2 mmol) in methanol (40 mL). After the addition was completed, stirring was continued for 2 h. A yellow coloured precipitate was filtered and washed with ethanol, CHCl_3 and diethyl ether, respectively. It was then dried in air. Yield: 0.55 g (51%). Anal. Calc. for $\text{NiC}_{21}\text{H}_{17}\text{N}_5\text{O}_8 \cdot \text{H}_2\text{O}$: C, 46.41; H, 3.50; N, 12.89. Found: C, 46.52; H, 3.62; N, 12.93%. ^1H NMR (DMSO- d_6 , δ ppm): $\delta = 3.41$ (H_2O), $\delta = 4.60$ (OCH_2), $\delta = 6.97$ – 7.96 (Ar-H), $\delta = 10.31$ ($\text{HC}=\text{N}$). Selected IR data (KBr, $\nu \text{ cm}^{-1}$): 3383 ($\nu(\text{H}_2\text{O})$), 1658 ($\nu(\text{C}=\text{N})$), 1598 ($\text{C}=\text{N}(\text{py})$). $A_{\text{M}} = 39 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$. UV–Vis (λ_{max} , nm) (DMF–DMSO (1:1)): 274, 323, 367. Mass spectra: 543, $[\text{Ni}(\text{L})(\text{NO}_3)_2 \cdot \text{H}_2\text{O}]^+$.

2.4.3. Synthesis of the $[\text{Pb}(\text{L})(\text{NO}_3)][\text{NO}_3] \cdot 2\text{H}_2\text{O}$

To a stirred solution of 1,2-bis(2-carboxyaldehyde phenoxy)ethane (0.54 g, 2 mmol) and $\text{Pb}(\text{NO}_3)_2$ (0.66 g, 2 mmol) in methanol (60 mL) was added dropwise 2,6-di-

aminopyridine (0.22 g, 2 mmol) in methanol (40 mL). After the addition was completed, the stirring was continued for 2 h. A yellow coloured precipitate was filtered and washed with ethanol, CHCl_3 and diethyl ether, respectively. Then dried in air. Yield: 0.62 g (45%). Anal. Calc. for $\text{PbC}_{21}\text{H}_{17}\text{N}_5\text{O}_8 \cdot \text{H}_2\text{O}$: C, 35.49; H, 2.96; N, 9.86. Found: C, 35.54; H, 3.14; N, 9.95%. ^1H NMR could not be taken because of the low solubility. Selected IR data (KBr, ν cm^{-1}): 3383 $\nu(\text{H}_2\text{O})$, 1651 $\nu(\text{C}=\text{N})$, 1598 ($\text{C}=\text{N}(\text{py})$). $A_M = 81 \Omega^{-1} \text{mol}^{-1} \text{cm}^2$. UV–Vis (λ_{max} , nm) (DMF–DMSO (1:1)): 275, 321, 379. Mass spectra: 707 $[[\text{Pb}(\text{L})(\text{NO}_3)]][\text{NO}_3] \cdot 2\text{H}_2\text{O} - 3\text{H}^+$.

2.4.4. Synthesis of the $[\text{Co}(\text{L})(\text{NO}_3)_2(\text{OH})(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$

To a stirred solution of 1,2-bis(2-carboxyaldehyde phenoxy)ethane (0.54 g, 2 mmol) and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.58 g, 2 mmol) in methanol (60 mL) was added dropwise 2,6-diaminopyridine (0.22 g, 2 mmol) in methanol (40 mL). After the addition was completed, the stirring was continued for 2 h. A yellow coloured precipitate was filtered and washed with ethanol, CHCl_3 and diethyl ether, respectively. Then dried in air. Yield: 0.57 g (48%). Anal. Calc. for $\text{CoC}_{21}\text{H}_{20}\text{N}_5\text{O}_{10} \cdot 2\text{H}_2\text{O}$: C, 42.34; H, 4.19; N, 11.32. Found: C, 42.21; H, 4.02; N, 11.25%. ^1H NMR (DMSO- d_6 , δ ppm): $\delta = 3.41$ (H_2O), $\delta = 4.60$ (OCH_2), $\delta = 6.99$ – 7.96 (Ar-H), $\delta = 10.31$ ($\text{HC}=\text{N}$). Selected IR data (KBr, ν cm^{-1}): 3381 $\nu(\text{H}_2\text{O})$, 1657 $\nu(\text{C}=\text{N})$, 1598 ($\text{C}=\text{N}(\text{py})$). $A_M = 26 \Omega^{-1} \text{mol}^{-1} \text{cm}^2$. UV–Vis (λ_{max} , nm) (DMF–DMSO (1:1)): 276, 323, 380. Mass spectra: 599 $[[\text{Co}(\text{L})(\text{NO}_3)_2(\text{OH})(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O} + 2\text{H}^+]^+$.

2.4.5. Synthesis of the $[\text{La}(\text{L})(\text{NO}_3)_3(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$

To a stirred solution of 1,2-bis(2-carboxyaldehyde phenoxy)ethane (0.54 g, 2 mmol) and $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.87 g, 2 mmol) in methanol (60 mL) was added dropwise 2,6-diaminopyridine (0.22 g, 2 mmol) in methanol (40 mL). After the addition was completed, the stirring was continued for 2 h. A yellow coloured precipitate was filtered and washed with ethanol, CHCl_3 and diethyl ether, respectively. Then dried in air. Yield: 0.59 g (42%). Anal. Calc. for $\text{LaC}_{21}\text{H}_{20}\text{N}_6\text{O}_{12} \cdot \text{H}_2\text{O}$: C, 35.80; H, 3.10; N, 11.81. Found: C, 35.76;

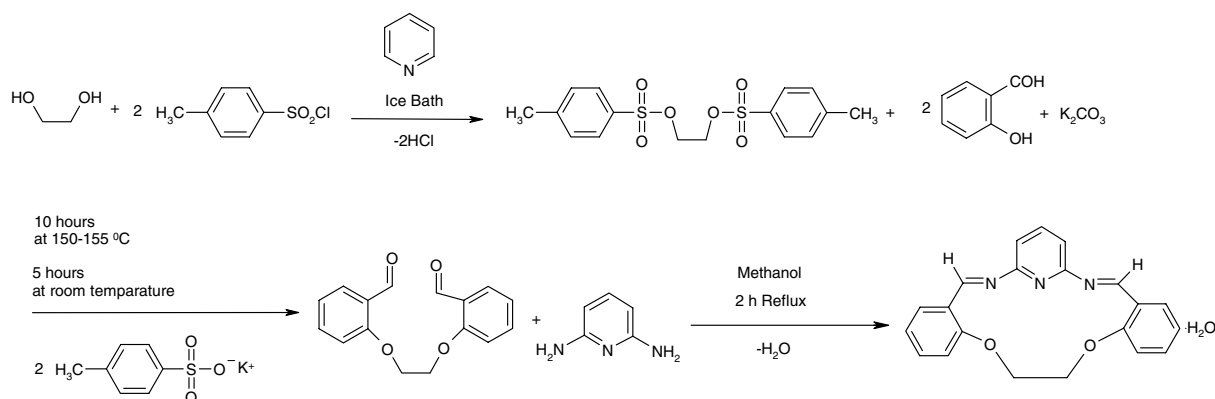
H, 2.98; N, 11.93%. ^1H NMR (DMSO- d_6 , δ ppm): $\delta = 3.41$ (H_2O), $\delta = 4.60$ (OCH_2), $\delta = 6.99$ – 7.96 (Ar-H), $\delta = 10.31$ ($\text{HC}=\text{N}$). Selected IR data (KBr, ν cm^{-1}): 3380 $\nu(\text{H}_2\text{O})$, 1657 $\nu(\text{C}=\text{N})$, 1598 ($\text{C}=\text{N}(\text{py})$). $A_M = 30 \Omega^{-1} \text{mol}^{-1} \text{cm}^2$. UV–Vis (λ_{max} , nm) (DMF–DMSO (1:1)): 274, 321, 378. Mass spectra: 609 $[\text{La}(\text{L})(\text{NO}_3)_2 + 3\text{H}^+]^+$.

3. Results and discussion

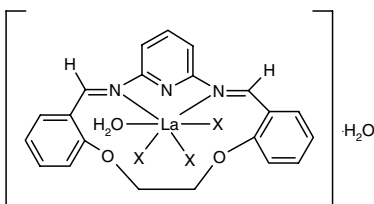
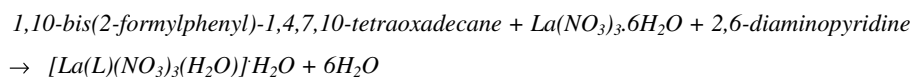
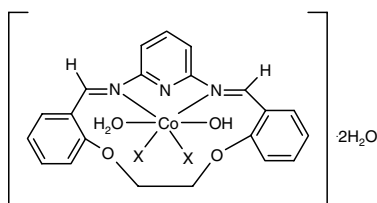
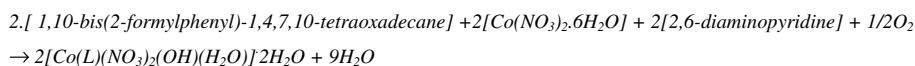
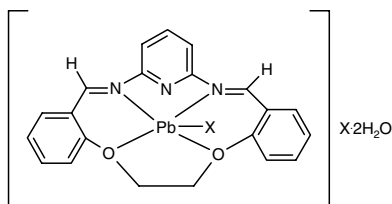
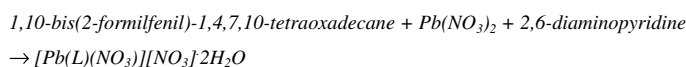
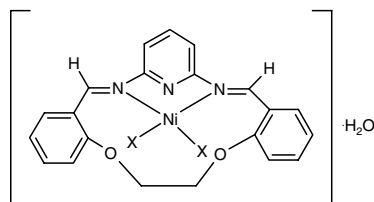
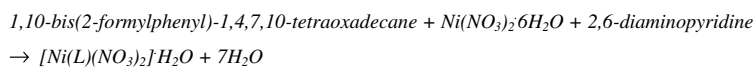
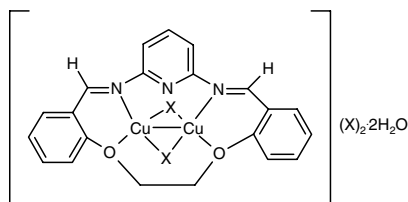
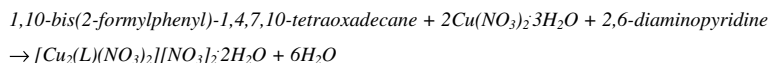
The ligand and complexes have been synthesized (Schemes 1 and 2) and characterized by elemental analysis, IR, ^1H and ^{13}C NMR data, electronic spectra, magnetic susceptibility measurements, molar conductivity, mass spectra, thermogravimetric analyses and cyclic voltammeter. The corresponding data for the ligand and complexes are presented in Tables 1–4.

3.1. IR spectra

The IR spectrum of the ligand (L) shows a $\nu(\text{C}=\text{N})$ peak at 1685 cm^{-1} , and the absence of a $\nu(\text{C}=\text{O})$ peak at around 1700 cm^{-1} is indicative of Schiff's base condensation. The IR spectra of all complexes show $\nu(\text{C}=\text{N})$ bands at 1615 – 1657 cm^{-1} [2,21] and it is found that the $\nu(\text{C}=\text{N})$ bands in the complexes are shifted by about 70 – 29 cm^{-1} to lower energy regions compared to that in the free ligand (L). This phenomenon appears to be due to the coordination of azomethine nitrogen to the metal ion [22–24]. Also, a weak $\nu(\text{H}_2\text{O})$ band of free ligand at about 3380 cm^{-1} is observed because of hydrated water molecule. The IR spectra of the complexes are characterized by the appearance of a broad band in the region at 3328 – 3383 cm^{-1} due to OH groups [25–27]. 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 bidentate nitrate groups. An intense band at 1384 cm^{-1} is attributed to the presence of the ionic nitrate [28–30]. The IR spectra of the complexes clearly demonstrated that the COC and CCO stretching vibrations are altered compared to ligands 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 the complex formation [30,31].



Scheme 1. Synthesis of the ligand.



Scheme 2. Synthesis of the complexes (X: NO₃).

3.2. NMR spectra

¹H NMR and ¹³C NMR of the ligand and ¹H NMR of the complexes in DMSO-*d*₆ solution show that they are

NMR active. However, ¹³C NMR of the complexes could not be taken because of the low solubility degree of the complexes in common solvents. The ¹H NMR spectrum of the free ligand showed a singlet at 10.4 ppm due to the

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

Compound	(Calc.) found					A_M ($\Omega^{-1} \text{ cm}^2$ mol^{-1})	Formula weight	MS/ EI	Assignment	
	%C	%H	%N							
$\text{C}_{21}\text{H}_{17}\text{N}_3\text{O}_2 \cdot \text{H}_2\text{O}$	(69.80)	70.07	(5.26)	5.34	(11.63)	12.06	–	361	339	$[[\text{L}]-4\text{H}]^+$
$[\text{Cu}_2(\text{L})(\text{NO}_3)_2][\text{NO}_3]_2 \cdot 2\text{H}_2\text{O}$	(33.42)	33.24	(2.79)	2.58	(13.00)	13.25	146	754	719	$[[\text{Cu}_2(\text{L})(\text{NO}_3)_2][\text{NO}_3]_2+\text{H}]^+$
$[\text{Ni}(\text{L})(\text{NO}_3)_2] \cdot \text{H}_2\text{O}$	(46.41)	46.52	(3.50)	3.62	(12.89)	12.93	39	543	543	$[\text{Ni}(\text{L})(\text{NO}_3)_2 \cdot \text{H}_2\text{O}]^+$
$[\text{Pb}(\text{L})(\text{NO}_3)_2][\text{NO}_3] \cdot 2\text{H}_2\text{O}$	(35.49)	35.54	(2.96)	3.14	(9.86)	9.95	81	728	707	$[[\text{Pb}(\text{L})(\text{NO}_3)_2][\text{NO}_3] \cdot 2\text{H}_2\text{O}-3\text{H}]^+$
$[\text{Co}(\text{L})(\text{NO}_3)_2(\text{OH})(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$	(42.34)	42.21	(4.19)	4.02	(11.32)	11.25	26	623	599	$[[\text{Co}(\text{L})(\text{NO}_3)_2(\text{OH})(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}+\text{H}]^+$
$[\text{La}(\text{L})(\text{NO}_3)_3(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$	(35.80)	35.76	(3.10)	2.98	(11.81)	11.93	30	704	609	$[\text{La}(\text{L})(\text{NO}_3)_3+3\text{H}]^+$

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

Compound	$\nu(\text{C}=\text{N})$	$\nu(\text{C}=\text{N})$ pyridine	$\nu(\text{H}_2\text{O})$	Ionic $\nu(\text{NO}_3^-)$
$\text{C}_{23}\text{H}_{21}\text{N}_3\text{O}_3 \cdot \text{H}_2\text{O}$	1685	1598	3381	–
$[\text{Cu}_2(\text{L})(\text{NO}_3)_2][\text{NO}_3]_2 \cdot 2\text{H}_2\text{O}$	1615	1598	3328	1384
$[\text{Ni}(\text{L})(\text{NO}_3)_2] \cdot \text{H}_2\text{O}$	1658	1598	3383	–
$[\text{Pb}(\text{L})(\text{NO}_3)_2][\text{NO}_3] \cdot 2\text{H}_2\text{O}$	1651	1598	3383	1384
$[\text{Co}(\text{L})(\text{NO}_3)_2(\text{OH})(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$	1657	1598	3381	–
$[\text{La}(\text{L})(\text{NO}_3)_3(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$	1657	1598	3380	–

imine protons, multiplet in the range 7.1–8.0 ppm due to the aromatic protons, and H_2O proton at 3.4 ppm. ^{13}C NMR spectrum of the free ligand showed at 161.3 ppm due to the imine carbon, at 65.6 ppm due to OCH_2 carbon and at 189.8 ppm due to the pyridine carbon (Fig. 1). The

^1H NMR spectra of the complexes exhibited almost the same values as that of the ligand. Although we expected a shift on the position of $\text{CH}=\text{N}$ signal for the NMR spectra of the complexes, a significant shift could not be observed. But the $\text{CH}=\text{N}$ signal is observed in low intensity compared to that of the ligand.

3.3. Electronic absorption spectroscopy

The electronic spectrum of the ligand (L) in DMSO–DMF (1:1) shows absorption bands at 276, 321 and 376 nm. The bands are indicative of benzene and other chromophore moieties present in the ligand. The absorption bands of the complexes are shifted to longer wave numbers compared to that of the ligand as expected [31,32]. No d–d transitions for the complexes were

Table 3
Voltammetric data for the complexes in DMSO-TEAP

Complexes	$\text{M}^{3+}/\text{M}^{2+}$ $E_{1/2}^a$ (V)	ΔE_p^b (V)	M^{2+}/M^+ $E_{1/2}^a$ (V)	ΔE_p^b (V)	L/L^- $E_{1/2}^a$ (V)
$[\text{Co}(\text{L})(\text{NO}_3)_2(\text{OH})(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$	–0.612	0.128			
$[\text{Ni}(\text{L})(\text{NO}_3)_2] \cdot \text{H}_2\text{O}$			–1.38	0.120	–0.749
$[\text{Cu}_2(\text{L})(\text{NO}_3)_2][\text{NO}_3]_2 \cdot 2\text{H}_2\text{O}$			0.155	0.250	–0.480

^a Anodic peak potential for oxidation and cathodic peak potential for reduction in case of irreversible processes.

^b $\Delta E_p = E_{pc} - E_{pa}$ at 0.100 V s^{-1} scan rate.

Table 4
TGA data of the complexes

Compounds	First step, °C	Second step, °C	Third step, °C
	Weight loss % Calculated (found) Decomposition group	Weight loss % Calculated (found) Decomposition group	Weight loss % Calculated (found) Decomposition group
$[\text{CoL}(\text{NO}_3)_2(\text{OH})(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$	41.0–329.0 12.08 (12.00) 3 H_2O and OH		
$[\text{NiL}(\text{NO}_3)_2] \cdot \text{H}_2\text{O}$	42.0–160.0 3.31 (2.92) H_2O		
$[\text{Cu}_2\text{L}(\text{NO}_3)_2][\text{NO}_3]_2 \cdot 2\text{H}_2\text{O}$	33.3–128.6 4.77 (4.55) $2\text{H}_2\text{O}$		
$[\text{PbL}(\text{NO}_3)_2][\text{NO}_3] \cdot 2\text{H}_2\text{O}$	129.0–315.0 5.06 (5.71) $2\text{H}_2\text{O}$	315.0–420.0 17.44 (18.09) 2NO_3	
$[\text{LaL}(\text{NO}_3)_3(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$	46.0–146.0 2.56 (2.92) H_2O	146.0–338.0 20.17 (20.58) H_2O and 2NO_3	338.0–445.0 8.81 (10.10) NO_3

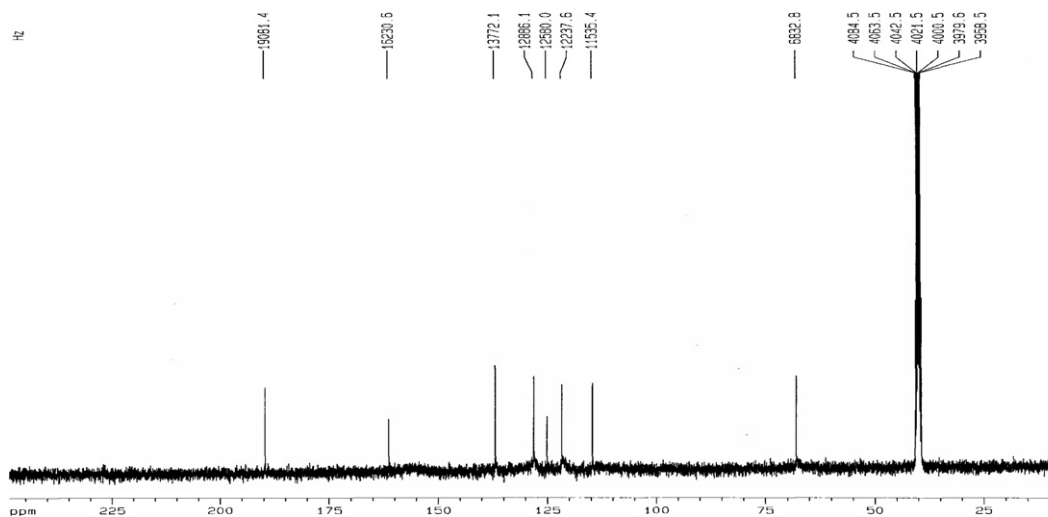
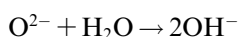
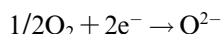
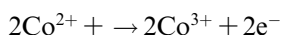


Fig. 1. ^{13}C NMR spectra of 1,3,5-triaza-2,4,7,8:13,14-tribenzo-9,12-dioxacyclopentadeca-1,5-diene (L).

observed probably due to having low solubility of complexes. A moderately intensive band observed in the range of 320–380 nm is due to $\pi\text{--}\pi^*$ transition, and the strong band observed in the range of 270–280 nm is due to $n\text{--}\pi^*$ [33] for these complexes.

3.4. Magnetic and conductivity studies

The observed room-temperature magnetic moment values for the binuclear Cu(II) and the other mononuclear complexes are found to be diamagnetic. The diamagnetic behaviour of the binuclear complex may be explained by a very strong anti-ferromagnetic interaction in the Cu–Cu pair. Co(II) complex was oxidized to Co(III) complex by O_2 in air [34].



The conductivity data in DMF–DMSO are reported in the range of 2:1 and 1:1 electrolytes in these solvents. The complexes $[\text{Cu}_2(\text{L})(\text{NO}_3)_2][\text{NO}_3]_2 \cdot 2\text{H}_2\text{O}$ and $[\text{Pb}(\text{L})(\text{NO}_3)][\text{NO}_3] \cdot 2\text{H}_2\text{O}$ have values of $\Lambda_{\text{M}} = 146$ and $81 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$, indicating 2:1 and 1:1 electrolytes, respectively. The other complexes are nonelectrolytes [35]. It is seen that the complex formation reaction between ligand and relatively large Pb(II) and La(III) metal ions results in the $[\text{Pb}(\text{L})(\text{NO}_3)][\text{NO}_3] \cdot 2\text{H}_2\text{O}$ and $[\text{La}(\text{L})(\text{NO}_3)_3(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$ complexes. The binding mode of the ligand for the $[\text{Pb}(\text{L})(\text{NO}_3)][\text{NO}_3] \cdot 2\text{H}_2\text{O}$ complex is different than that of the $[\text{La}(\text{L})(\text{NO}_3)_3(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$ complexes. In the first case, the ligand behaves as a tetradentate ligand with the lone electron pairs of azomethine nitrogen atoms and the lone electron pairs of two oxygen atoms in ether groups. In the second case, the ligand behaves as a bidentate ligand with the lone electron pairs of azomethine nitro-

gen atoms. The long distance binding process can be favored for too large Pb(II) metal ion but not La(III) metal ion due to having smaller ion size than Pb(II) metal ion. So its coordination is satisfied with three NO_3^- and one H_2O in the second case. A similar binding mode was observed in the literature for Pb(II) metal ions [30]. The absorptions of the coordinated nitrate ions, at ca. 1460–1452 (ν_5), 1300 (ν_1) and 1040 (ν_2) cm^{-1} , suggest the presence of the coordinated nitrate groups while an intense band at ca. 1384 cm^{-1} can be attributed to the ionic nitrate counterions [29,30]. Also, the conductivity measurements of the lead(II) complex in DMF–DMSO resulted in Λ_{M} value of $89 \Omega^{-1} \text{mol}^{-1} \text{cm}^2$, which indicate that it is of the 1:1 electrolyte type. These results clearly verify the different binding mode of ligand in the case of the Pb(II) metal ion. As expected, in the case of the relatively small (Ni(II) and Co(III)) metal 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 NO_3^- , H_2O , and OH^- ligands. The conductivity measurements showed that these complexes are nonelectrolyte. On the other hand, the diamagnetic behaviour of the binuclear complex can be explained by a very strong anti-ferromagnetic interaction in the Cu–Cu pair [36]. Also, the structure was supported with the other spectroscopic data. Furthermore, the controlled potential coulometric (CPC) study indicated that the number of electrons transferred for the electrochemical reaction of the complex was two for the reduction process based on the copper metal as seen from the electrochemical study. The structure of the binuclear complex has been presented in Scheme 2. Some Co(II), Ni(II), Ag(II), Zn(II) or Pb(II) complexes prepared with similar ligands have been known from the literature [28]. 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

CH₃CN and the crystals were unsuitable for single-crystal X-ray structure determination. Suggested structure for Cu(II) complex is bipyramidal, those for La(III) and Co(III) complexes are octahedral, that for Pb(II) complex is square pyramidal, and that for Ni(II) complex is square planar.

3.5. Electrochemistry

The electrochemical behaviours of the cobalt(III), nickel(II), and copper(II) complexes were studied using cyclic voltammetric (CV) technique in DMSO solution containing 0.1 M TEAP. All CVs and their data are depicted in Fig. 2 and Table 3. Fig. 2a shows the CV of the cobalt complex, which displayed irreversible one-electron reduction in DMSO containing Ag/AgCl electrode system with a peak separation value ($\Delta E_p = 0.230$ V). The reduction process could be referred to the metal-based Co(III)/Co(II) couples in the complex. The cathodic peak potential of complex is displayed at $E_{pc} = -0.720$ V versus Ag/AgCl.

Fig. 2b shows the CV of the copper complex which exhibits one irreversible reduction peak as a result of a large peak separation value ($\Delta E_p = 0.280$ V) at 0.100 V s^{-1} scan rate. This reduction wave is assigned to the Cu(II)/Cu(I) species. The cathodic electrode potentials are displayed at $E_{pc} = -0.010$ V. The controlled potential coulometric (CPC) study indicated that the number of electrons transferred for the electrochemical reaction of the complex was two for the reduction process based on the copper metal [36–41].

Fig. 2c shows the CV of the nickel complex, which exhibits a quasi-reversible one-electron reduction in DMSO containing Ag/AgCl electrode system at 0.100 V s^{-1} scan rate with a corresponding anodic wave. This reduction wave is assigned to the Ni(II)/Ni(I) couples. The quasi-reversibility of the reduction process is confirmed with the corresponding peak separation value between the cathodic peak potential and the anodic peak potential ($\Delta E_p = 0.125$ V) and almost the unity of the ratio of the anodic peak current-to-cathodic peak current. The half-wave potential of the nickel complex was located at $E_{1/2} = -1.38$ V versus Ag/AgCl.

3.6. TGA studies

The thermal stability of the complexes was investigated using TGA. The thermogravimetric analysis (TGA) (Table 4) and curves were obtained at a heating rate of $10 \text{ }^\circ\text{C/min}$ in a nitrogen atmosphere over a temperature range of $20\text{--}900 \text{ }^\circ\text{C}$.

The Co(III) complexes were stable up to $41.0 \text{ }^\circ\text{C}$ and their decomposition started at this temperature. In the decomposition process of the Co(III) complex, the mass losses corresponded to $3\text{H}_2\text{O}$ and OH leaving in the first stage of the decomposition. The decomposition of the Co(III) complex is irreversible.

The Ni(II) complexes were stable up to $42.0 \text{ }^\circ\text{C}$ and their decomposition started at this temperature. In the decom-

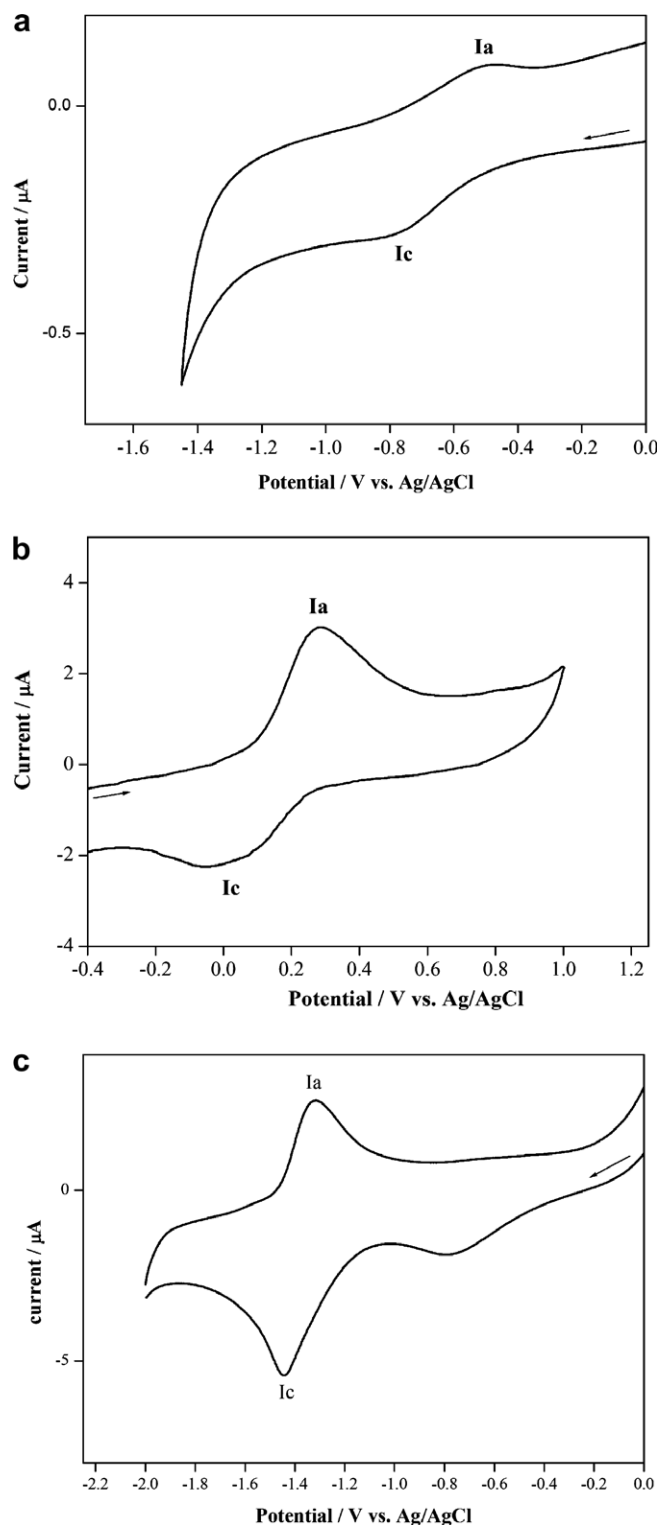


Fig. 2. Cyclic voltammograms of complexes, (a) cobalt(III), (b) nickel(II) and (c) copper(II) complexes in DMSO/0.1 M TEAP at 0.100 V s^{-1} scan rate.

position process of the Ni(II) complex, the mass losses corresponded to H_2O leaving in the first stage of the decomposition. The decomposition of the Ni(II) complex is irreversible.

plex, 2.92% weight loss was observed at 146.0 °C. In the TGA curve of the Cu(II) complex, 4.55% weight loss was observed at 128.6 °C. This shows that the complex contains 1, 2, 1 and 2 mol of water of crystallization per complex molecule, respectively. The IR spectra of the complexes are characterized by the appearance of a broad band in the region 3328–3383 cm^{-1} due to the $\nu(\text{O-H})$ frequency of water of crystallization. This water content was also identified by the elemental analyses. This decomposition process of Ni(II), Pb(II), La(III) and Cu(II) complexes was also confirmed by TGA data. As it can be seen in Table 2, the most stable complex is Pb(II) complex.

In the TGA curves of the Co(III) complex, 12.00% weight loss was observed at 329.0 °C. This shows that the complex contains 2 mol of water of crystallization per com-

plex molecule, in addition to 1 mol of water of coordination and hydroxyl ligands.

In the TGA curve of the La(III) complex, 2.92% weight loss was observed at 338.0 °C. This shows that the complex contains 1 mol of water of crystallization per complex molecule, in addition, 1 mol of water of coordination and 2 mol nitrate ligands (20.58%). In addition, in the TGA curve of the La(III) complex, 10.10% weight loss was observed at 445.0 °C. This shows that the complex contains 1 mol of nitrate ligands.

The weight losses for Cu(II), Ni(II), Co(III), Pb(II) and La(III) complexes were found to be approximately the same, when expressed as the percentages calculated stoichiometrically from their chemical formulas given in Table 4.

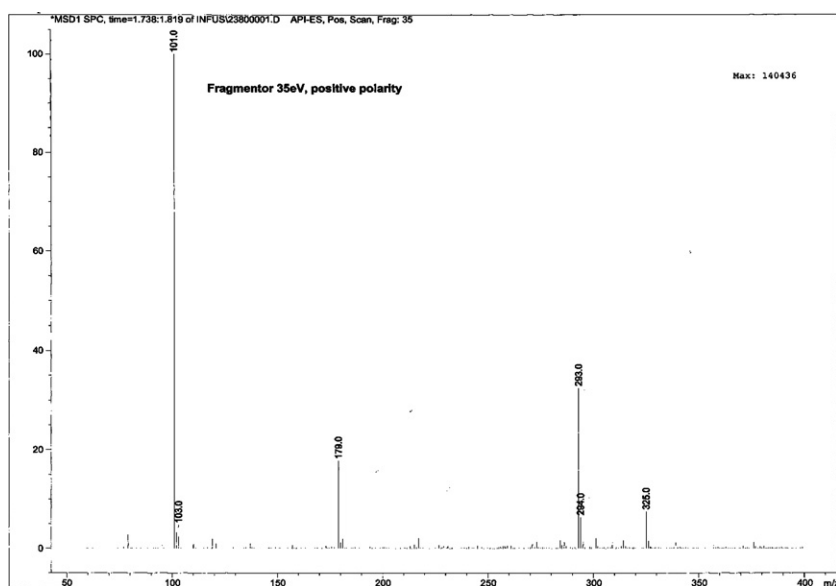


Fig. 4. The mass spectra of the ligand.

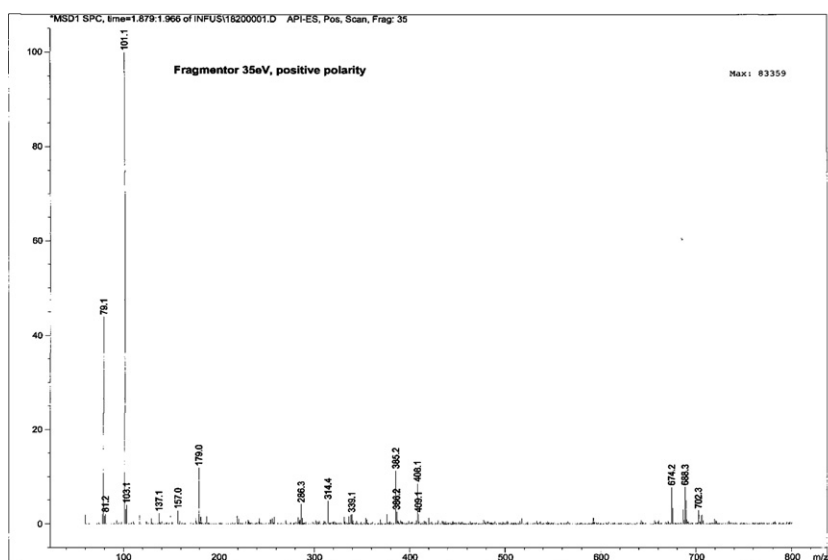


Fig. 5. The mass spectra of $[\text{Cu}_2(\text{L})(\text{NO}_3)_2][\text{NO}_3]_2 \cdot 2\text{H}_2\text{O}$ (see Fig. 1).

Single crystals of the complexes could not be isolated from any solutions, thus no definitive structure could be described. However, the analytical, spectroscopic and magnetic data enable us to propose the possible structures.

3.7. Mass spectra

The fragment of the mass spectrum of the ligand(L): 101 ($[\text{C}_7\text{NH}_3]^+$, 100%), 103 ($[\text{C}_7\text{NH}_5]^+$, 4.8%), 179 ($[\text{C}_{12}\text{N}_2\text{H}_7]^+$, 17.8%), 293 ($[\text{L}-(\text{OCH}_2\text{CH}_2)-6\text{H}]^+$, 32.4%), 325 ($[\text{L}-(\text{O})-2\text{H}]^+$, 7.5%), 339 ($[\text{L}-4\text{H}]^+$, 1.2%).

The fragment of the mass spectrum of $[\text{Cu}_2(\text{L})(\text{NO}_3)_2][\text{NO}_3]_2 \cdot 2\text{H}_2\text{O}$: 79 ($[\text{C}_6\text{H}_6+\text{H}]^+$, 44%), 101 ($[\text{C}_7\text{NH}_3]^+$, 100%), 103 ($[\text{C}_7\text{NH}_5]^+$, 4.0%), 179 ($[\text{C}_{12}\text{N}_2\text{H}_7]^+$, 11.9%), 286 ($[\text{L}-(\text{OCH}_2\text{CH}_2\text{O})+3\text{H}]^+$, 4.2%), 314 ($[\text{L}-(\text{OCH}_2)+\text{H}]^+$, 4.9%), 339 ($[\text{L}-4\text{H}]^+$, 2.1%), 408 ($[\text{Cu}(\text{L})+\text{H}]^+$, 8.6%), 409 ($[\text{Cu}(\text{L})+2\text{H}]^+$, 2.1%), 674 ($[[\text{Cu}_2(\text{L})(\text{NO}_3)_2](\text{NO}_3) \cdot \text{H}_2\text{O}]^+$, 7.8%), 688 ($[[\text{Cu}_2(\text{L})(\text{NO}_3)_2](\text{NO}_3)_2-(\text{CH}_2\text{CH}_2)-2\text{H}]^+$, 7.8%), 702 ($[[\text{Cu}_2(\text{L})(\text{NO}_3)_2](\text{NO}_3)_2-(\text{CH}_2)-2\text{H}]^+$, 2.9%), 719 ($[[\text{Cu}_2(\text{L})(\text{NO}_3)_2][\text{NO}_3]_2+\text{H}]^+$, 1.1%).

The fragment of the mass spectrum of $[\text{Ni}(\text{L})(\text{NO}_3)_2] \cdot \text{H}_2\text{O}$: 79 ($[\text{C}_6\text{H}_6+\text{H}]^+$, 4.2%), 101 ($[\text{C}_7\text{NH}_3]^+$, 100%), 103 ($[\text{C}_7\text{NH}_5]^+$, 4.2%), 179 ($[\text{C}_{12}\text{N}_2\text{H}_7]^+$, 17.6%), 286 ($[\text{L}-(\text{OCH}_2\text{CH}_2\text{O})+3\text{H}]^+$, 5.6%), 293 ($[\text{L}-(\text{CH}_2\text{CH}_2\text{O})-6\text{H}]^+$, 15.7%), 310 ($[\text{L}-(\text{OCH}_2)-3\text{H}]^+$, 0.9%), 314 ($[\text{L}-(\text{OCH}_2)+\text{H}]^+$, 3.1%), 325 ($[\text{L}-(\text{O})-2\text{H}]^+$, 5.4%), 339 ($[\text{L}-4\text{H}]^+$, 26.1%), 340 ($[\text{L}-3\text{H}]^+$, 5.0%), 371 ($[\text{Ni}(\text{L})-(\text{CH}_2\text{CH}_2)-2\text{H}]^+$, 3.4%), 422 ($[\text{Ni}(\text{L})(\text{NO}_3)-(\text{OCH}_2\text{CH}_2)+2\text{H}]^+$, 3.1%), 462 ($[\text{Ni}(\text{L})(\text{NO}_3)-\text{H}]^+$, 1.2%), 543 ($[\text{Ni}(\text{L})(\text{NO}_3)_2 \cdot \text{H}_2\text{O}]^+$, 0.8%).

The fragment of the mass spectrum of $[\text{Pb}(\text{L})(\text{NO}_3)]_2[\text{NO}_3]_2 \cdot 2\text{H}_2\text{O}$: 79 ($[\text{C}_6\text{H}_6+\text{H}]^+$, 4.5%), 101 ($[\text{C}_7\text{NH}_3]^+$, 100%), 103 ($[\text{C}_7\text{NH}_5]^+$, 4.5%), 179 ($[\text{C}_{12}\text{N}_2\text{H}_7]^+$, 19.0%), 293 ($[\text{L}-(\text{CH}_2\text{CH}_2\text{O})-6\text{H}]^+$, 6.9%), 314 ($[\text{L}-(\text{OCH}_2)+\text{H}]^+$, 4.4%), 339 ($[\text{L}-4\text{H}]^+$, 16.2%), 348 ($[\text{L}+5\text{H}]^+$, 3.9%), 707 ($[[\text{Pb}(\text{L})(\text{NO}_3)]_2[\text{NO}_3]_2 \cdot 2\text{H}_2\text{O}-3\text{H}]^+$, 1.5%).

The fragment of the mass spectrum of $[\text{Co}(\text{L})(\text{NO}_3)_2(\text{OH})(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$: 101 ($[\text{C}_7\text{NH}_3]^+$, 41.4%), 103 ($[\text{C}_7\text{NH}_5]^+$, 4.5%), 179 ($[\text{C}_{12}\text{N}_2\text{H}_7]^+$, 9.8%), 293 ($[\text{L}-(\text{CH}_2\text{CH}_2\text{O})-4\text{H}]^+$, 40.1%), 309 ($[\text{L}-(\text{OCH}_2)-4\text{H}]^+$, 5.0%), 325 ($[\text{L}-(\text{O})-2\text{H}]^+$, 22.7%), 339 ($[\text{L}-4\text{H}]^+$, 27.5%), 340 ($[\text{L}-3\text{H}]^+$, 100.0%), 375 ($[\text{Co}(\text{L})-(\text{CH}_2\text{CH}_2)+\text{H}]^+$, 13.9%), 376 ($[\text{Co}(\text{L})-(\text{CH}_2\text{CH}_2)+2\text{H}]^+$, 4.0%), 453 ($[\text{Co}(\text{L})(\text{NO}_3)-(\text{CH}_2)+3\text{H}]^+$, 3.7%), 599 ($[[\text{Co}(\text{L})(\text{NO}_3)_2(\text{OH})(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}+2\text{H}]^+$, 1.8%).

The fragment of the mass spectrum of $[\text{La}(\text{L})(\text{NO}_3)_3(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$: 79 ($[\text{C}_6\text{H}_6+\text{H}]^+$, 3.9%), 101 ($[\text{C}_7\text{NH}_3]^+$, 100%), 103 ($[\text{C}_7\text{NH}_5]^+$, 5.0%), 179 ($[\text{C}_{12}\text{N}_2\text{H}_7]^+$, 18.1%), 286 ($[\text{L}-(\text{OCH}_2\text{CH}_2\text{O})+3\text{H}]^+$, 10.3%), 293 ($[\text{L}-(\text{CH}_2\text{CH}_2\text{O})-6\text{H}]^+$, 39.8%), 310 ($[\text{L}-(\text{OCH}_2)-3\text{H}]^+$, 0.5%), 314 ($[\text{L}-(\text{OCH}_2)+\text{H}]^+$, 5.6%), 325 ($[\text{L}-(\text{O})-2\text{H}]^+$, 30.0%), 339 ($[\text{L}-4\text{H}]^+$, 18.5%), 340 ($[\text{L}-3\text{H}]^+$, 4.2%), 363 ($[\text{L} \cdot \text{H}_2\text{O}+\text{H}]^+$, 4.0%), 479 ($[\text{La}(\text{L})-3\text{H}]^+$, 4.3%), 543 ($[\text{La}(\text{L})(\text{NO}_3)-\text{H}]^+$, 4.9%), 582 ($[\text{La}(\text{L})(\text{NO}_3)_2-(\text{CH}_2\text{CH}_2)+4\text{H}]^+$, 1.0%), 609 ($[\text{La}(\text{L})(\text{NO}_3)_2+3\text{H}]^+$, 1.6%), 611 ($[\text{La}(\text{L})(\text{NO}_3)_2+5\text{H}]^+$, 1.6%). The mass spectra of the ligand and

its copper(II) complex, and the fragments observed in the mass spectrum of the copper complex are shown in Figs 3–5.

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