Journal of Molecular Structure 891 (2008) 157–166

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

Synthesis and spectral studies of macrocyclic Cu(II), Ni(II) and Co(II) complexes by template reaction of 1,4-bis(3-aminopropoxy)butane with metal(II) nitrate and salicylaldehyde derivatives

Salih Ilhan [a,*], Hamdi Temel [b]

[a] Department of Chemistry, Faculty of Art and Sciences, Siirt University, Siirt, Turkey
[b] Department of Chemistry, Faculty of Education, Dicle University, Diyarbakir, Turkey

ARTICLE INFO

Article history:
Received 20 September 2007
Received in revised form 11 March 2008
Accepted 12 March 2008
Available online 21 March 2008

Keywords:
Macrocyclic Schiff base
Macrocyclic Schiff base complex
Salicylaldehyde derivatives
1,2-Bis(2-formylphenyl)ethane or
1,3-bis(2-formylphenyl)propane

ABSTRACT

Six new macrocyclic complexes were synthesized by template reaction of salicylaldehyde derivatives with 1,4-bis(3-aminopropoxy)butane and metal(II) nitrate. The metal to ligand ratio of the complexes was found to be 1:1. The Cu(II) complexes are proposed to be square planar and the Ni(II) and Co(II) complexes are proposed to be tetrahedral geometry. Macrocyclic complexes are 1:2 electrolytes as shown by their molar conductivities (Λ_M) in DMF (dimethylformamide) of 10^{-3} M solution. The structure of metal complexes is proposed from elemental analysis, FTIR, UV–vis, magnetic susceptibility measurements, molar conductivity measurements and mass spectra.

1. Introduction

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 [1–3] Macrocyclic ligands containing a heteroatom are important complexing agents for cations, anions and molecules [4,5]. The stability of macrocyclic metal complexes 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]. Synthetic macrocycles are a growing class of compounds with varying chemistry a wide range of different molecular topologies and sets of donor atoms [7–13]. The chemical properties of macrocyclic complexes can be tuned to force metal ions to adopt unusual coordination geometry. Transition metal macrocyclic complexes have received much attention as an active part of metalloenzymes [14] as biomimic model compounds [15] due to their resemblance with natural proteins like hemerythrin and enzymes. Synthesis of these Schiff base complexes is achieved through the template reaction [16–19] or transmetallation reactions [20–23] which are used when the transition metal cations are ineffective as templates. The toxicity of these metals on a biological system is connected with the displacing the essential metal ions in biomolecules, blocking the functional groups and inhibiting or enhancing their enzymatic activities. The synthesis of potential chelating agents for effective sequestering and removing toxic metal ions from the human body is a field of growing interest [24]. In the present work, we have synthesized six macrocyclic Schiff base complexes by template effect by reaction of metal(II) nitrate with 1,4-bis(3-aminopropoxy)butane and salicylaldehyde derivatives. Spectral, magnetic 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. IR spectra were recorded on a PERKIN ELMER SPECTRUM RX1 FTIR spectrophotometer on KBr pellets 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 200–900 nm. Molar conductivity was measured with a WTW LF model 330 conductivity meters, using prepared solution of the complexes in DMF solvent. Magnetic

---

* Corresponding author.
E-mail address: salihilhan@dicle.edu.tr (S. Ilhan).

0022-2860/$ - see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.molstruc.2008.03.016

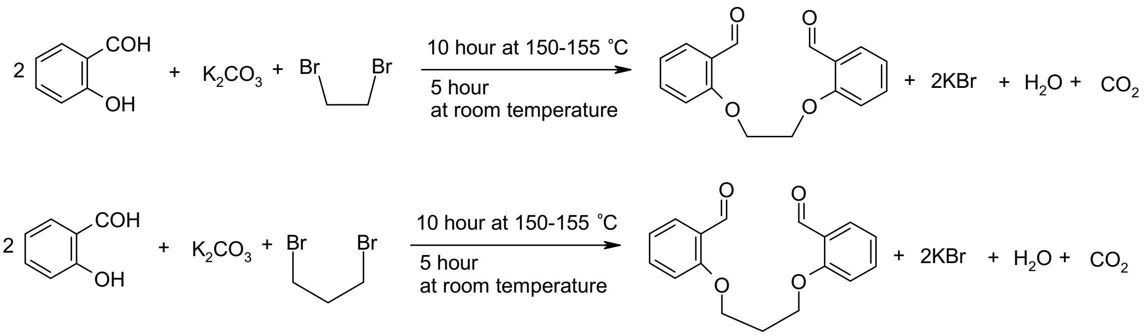

Fig. 1. Synthesis of 1,2-bis(2-formylphenyl)ethane or 1,3-bis(2-formylphenyl)propane.

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

Compound	Yield	(calcd.)			λ_M (Ω^1 cm^2 mol^{-1})	F.W.	MS/EI	Assigment	μ_{eff} (BM)
	Gram (%)	Found %C	%H	%N					
$[NiL^1][NO_3]_2{\cdot}2H_2O$	0.23	(47.49)	(5.78)	(8.52)	167	657	621	$[[NiL^1][NO_3]_2]^+$	2.81
	(17.4)	47.67	6.04	8.29					
$[CoL^1][NO_3]_2{\cdot}3H_2O$	0.29	(46.15)	(5.92)	(8.28)	179	675	559	$[[CoL^1](NO_3)]^+$	3.96
	(21.4)	46.34	6.18	8.32					
$[CuL^1][NO_3]_2{\cdot}2H_2O$	0.31	(47.06)	(5.73)	(8.45)	184	663	627	$[[CuL^1](NO_3)_2+H]^+$	2.02
	(23.3)	47.14	6.02	8.34					
$[NiL^2][NO_3]_2{\cdot}2H_2O$	0.19	(48.36)	(5.97)	(8.36)	191	671	636	$[[NiL^2](NO_3)_2+H]^+$	2.64
	(14.5)	48.44	6.12	8.55					
$[CoL^2][NO_3]_2{\cdot}4H_2O$	0.30	(45.83)	(6.22)	(7.92)	171	709	636	$[[CoL^2](NO_3)_2+H]^+$	3.78
	(21.2)	46.94	6.17	7.85					
$[CuL^2][NO_3]_2{\cdot}3H_2O$	0.39	(47.09)	(6.10)	(8.14)	186	694	579	$[CuL^2](NO_3)+H]^+$	2.17
	(28.0)	46.94	5.96	8.26					

Susceptibilities were determined on a Sherwood Scientific Magnetic Susceptibility Balance (Model MK1) at room temperature (20 °C) using $Hg[Co(SCN)_4]$ as a calibrant; diamagnetic corrections were calculated from Pascal's constants [25]. Electrospray ionization mass spectrometric analysis (ESI-MS) was obtained on the AGILENT 1100 MSD spectrometer.

2.2. Materials

The salicylaldehyde derivatives used in the synthesis were prepared from salicylaldehyde, 1,2-dibromoethane or 1,3-dibromopropane and K_2CO_3 as shown in Fig. 1 and according to the literature method [26,27]. All the chemicals and solvents were of analytical grade and used as received.

To a stirred solution of salicylaldehyde derivatives (2 mmol) and $M(NO_3)_2{\cdot}nH_2O$ (2 mmol) in methanol (60 mL) was added dropwise 1,4-bis(3-aminopropoxy)butane (2 mmol) in methanol (40 mL). After the addition was completed, the stirring was continued for 2 h. Then precipitate was filtered and washed with methanol, then dried in air (M = Cu; $n = 3$ or M = Co, Ni; $n = 6$).

2.2.1. Characterization of $[NiL^1](NO_3)_2{\cdot}2H_2O$

Yield: 0.23 g (17.4%). Anal. Calcd. for $NiC_{26}H_{34}N_4O_{10}{\cdot}2H_2O$:·C, 47.49, H, 5.78, N, 8.52. Found: C, 47.67, H, 6.04, N, 8.29. Selected IR data (KBr, ν cm^{-1}): 3368 ν(H_2O) 3135 ν(Ar—CH), 2967, 2881 ν(Alph.-CH), 1634 ν(C=N), 1452, 1450 ν(Ar—C=C), 1384, 1109, 661 ν(NO_3^-), 1278, 1242 ν(Ar—O), 1146, 1041 ν(R—O), 752 ν(Substituted benzene), 528 ν(Ni—O) 475 ν(Ni—N). $\Lambda_M = 167\ \Omega^{-1}$ cm^2 mol^{-1} (in DMF). UV–vis (λ_{max}, nm) in DMF: 242, 265, 326, 568. Mass spectrum (m/z): 621 $[[NiL^2](NO_3)_2+H]^+$, $\mu_{eff} = 2.81$ B.M.

2.2.2. Characterization of $[CoL^1](NO_3)_2{\cdot}3H_2O$

Yield: 0.29 g (21.4%). Anal. Calcd. for $CoC_{26}H_{34}N_4O_{10}{\cdot}3H_2O$: C, 46.15, H, 5.92, N, 8.28. Found: C, 46.34, H, 6.18, N, 8.32. Selected IR data (KBr, ν cm^{-1}): 3361 ν(H_2O), 3076 ν(Ar—CH), 2933, 2881 ν(Alph.-CH), 1635 ν(C=N), 1491, 1456 ν(Ar—C=C), 1384, 1161, 654 ν(NO_3^-), 1292, 1247 ν(Ar—O), 1162, 1043, ν(R—O), 756 ν(Substituted benzene), 552 ν(Co—O) 511 ν(Co—N). $\Lambda = 179\ \Omega^{-1}$ cm^2 mol^{-1} (in DMF). UV–vis (λ_{max}, nm) in DMF: 238, 272, 307, 651. Mass spectrum (m/z): 559 $[[CoL^1](NO_3)]^+$. $\mu_{eff} = 3.96$ B.M.

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

Compound	ν(H_2O)	ν(C=N)	Ionic ν(NO_3^-)	ν(R—O)	ν(Ar—O)	ν(M—O)	ν(M—N)
$[NiL^1][NO_3]_2{\cdot}2H_2O$	3368 s	1634 m	1384 m	1146, 1041 m	1278, 1242 s	528 w	475 w
$[CoL^1][NO_3]_2{\cdot}3H_2O$	3361 s	1635 m	1384 m	1162, 1043 m	1292, 1247 s	552 w	511 w
$[CuL^1][NO_3]_2{\cdot}2H_2O$	3342 s	1634 m	1384 m	1193, 1091 m	1287, 1243 s	517 w	476 w
$[NiL^2][NO_3]_2{\cdot}2H_2O$	3338 s	1636 m	1384 m	1177, 1052 m	1288, 1246 s	516 w	471 w
$[CoL^2][NO_3]_2{\cdot}4H_2O$	3356 s	1636 m	1384 m	1092, 1038 m	1311, 1239 s	535 w	502 w
$[CuL^2][NO_3]_2{\cdot}3H_2O$	3349 s	1635 m	1384 m	1191, 1046 m	1288, 1246 s	515 w	473 w

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

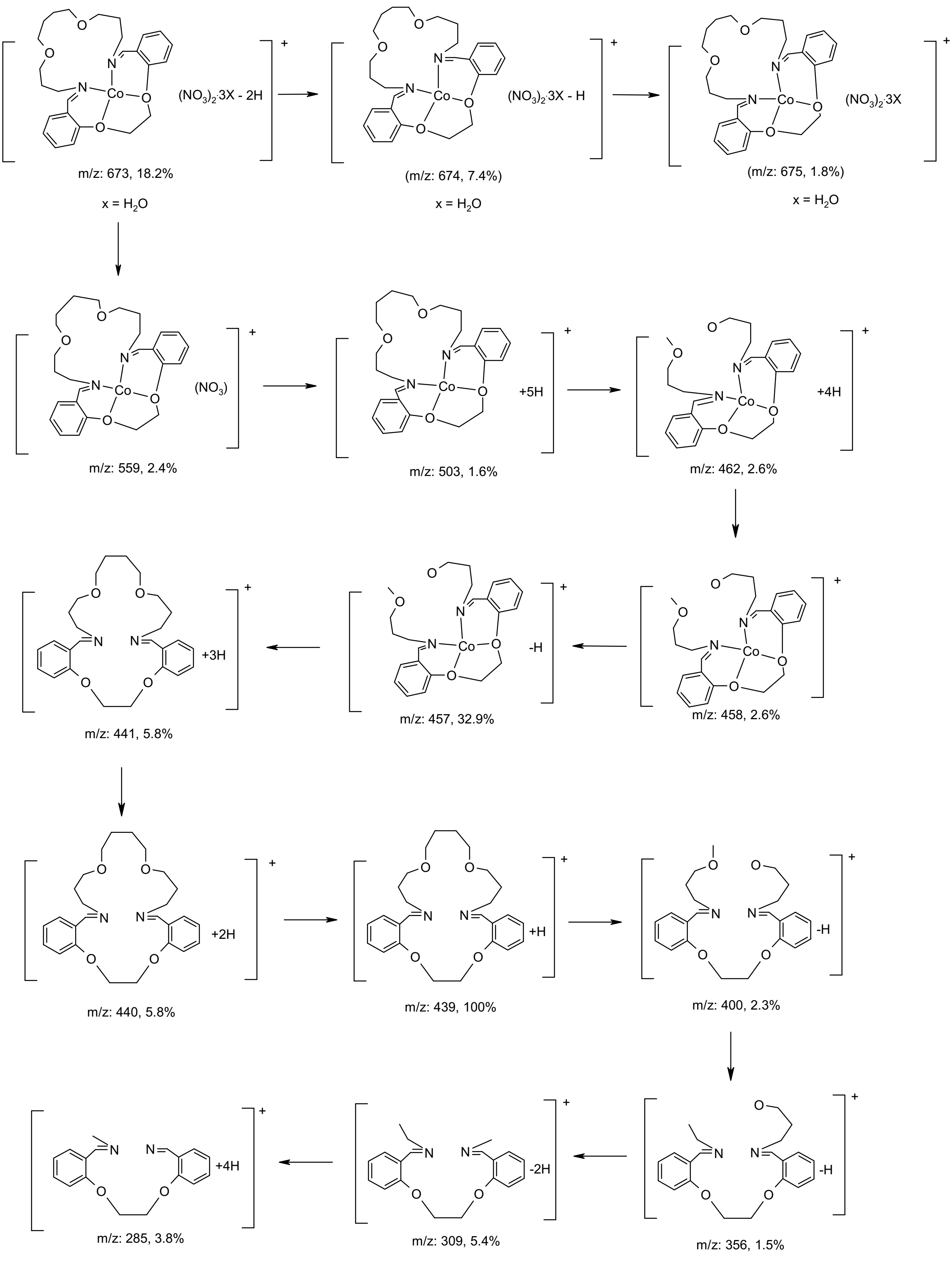

Fig. 2. The fragments observed in the mass spectrum of the $[CoL^1](NO_3)_2{\cdot}3H_2O$.

2.2.3. Characterization of $[CuL^1](NO_3)_2{\cdot}2H_2O$

Yield: 0.31 g (23.3%). Anal. Calcd. for $CuC_{26}H_{34}N_4O_{10}{\cdot}2H_2O$: C, 47.06, H, 5.73, N, 8.45. Found: C, 47.14, H, 6.02, N, 8.34. Selected IR data (KBr, ν cm^{-1}): 3342 ν(H_2O), 3070 ν(Ar—CH), 2937, 2831 ν(Alph.-CH), 1634 ν(C=N), 1490, 1455 ν(Ar—C=C), 1384, 1156, 667 ν(NO_3^-), 1287, 1243 ν(Ar—O), 1193, 1091, ν(R—O), 757 ν(Substituted benzene), 517 ν(Cu—O) 476 ν(Cu—N). $\Lambda = 184\ \Omega^{-1}\ cm^2\ mol^{-1}$ (in DMF). UV–vis (λ_{max}, nm) in DMF: 232, 266, 317, 693. Mass spectrum (*m/z*): 627 $[[CuL^1](NO_3)_2{+}H]^+$. $\mu_{eff} = 2.02$ B.M.

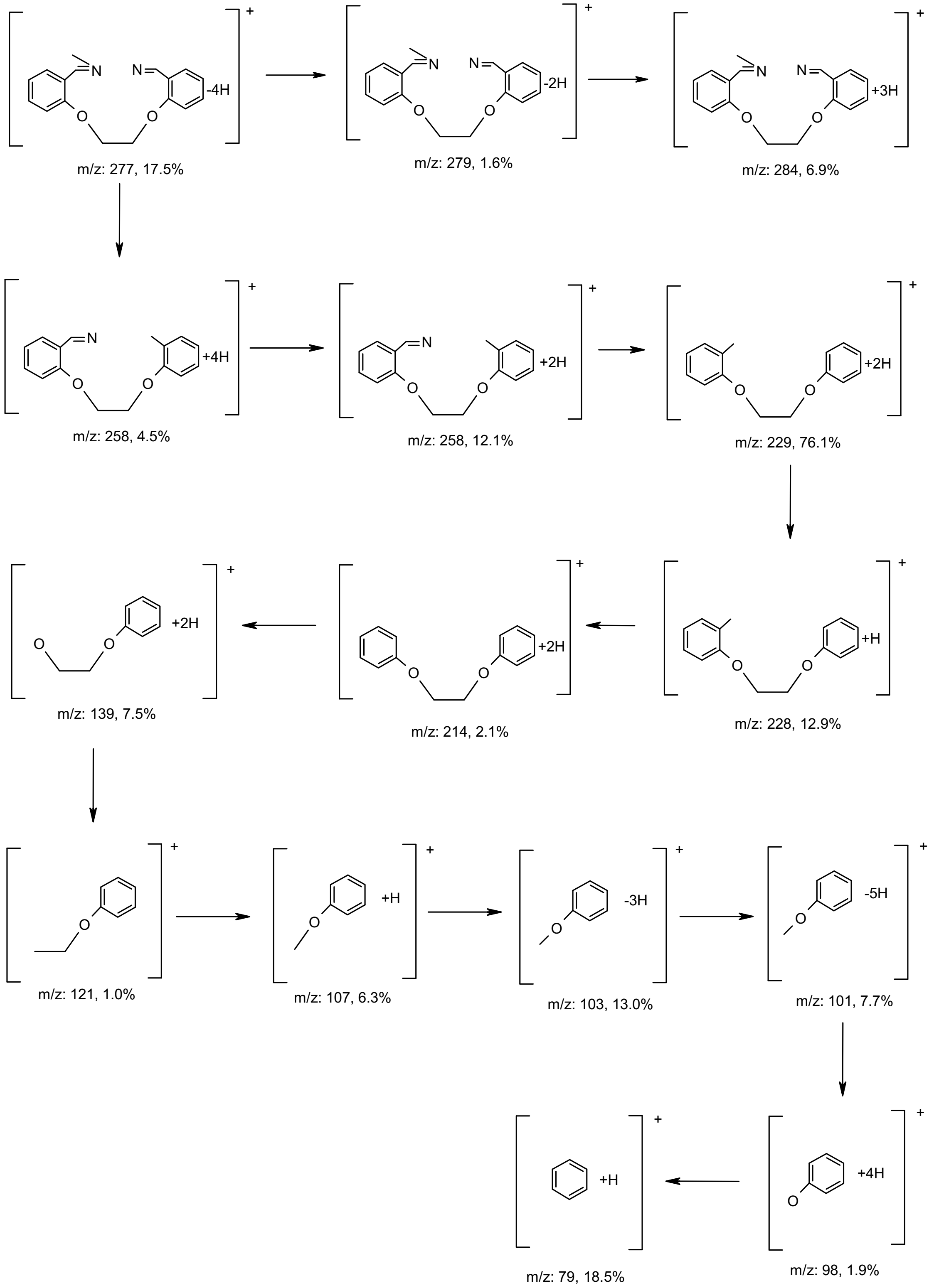

Fig. 2 (*continued*)

2.2.4. Characterization of [NiL^2](NO$_3$)$_2$·2H$_2$O

Yield: 0.19 g (14.5%). Anal. Calcd. for $NiC_{27}H_{36}N_4O_{10}\cdot 2H_2O$: C, 48.36, H, 5.97, N, 8.36. Found: C, 48.44, H, 6.12, N, 8.55. Selected IR data (KBr, ν cm^{-1}): 3338 ν(H$_2$O), 3054 ν(Ar—CH), 2936, 2858 ν(Alph.-CH), 1636 ν(C=N), 1489, 1454 ν(Ar—C=C), 1384, 1161, 626 ν(NO$_3^-$), 1288, 1246 ν(Ar—O), 1177, 1052, ν(R—O), 758 ν(Substituted benzene), 516 ν(Ni—O) 471 ν(Ni—N). $\Lambda = 191\ \Omega^{-1}\ cm^2\ mol^{-1}$ (in DMF). UV–vis (λ_{max}, nm) in DMF: 243, 282, 312, 667. Mass spectrum (*m*/*z*): 636 [[NiL^2](NO$_3$)$_2$+H]$^+$. $\mu_{eff} = 2.64$ B.M.

2.2.5. Characterization of [CoL^2](NO$_3$)$_2$·4H$_2$O

Yield: 0.30 g (21.2%). Anal. Calcd. for $CoC_{27}H_{36}N_4O_{10}\cdot 4H_2O$: C, 45.83, H, 6.22, N, 7.92. Found: C, 45.94, H, 6.17, N, 7.85. Selected IR data (KBr, ν cm^{-1}): 3356 ν(H$_2$O), 3125 ν(Ar—CH), 2923, 2862

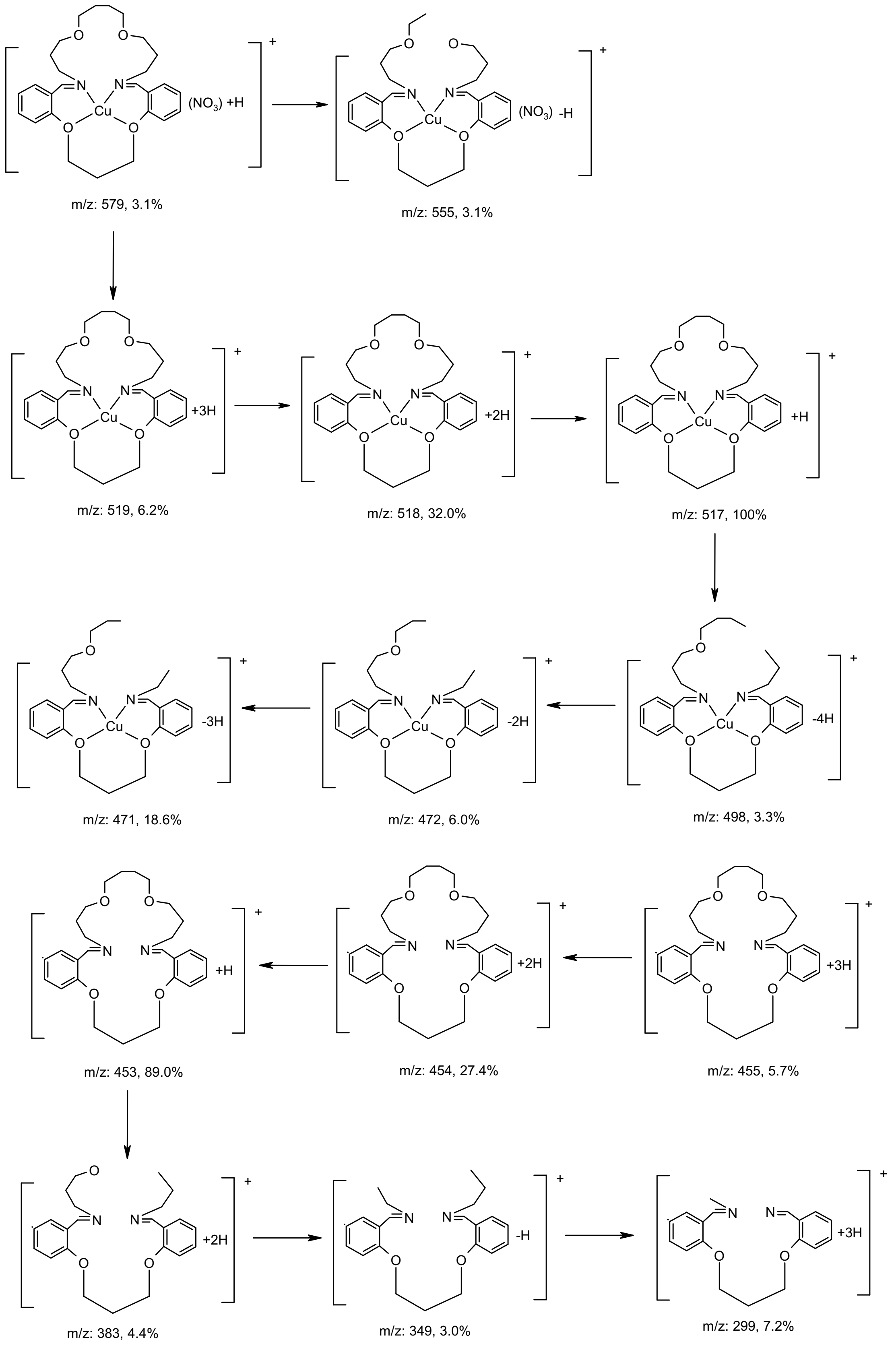

Fig. 3. The fragments observed in the mass spectrum of the $[CuL^2](NO_3)_2{\cdot}3H_2O$.

ν(Alph.-CH), 1634 ν(C=N), 1490, 1455 ν(Ar—C=C), 1384, 1163, 654 ν(NO_3^-), 1311, 1239 ν(Ar—O), 1092, 1038, ν(R—O), 753 ν(Substituted benzene), 535 ν(Co—O) 502 ν(Co—N). $\Lambda = 171\ \Omega^{-1}\ cm^2\ mol^{-1}$ (in DMF). UV–vis (λ_{max}, nm) in DMF: 238, 268, 322, 649. Mass spectrum (*m*/*z*): 636 $[[CoL^2](NO_3)_2{+}H]^+$. $\mu_{eff} = 3.78$ B.M.

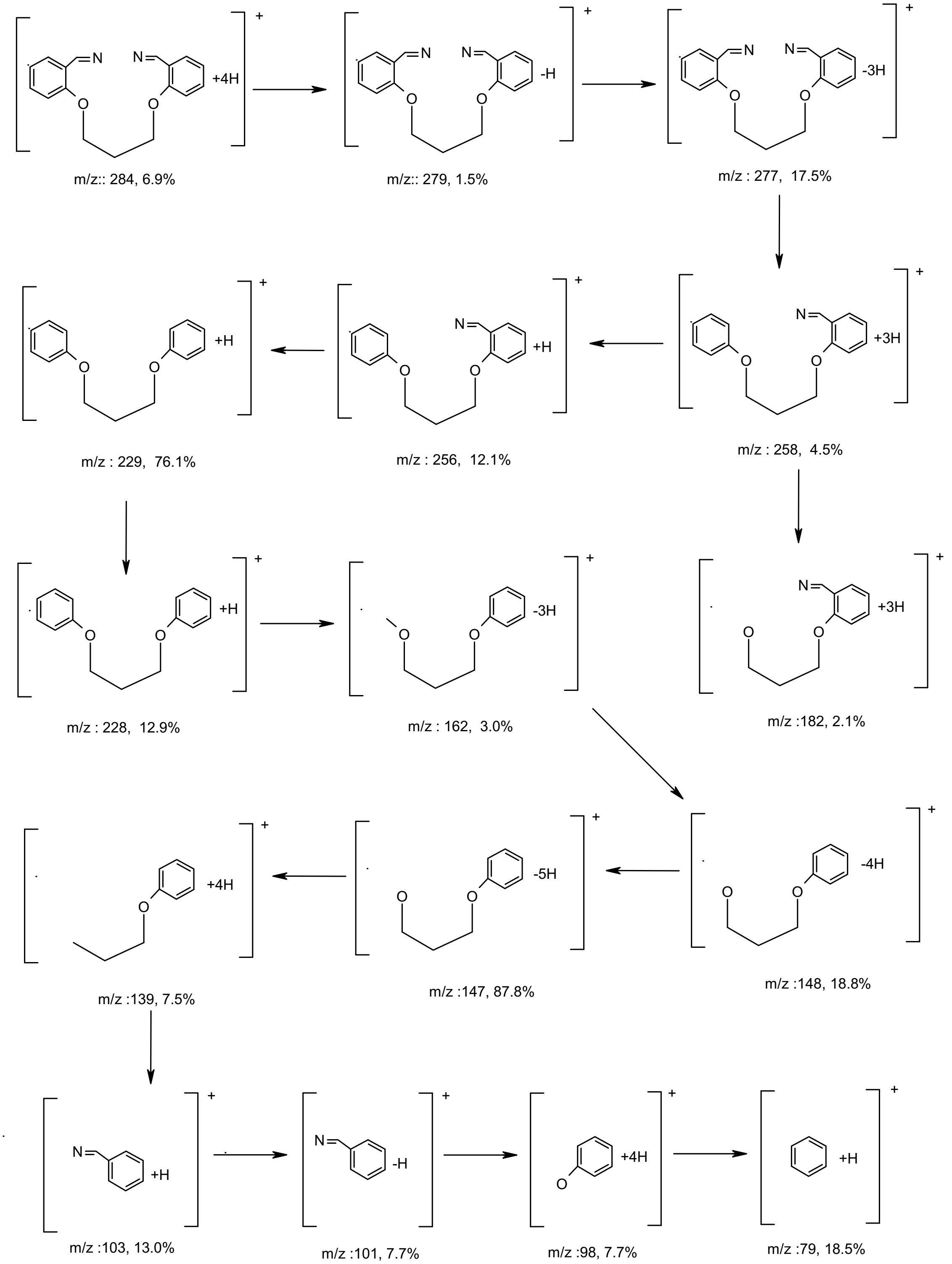

Fig. 3 (*continued*)

2.2.6. Characterization of [CuL^2](NO$_3$)$_2$·3H$_2$O

Yield: 0.39 g (28.0%). Anal. Calcd. for $CuC_{27}H_{36}N_4O_{10}\cdot 3H_2O$: C, 47.09, H, 6.10, N, 8.14. Found: C, 46.94, H, 5.96, N, 8.26. Selected IR data (KBr, ν cm^{-1}): 3449 ν(H$_2$O), 3066 ν(Ar—CH), 2935, 2872 ν(Alph.-CH), 1635 ν(C=N), 1490, 1456 ν(Ar—C=C), 1384, 1107, 664 ν(NO$_3$$^-$), 1288, 1246 ν(Ar—O), 1191, 1046, ν(R—O), 754 ν(Substituted benzene), 515 ν(Cu—O) 473 ν(Cu—N). $\Lambda = 186\ \Omega^{-1}\ cm^2\ mol^{-1}$ (in DMF). UV–vis (λ_{max}, nm) in DMF: 240, 276, 309, 668. Mass spectrum (*m*/*z*): 579 [[CuL^2](NO$_3$)+H]$^+$. $\mu_{eff} = 2.17$ B.M.

3. Results and discussion

In this work, the reaction between 1,2-bis(2-formylphenyl)ethane or 1,3-bis(2-formylphenyl)propane with metal(II) nitrate and 1,4-bis(3-aminopropoxy)butane in methanol, gave [1+1] macrocy-

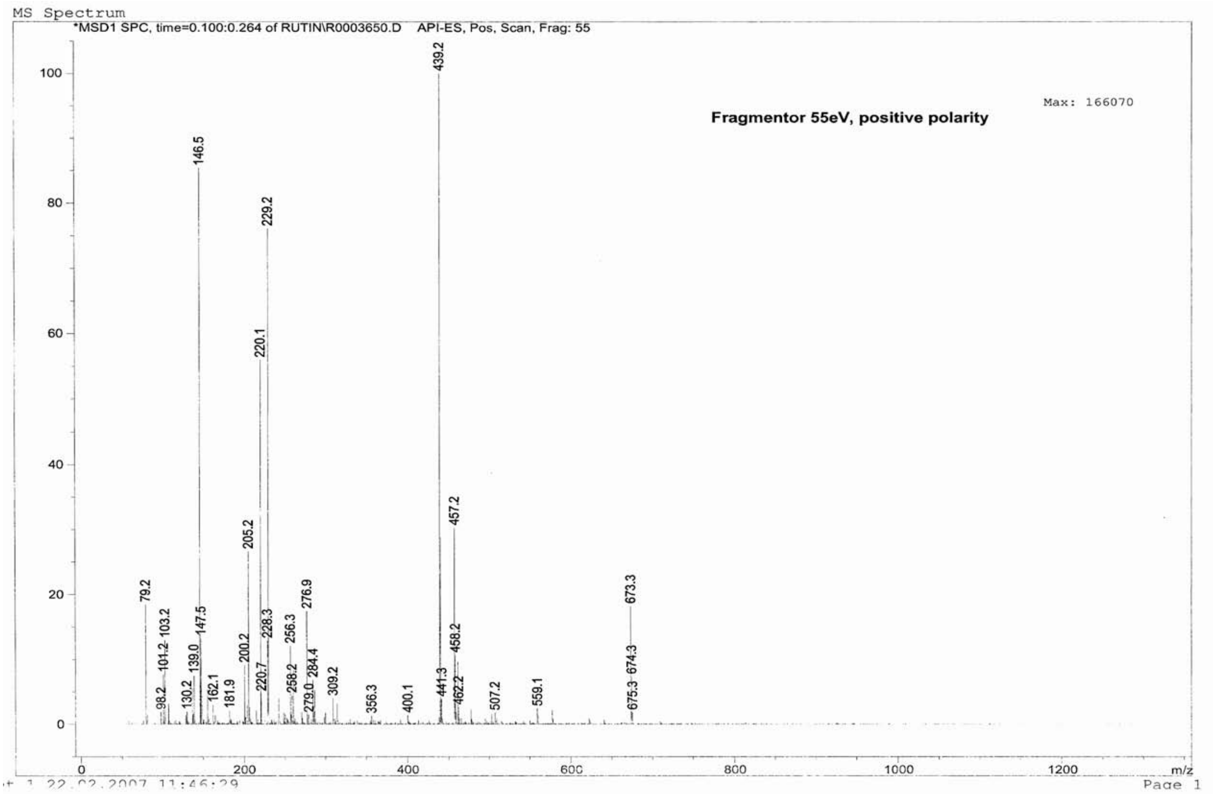

Fig. 4. The mass spectra of the $[CoL^1][NO_3]_2 \cdot 3H_2O$.

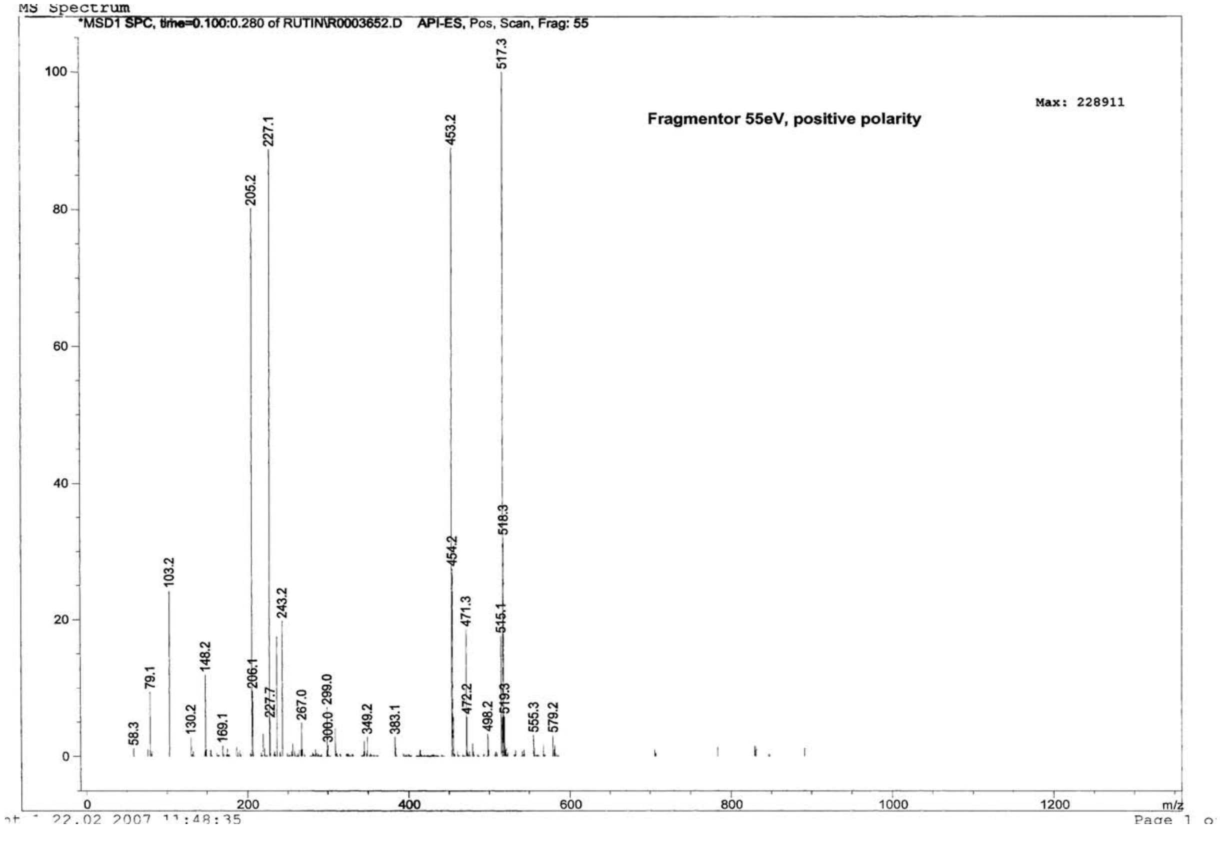

Fig. 5. The mass spectra of the $[CuL^2][NO_3]_2 \cdot 3H_2O$.

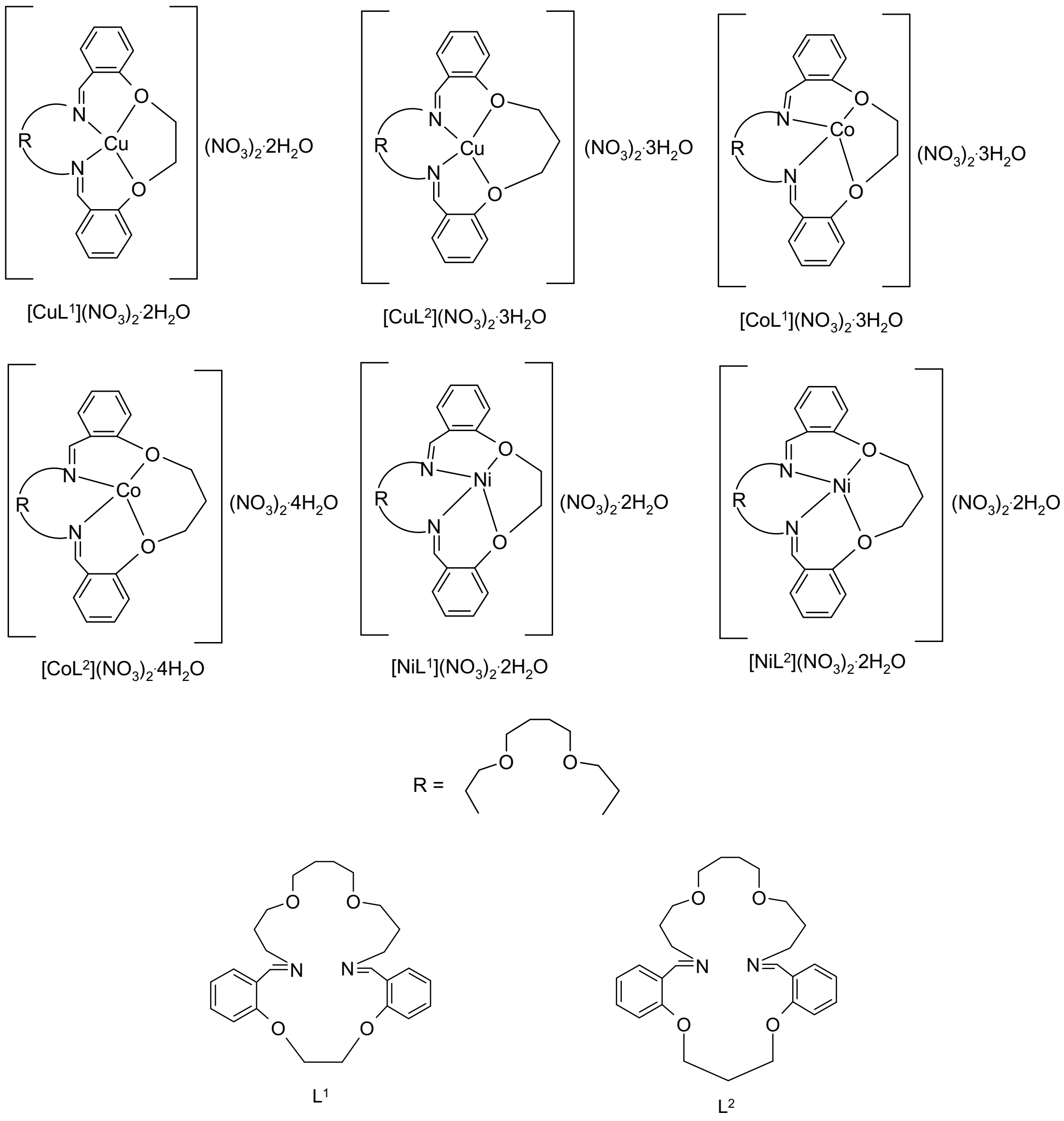

Fig. 6. Suggested Structure of the complexes.

clic Schiff base complexes as the product. The macrocyclic complexes were characterized by elemental analysis, FTIR, UV–vis, conductivity measurements, magnetic susceptibility and mass and spectra. The mass spectra of the complexes play an important role in confirming the monomeric [1+1] (dicarbonyl and diamine) nature of complexes (Table 1). The crystals were unsuitable for single-crystal X-ray structural determination and are insoluble in most common solvents as: water, ethanol, ethyl acetate and/or acetonitrile.

3.1. FTIR spectra

The characteristic infrared spectral data are given in the experimental section. Infrared spectra of the complexes were recorded in KBr pellet from 4000 to 400 cm^{-1}. The broad bands at *ca.* 3350 cm^{-1} in the spectra of all complexes can be attributed to stretching vibrations of water molecule υ(H_2O) [28]. A medium band observed in the IR spectra of the complexes in the 1636–1634 cm^{-1} region which is attributed to the υ(C=N) stretch, indicating coordination of the azomethine nitrogen to metal [29]. The absorptions of the nitrate ions, at *ca.* 1460–1452 (ν_5), 1300 (ν_1) and 1040 (ν_2) cm^{-1}, suggest the presence of bidentate nitrate groups: a intense band at *ca.* 1384 cm^{-1} attributable to ionic nitrate, is also present [29–31]. The spectra of all the complexes are dominated by bands at 2965–2855 cm^{-1} due to ν(Alph.-CH) groups [30]. Conclusive evidence of the bonding is also shown by the observation that new bands in the IR spectra of the complexes appear at 552–515 and 511–471 cm^{-1} assigned to ν(M—O) and ν(M—N) stretching vibrations [31] (Table 2).

3.2. Electronic absorption spectroscopy

Electronic absorption spectral data of the complexes in dimethylformamide (DMF) at room temperature are presented in experimental section. The electronic spectra of complexes in DMF show four bands in the visible–ultraviolet region. The absorption bands below 300 nm are practically identical and can be attributed to $\pi \rightarrow \pi^*$ transitions in the benzene ring and azomethine (—C=N) groups [32]. The absorption bands observed within the 300–330 nm range are most probably due to the transitions of $n \rightarrow \pi^*$ of imine groups [33]. The general character of these spectra is very similar to that of the corresponding complexes of unsymmetrical desubstituted phenoxy groups. This is probably due to the fact that metal-to-ligand charge transfer and ligand-to-metal charge transfer transitions have similar energy differences [34]. The electronic spectra of the Cu(II) complexes show an absorption band at 668–693 nm attributed to the $^2E_g \rightarrow {}^2T_{2g}$ transition, characteristic for square planar geometry [31,34]. The energy of the band assigned to d–d transitions can provide a rough estimate of the ligand field strength, since one of the electronic transitions comprised in the band envelope is $\mathrm{d_x2\text{-}_y2{-}d_{xy}}$ and the energy associated with this transition is 10Dq-C [31,34]. The electronic spectra of the Ni(II) and Co(II) complexes show an absorption band at 568–668 nm attributed to the $^2E_g \rightarrow {}^2T_{2g}$ transition, characteristic for tetragonally elongated octahedral or square planar geometry [31,34]. The electronic absorption bands of the presented Ni(II) and Co(II) complexes in the visible region exhibit solvent dependence behavior. The observed red shifts in the low-energy d–d band of Ni(II) and Co(II) complexes in DMF can be interpreted in terms of weak ligand field strength [27,31,34].

3.3. Magnetic studies

The metal–ligand mole ratio was found to be 1:1, according to elemental analysis and mass spectra. Since all of the complexes are paramagnetic, their NMR spectra could not be obtained. The magnetic moments of the Cu(II) complexes carried out at room temperature are in the range 2.02–2.17 BM, which are typical for Cu(II) complexes having one unpaired electron at this temperature. Magnetic susceptibility measurements provide sufficient data to characterize the structure of the Ni(II) and Co(II) complexes. The magnetic moment measurements of compounds were carried out at 25 °C. The magnetic moments of the Ni(II) complexes carried out at room temperature are in the range 2.64–2.81 B.M, which are typical for Ni(II) complexes having two unpaired electron [31,34]. The room temperature magnetic moment (3.78–3.96 B.M) determined for Co(II) metal complexes, are close to the spin-only magnetic moment ($\mu = 3.87$ B.M) for three unpaired electrons. This result and the absorption bands observed for the electronic spectra of Ni(II) and Co(II) complexes also support the tetrahedral geometry for Ni(II) and Co(II) complexes.

3.4. Conductivity measurements

The complexes are 1:2 electrolytes as shown by their molar conductivities (Λ_M) in DMF (dimethylformamide) at 10^{-3} M, which are in the range 161–191 $\Omega^{-1}\,\mathrm{cm}^2\,\mathrm{mol}^{-1}$. The molar conductivities of the compounds in DMF are in the range reported for 1:2 electrolytes [35–38].

3.5. Mass spectra

The fragments observed in the mass spectrum of the complexes are useful for characterization of the complexes [39–43]. Therefore, fragments observed in the mass spectrum of the complexes were given below and shown in figures (Figs. 2–5).

$[\mathrm{NiL}^1](\mathrm{NO}_3)_2{\cdot}2\mathrm{H}_2\mathrm{O}$: (622, 7.2%, $[[\mathrm{NiL}^1](\mathrm{NO}_3)_2+\mathrm{H}]^+$), (621, 3.1%, $[[\mathrm{NiL}^1](\mathrm{NO}_3)]^+$), (561, 5.4%, $[[\mathrm{NiL}^1](\mathrm{NO}_3)+\mathrm{H}]^+$), (560, 13.7%, $[[\mathrm{NiL}^1](\mathrm{NO}_3)]^+$), (500, 23.7%, $[\mathrm{NiL}^1+2\mathrm{H}]^+$), (499, 54.5%, $[\mathrm{NiL}^1+\mathrm{H}]^+$), (498, 100%, $[\mathrm{NiL}^1]^+$), (441, 16.1%, $[\mathrm{L}^1+3\mathrm{H}]^+$), (440, 46.1%, $[\mathrm{L}^1+2\mathrm{H}]^+$), (439, 83.3%, $[\mathrm{L}^1+\mathrm{H}]^+$), (438, 29.3%, $[\mathrm{L}^1+\mathrm{H}]^+$), (424, 19.4%, $[\mathrm{L}^1{-}(\mathrm{CH}_2)]^+$), (96, 8.2%, $[\mathrm{C}_6\mathrm{H}_6\mathrm{O}+2\mathrm{H}]^+$), (79, 27.3%, $[\mathrm{C}_6\mathrm{H}_6+\mathrm{H}]^+$).

$[\mathrm{CoL}^1](\mathrm{NO}_3)_2{\cdot}3\mathrm{H}_2\mathrm{O}$: see Figs. 2 and 4.

$[\mathrm{CuL}^1](\mathrm{NO}_3)_2{\cdot}2\mathrm{H}_2\mathrm{O}$: (627, 11.3%, $[[\mathrm{CuL}^1](\mathrm{NO}_3)_2+\mathrm{H}]^+$), (626, 4.2%, $[[\mathrm{CuL}^1](\mathrm{NO}_3)_2]^+$), (625, 2.1%, $[[\mathrm{CuL}^1](\mathrm{NO}_3)_2{-}\mathrm{H}]^+$), (624, 1.6%, $[[\mathrm{CuL}^1](\mathrm{NO}_3)_2{-}2\mathrm{H}]^+$), (565, 8.4%, $[[\mathrm{CuL}^1](\mathrm{NO}_3)+\mathrm{H}]^+$), (564, 12.3%, $[[\mathrm{CuL}^1](\mathrm{NO}_3)]^+$), (563, 3.1%, $[[\mathrm{CuL}^1](\mathrm{NO}_3){-}\mathrm{H}]^+$), (503, 15.2%, $[\mathrm{CuL}^1+\mathrm{H}]^+$), (502, 32.8%, $[\mathrm{CuL}^1]^+$), (489, 40.3%, $[\mathrm{CuL}^1{-}(\mathrm{CH}_2)+\mathrm{H}]^+$), (488, 59.1%, $[\mathrm{CuL}^1{-}(\mathrm{CH}_2)]^+$), (441, 48.3%, $[\mathrm{L}^1+3\mathrm{H}]^+$), (440, 77.5%, $[\mathrm{L}^1+2\mathrm{H}]^+$), (439, 100%, $[\mathrm{L}^1+\mathrm{H}]^+$), (438, 9.3%, $[\mathrm{L}^1]^+$), (424, 10.9%, $[\mathrm{L}^1{-}(\mathrm{CH}_2)]^+$), (408, 5.9%, $[\mathrm{L}^1{-}(\mathrm{OCH}_2)]^+$), (98, 17.2%, $[\mathrm{C}_6\mathrm{H}_6\mathrm{O}+4\mathrm{H}]^+$), (79, 9.7%, $[\mathrm{C}_6\mathrm{H}_6+\mathrm{H}]^+$).

$[\mathrm{NiL}^2](\mathrm{NO}_3)_2{\cdot}2\mathrm{H}_2\mathrm{O}$: (637, 13.2%, $[[\mathrm{NiL}^2](\mathrm{NO}_3)_2+\mathrm{H}]^+$), (636, 20.2%, $[[\mathrm{NiL}^2](\mathrm{NO}_3)_2]^+$), (574, 8.1%, $[[\mathrm{NiL}^2](\mathrm{NO}_3)]^+$), (573, 4.3%, $[[\mathrm{NiL}^2](\mathrm{NO}_3){-}\mathrm{H}]^+$), (514, 44.9%, $[\mathrm{NiL}^2+2\mathrm{H}]^+$), (512, 67.9%, $[\mathrm{NiL}^2+\mathrm{H}]^+$), (511, 100%, $[\mathrm{NiL}^2]^+$), (498, 11.5%, $[\mathrm{NiL}^2\text{-}(\mathrm{O})+\mathrm{H}]^+$), (483, 20.5%, $[\mathrm{NiL}^2{-}(\mathrm{OCH}_2)]^+$), (456, 13.2%, $[\mathrm{L}^2+3\mathrm{H}]^+$), (455, 29.1%, $[\mathrm{L}^2+2\mathrm{H}]^+$), (454, 42.6%, $[\mathrm{L}^2+\mathrm{H}]^+$), (439, 9.2%, $[\mathrm{L}^2{-}(\mathrm{CH}_2)]^+$), (423, 5.2%, $[\mathrm{L}^2{-}(\mathrm{OCH}_2)]^+$), (419, 14.2%, $[\mathrm{L}^2{-}(\mathrm{OCH}_2\mathrm{CH}_2)]^+$), (405, 23.2%, $[\mathrm{L}^2{-}(\mathrm{OCH}_2\mathrm{CH}_2\mathrm{CH}_2)]^+$), (96, 8.2%, $[\mathrm{C}_6\mathrm{H}_6\mathrm{O}+2\mathrm{H}]^+$), (79, 27.3%, $[\mathrm{C}_6\mathrm{H}_6+\mathrm{H}]^+$).

$[\mathrm{CoL}^2](\mathrm{NO}_3)_2{\cdot}4\mathrm{H}_2\mathrm{O}$: (637, 6.2%, $[[\mathrm{CoL}^2](\mathrm{NO}_3)_2+\mathrm{H}]^+$), (636, 22.9%, $[[\mathrm{CoL}^2](\mathrm{NO}_3)_2]^+$), (635, 6.3%, $[[\mathrm{CoL}^2](\mathrm{NO}_3)_2{-}\mathrm{H}]^+$), (574, 5.1%, $[[\mathrm{CoL}^2](\mathrm{NO}_3)]^+$), (573, 2.3%, $[[\mathrm{CoL}^2](\mathrm{NO}_3){-}\mathrm{H}]^+$), (514, 25.3%, $[\mathrm{CoL}^2+2\mathrm{H}]^+$), (513, 47.9%, $[\mathrm{CoL}^2+\mathrm{H}]^+$), (512, 61.3%, $[\mathrm{CoL}^2]^+$), (498, 13.2%, $[\mathrm{CoL}^2{-}(\mathrm{CH}_2)]^+$), (497, 7.2%, $[\mathrm{CoL}^2{-}(\mathrm{O})+\mathrm{H}]^+$), (482, 10.3%, $[\mathrm{CoL}^2{-}(\mathrm{OCH}_2)\text{-}\mathrm{H}]^+$), (456, 34.7%, $[\mathrm{L}^2+3\mathrm{H}]^+$), (455, 62.1%, $[\mathrm{L}^2+2\mathrm{H}]^+$), (454, 100%, $[\mathrm{L}^2+\mathrm{H}]^+$), (439, 4.2%, $[\mathrm{L}^2{-}(\mathrm{CH}_2)]^+$), (423, 11.4%, $[\mathrm{L}^2{-}(\mathrm{OCH}_2)]^+$), (419, 14.2%, $[\mathrm{L}^2{-}(\mathrm{OCH}_2\mathrm{CH}_2)]^+$), (96, 8.2%, $[\mathrm{C}_6\mathrm{H}_6\mathrm{O}+2\mathrm{H}]^+$), (81, 2.3%, $[\mathrm{C}_6\mathrm{H}_6+\mathrm{H}]^+$), (80, 9.1%, $[\mathrm{C}_6\mathrm{H}_6+\mathrm{H}]^+$), (79, 18.8%, $[\mathrm{C}_6\mathrm{H}_6+\mathrm{H}]^+$).

$[\mathrm{CuL}^1](\mathrm{NO}_3)_2{\cdot}2\mathrm{H}_2\mathrm{O}$: See Figs. 3 and 5.

4. Conclusion

The novel six Schiff base macrocyclic complexes were prepared and characterized by elemental analyses, FTIR and UV–vis spectra, conductivity measurements, magnetic susceptibilities and mass spectra. General structures of the complexes were shown in Fig. 6. The Ni(II) and Co(II) complexes probability show tetrahedral geometry and Cu(II) complexes probability show square planar geometry around the central metal ions.

References

[1] H. Khanmohammadi, S. Amani, H. Lang, T. Rueffer, Inorg. Chim. Acta 360 (2007) 579.
[2] K.P. Wainwright, Coord. Chem. Rev. 166 (1997) 35.
[3] S. Ilhan, H. Temel, I. Yilmaz, A. Kilic, Transition Met. Chem. 32 (2007) 344.
[4] R.M. Izatt, K. Pawlakm, J.S. Bradshaw, Chem. Rev. 95 (1995) 2529.
[5] A.A. Khandar, S.A. Hosseini-Yazdi, M. Khatamian, P. McArdle, S.A. Zarei, Polyhedron 26 (2007) 33.
[6] A.L. Vance, N.W. Alcock, D.H. Busch, J.A. Heppert, Inorg. Chem. 36 (1997) 5132.
[7] K.Y. Choi, H.Y. Lee, B. Park, J.H. Kim, J. Kim, M.W. Kim, J.W. Ryu, Polyhedron 20 (2001) 2003.
[8] T.W. Hambley, L.F. Lindoy, J.R. Reimers, P. Turner, W. Wei, A.N.W. Cooper, J. Chem. Soc. Dalton Trans. (2001) 614.
[9] S. Chandra, L.K. Gupta, J. Saudi Chem. Soc 8 (2004) 85.
[10] D.E. Fenton, R. Gauci, P.C. Junk, L.F. Lindoy, R.C. Luckay, G.V. Meehan, J.R. Price, P. Turner, G. Wei, J. Chem. Soc. Dalton Trans. 2185 (2002).
[11] S. Chandra, K. Gupta, Transition Met. Chem. 27 (2002) 196.
[12] S. Chandra, D. Jain, L.K. Gupta, J. Saudi Chem. Soc. (2003) 7.
[13] S. Chandra, L.K. Gupta, Spectrochim. Acta A 62 (2005) 307.
[14] A. Chaudhary, S. Dave, R. Swaroop, R.V. Singh, J. Ind. Chem. Soc. 79 (2002) 371.
[15] S. Chandra, L.K. Gupta, Spectrochim. Acta A 62 (2005) 307.
[16] L.F. Lindoy, D.H. Busch, W.L. Jolly (Eds.), Preparative Inorganic Reaction, vol. 6, Wiley-Interscience, New York, 1971, p. 1.
[17] C. Lodeiro, R. Batida, E. Bertolo, A. Macias, A. Rodriguez, Trans. Metal. Chem. 28 (2003) 388.
[18] J. de-Cabral, M.F. Cabral, M.G.B. Drew, F.S. Esho, O. Haas, S.M. Nelson, J. Chem. Soc. Chem. Commun. (1982) 1066.
[19] E.K. Barefield, F. Wagner, A. Herlinger, A.R. Dahl, Inorg. Synth. 16 (1976) 220.
[20] P. Comba, N.F. Curtis, G.A. Lawrance, A.M. Sargeson, B.W. Skelton, A.H. White, Inorg. Chem. 25 (1986) 4260.
[21] P. Comba, N.F. Curtis, G.A. Lawrance, M.A.O. Leary, B.W. Skelton, A.H. White, J. Chem. Soc. Dalton Trans. (1988) 497.
[22] L. Fabbrizzi, M. Licchelli, A.A.M. Lanfredi, O. Vassalli, F. Ugozzoli, Inorg. Chem. 35 (1996) 1582.
[23] S.M.E. Khalil, K.A. Bashir, J. Coord. Chem. 55 (6) (2002) 681.

[24] G. Shangguan, A.E. Martell, Z. Zhang, J.H. Reibenspies, Inorg. Chim. Acta 299 (2000) 47.

[25] A. Earnshaw, Introduction to Magnetochemistry, Academic Press, London, 1968. p.4.

[26] S. Ilhan, H. Temel, A. Kilic, J. Coord. Chem. 61 (2) (2008) 277.

[27] S. Ilhan, H. Temel, A. Kilic, Chin. J. Chem. 10 (2007) 1547.

[28] S. Ilhan, H. Temel, M. Aslanoglu, A. Kılıc, E. Tas, J. Chin. Chem. Soc. 53 (5) (2006) 1027.

[29] H. Temel, S. Ilhan, M. Sekerci, R. Ziyadanoğulları, Spectrosc. Lett. 35 (2) (2002) 219.

[30] Ü. Çakır, H. Temel, S. İlhan, H.İ. Uğraş, Spectrosc. Lett. 36 (5/6) (2003) 429.

[31] S. Ilhan, H. Temel, A. Kılıc, E. Tas, Transition Met. Chem. 32 (2007) 1012.

[32] S. Ilhan, H. Temel, M. Sekerci, Synt. React. Inorg. Met-Org. Chem. 32 (9) (2002) 1625.

[33] H. Temel, B. Ziyadanoğulları, H. Alp, I. Aydın, F. Aydın, S. İlhan, Russ. J. Coord. Chem. 32 (4) (2006) 282.

[34] H. Temel, S. Ilhan, A. Kılıc, E. Tas, J. Coord. Chem. (in press). 10.1080/00958970701502334.

[35] S. Ilhan, H. Temel, R. Ziyadanogullari, M. Sekerci, Transition Met. Chem. 32 (2007) 584.

[36] S. İlhan, H. Temel, Indian J. Chem. A 47A 47 (3) (2008) 378.

[37] S. İlhan, Indian J. Chem. 47A 47 (3) (2008) 374.

[38] S. Ilhan, H. Temel, I. Yilmaz, M. Sekerci, J. Organometal. Chem. 692 (18) (2007) 3855.

[39] S. Ilhan, H. Temel, I. Yilmaz, M. Sekerci, Polyhedron 26 (12) (2007) 2795.

[40] H. Temel, H. Alp, S. Ilhan, B. Ziyadanoğulları, İ. Yilmaz, Monatshefte fur Chemie 138 (2007) 1199.

[41] S. Ilhan, H. Temel, Transition Met. Chem. 32 (2007) 1039.

[42] H. Temel, H. Alp, S. Ilhan, B. Ziyadanoğulları, J. Coord. Chem. (in press). 10.1080/00958970701581734.

[43] H. Temel, S. İlhan, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 69 (2008) 896.