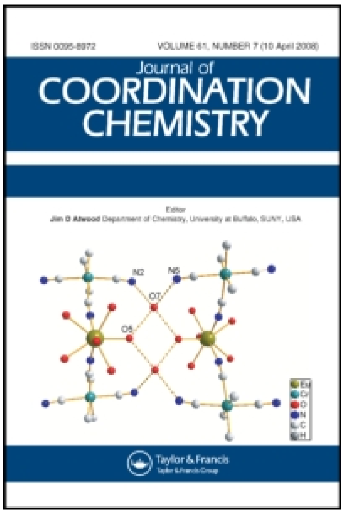

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Preparation and spectral characterization of new macrocyclic Ni(II) and Co(II) complexes derived from 1,4-<i>bis</i>(2-carboxyaldehydephenoxy)butane and various diamines

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Preparation and spectral characterization of new macrocyclic Ni(II) and Co(II) complexes derived from 1,4-*bis* (2-carboxyaldehydephenoxy)butane and various diamines

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Six new macrocyclic complexes were synthesized by the template effect from reaction of 1,4-*bis*(2-carboxyaldehydephenoxy)butane, $Ni(NO_3)_2 \cdot 6H_2O$ or $Co(NO_3)_2 \cdot 6H_2O$ and various diamines. The metal-to-ligand ratios of Ni(II) or Co(II) metal complexes were found to be 1 : 1. Coordination of the Schiff base to Ni(II) and Co(II) through the two nitrogen and two oxygen atom (ONNO) are expected to reduce the electron density in the azomethine link and hydroxyl group. The Ni(II) and Co(II) complexes are proposed to be tetrahedral and are 1 : 2 electrolytes as shown by their molar conductivities (Λ_M) in DMF (dimethyl formamide) at 10^{-3} M. The structures are proposed from elemental analysis, FT-IR, UV-VIS, magnetic susceptibility measurements, molar conductivity measurements, and mass spectra.

Keywords: Macrocyclic Schiff-base complexes; 1,4-*bis*(2-carboxyaldehydephenoxy)butane; Nickel(II) and Co(II) complexes; Mass spectra

1. Introduction

Schiff bases and their metal complexes have widely been studied because of their industrial, antifungal, and biological applications [1–3]. Transition metal complexes with macrocyclic ligands are well known for their enhanced kinetic and thermodynamic stability. Many tetradentate Schiff bases stabilize unusual oxidation states of metals [4–17]. It is well known that transition metals and group IIA metal ions act as templates for preparation of Schiff-base macrocyclic complexes. Typical experimental procedures yielding a wide range of macrocyclic complexes involve the reaction of a dicarbonyl compound with a diamine in the presence of an appropriate metal ion [18–20], through a template reaction [21–24]. Transmetallation reactions [25–28] are used when transition metal cations are ineffective as templates. Macrocyclic ligands containing various binding functionalities selectively bind, transform and transfer a large variety of

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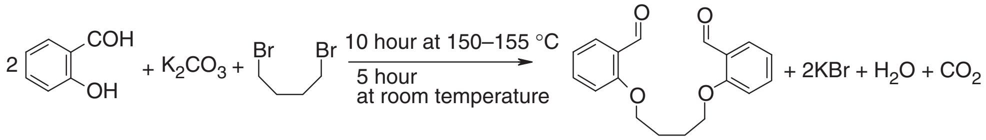

Scheme 1. 1,4-*bis*(2-carboxyaldehydephenoxy)butane.

substrates from charged species to neutral molecules. Structural factors such as ligand rigidity, the type of donor atoms, and their disposition have been shown to play significant roles in determining the binding features of macrocycles toward metal cations [29]. In our laboratory we have undertaken a systematic structural, spectroscopic and conductivity study on a series of Ni(II) and Co(II) macrocyclic complexes with N and O donor atoms. In the present work, we have synthesized six macrocyclic Schiff-base complexes by template reaction of 1,4-*bis*(2-carboxyaldehydephenoxy)butane and various diamines with $Ni(NO_3)_2 \cdot 6H_2O$, $Co(NO_3)_2 \cdot 6H_2O$; spectral and magnetic properties of the new compounds were studied in detail.

2. Experimental

The aldehyde used in the synthesis was prepared from salicylaldehyde, 1,4-dibromobutane and K_2CO_3 [30] (scheme 1). All chemicals and solvents were of analytical grade and used as received. 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 wavenumber range 4000–400 cm^{-1}. Electronic spectral studies were conducted on a PERKIN ELMER Model Lambda 25 UV-Visible spectrophotometer between 200–900 nm. Molar conductivity was measured with a WTW LF Model 330 conductivity meter using prepared solution of the complexes in DMF. Magnetic susceptibilities were determined on a Sherwood Scientific Magnetic Susceptibility Balance (Model MK1) at room temperature (20°C) using $Hg[Co(SCN)_4]$ as calibrant; diamagnetic corrections were calculated from Pascal's constants [31]. LC/MS-API-ES mass spectra were recorded using a AGILENT Model 1100 MSD mass spectrophotometer.

2.1. *Synthesis of Ni(II) and Co(II) metal complexes*

To a stirred solution of 1,4-*bis*(2-carboxyaldehydephenoxy)butane (1.5 g, 5 mmol) and $Ni(NO_3)_2 \cdot 6H_2O$ or $Co(NO_3)_2 \cdot 6H_2O$ (5 mmol) dissolved in methanol (60 mL), diamines (5 mmol) in methanol (40 mL) were added dropwise. After addition was complete, the stirring was continued for 2 h. Then precipitate was filtered, washed with methanol and dried in air.

2.2. *Spectral characterization of* $[NiL^1](NO_3)_2 \cdot 2H_2O$

Yield: 0.47 g (15.8%). Anal. Calcd for $NiC_{24}H_{30}N_4O_8 \cdot 2H_2O$: C, 48.32; H, 5.70; N, 9.40. Found: C, 48.46; H, 5.66; N, 9.28. Selected IR data (KBr, ν cm^{-1}): 3422 $\nu(H_2O)$, 3067 ν(Ar–CH), 2931, 2804 ν(Alph.–CH), 1637 ν(C=N), 1489, 1457 ν(Ar–C=C), 1162, 624 $\nu(NO_3^-)$, 1288, 1244 ν(Ar–O), 1193, 1070 ν(R–O), 757 ν(substituted benzene), 515 ν(Ni–O), 474 ν(Ni–N). $\Lambda_M = 138\,\Omega^{-1}\,mol^{-1}\,cm^2$ (in DMF). UV-vis (λ_{max}, nm, in DMF): 237, 246, 252, 258, 266, 281, 312, 665. Mass spectra: 597 $[[NiL^1](NO_3)_2 \cdot 2H_2O + H]^+$. $\mu_{eff} = 2.80$ B.M.

2.3. *Spectral characterization of* $[NiL^2](NO_3)_2 \cdot 4H_2O$

Yield: 1.65 g (52.2%). Anal. Calcd for $NiC_{24}H_{28}N_4O_8 \cdot 4H_2O$: C, 45.57; H, 5.70; N, 8.86. Found: C, 45.44; H, 5.57; N, 8.98. Selected IR data (KBr, ν cm^{-1}): 3336 $\nu(H_2O)$, 3077 ν(Ar–CH), 2938, 2860 ν(Alph.–CH), 1652 ν(C=N), 1489, 1459 ν(Ar–C=C), 1163, 654 $\nu(NO_3^-)$, 1287, 1245 ν(Ar–O), 1190, 1044, ν(R–O), 755 ν(substituted benzene), 528 ν(Ni–O), 500 ν(Ni–N). $\Lambda_M = 183\,\Omega^{-1}\,mol^{-1}\,cm^2$ (in DMF). UV-Vis (λ_{max}, nm, in DMF): 240, 267, 310, 314, 324, 559. Mass spectra: 632 $[[NiL^2](NO_3)_2 \cdot 4H_2O]^+$. $\mu_{eff} = 2.78$ B.M.

2.4. *Spectral characterization of* $[NiL^3](NO_3)_2 \cdot 12H_2O$

Yield: 0.86 g (19.9%). Anal. Calcd for $NiC_{28}H_{38}N_4O_8 \cdot 12H_2O$: C, 38.89; H, 7.16; N, 6.48. Found: C, 39.04; H, 7.25; N, 6.65. Selected IR data (KBr, ν cm^{-1}): 3436 $\nu(H_2O)$, 3084 ν(Ar–CH), 2931, 2802 ν(Alph.–CH), 1639 ν(C=N), 1491, 1454 ν(Ar–C=C), 1161, 622 $\nu(NO_3^-)$, 1288, 1244 ν(Ar–O), 1195, 1072, ν(R–O), 757 ν(substituted benzene), 512 ν(Ni–O), 473 ν(Ni–N). $\Lambda_M = 164\ \Omega^{-1}\,mol^{-1}\,cm^2$ (in DMF). UV-Vis (λ_{max}, nm, in DMF): 240, 245, 250, 257, 281, 307, 670. Mass spectra: 859 $[[NiL^3](NO_3)_2 \cdot 12H_2O)–5H]^+$. $\mu_{eff} = 2.69$ B.M.

2.5. *Spectral characterization of* $[CoL^1](NO_3)_2 \cdot 10H_2O$

Yield: 1.02 g (27.6%). Anal. Calcd for $CoC_{24}H_{30}N_4O_8 \cdot 10H_2O$: C, 38.81; H, 6.74; N, 7.55. Found: C, 38.96; H, 6.68; N, 7.49. Selected IR data (KBr, ν cm^{-1}): 3450 $\nu(H_2O)$, 3074 ν(Ar–CH), 2939, 2866 ν(Alph.–CH), 1638 ν(C=N), 1488, 1459 ν(Ar–C=C), 1162, 653 $\nu(NO_3^-)$, 1287, 1245 ν(Ar–O), 1192, 1045, ν(R–O), 755 ν(substituted benzene), 555 ν(Co–O), 516 ν(Co–N). $\Lambda_M = 191\,\Omega^{-1}\,mol^{-1}\,cm^2$ (in DMF). UV-Vis (λ_{max}, nm, in DMF): 249, 256, 266, 281, 312, 630. Mass spectra: 738 $[[CoL^1](NO_3)_2 \cdot 10H_2O–4H]^+$. $\mu_{eff} = 4.27$ B.M.

2.6. *Spectral characterization of* $[CoL^2](NO_3)_2 \cdot 3H_2O$

Yield: 1.95 g (62.9%). Anal. Calcd for $Co_2C_{24}H_{28}N_4O_8 \cdot 3H_2O$: C, 46.91; H, 5.54; N, 9.12. Found: C, 47.14; H, 5.65; N, 9.41. Selected IR data (KBr, ν cm^{-1}): 3467 $\nu(H_2O)$, 3125 ν(Ar–CH), 2938, 2860 ν(Alph.–CH), 1650 ν(C=N), 1489, 1459 ν(Ar–C=C), 1163, 654 $\nu(NO_3^-)$, 1288, 1245 ν(Ar–O), 1190, 1043, ν(R–O), 756 ν(substituted benzene), 531 ν(Co–O), 501 ν(Co–N). $\Lambda_M = 154\ \Omega^{-1}\,mol^{-1}\,cm^2$ (in DMF). UV-Vis (λ_{max}, nm, in DMF): 238, 250, 256, 266, 320, 496, 648. Mass spectra: 613 $[[CoL^2](NO_3)_2 \cdot 3H_2O–H]^+$. $\mu_{eff} = 3.98$ B.M.

2.7. *Spectral characterization of [CoL^3](NO$_3$)$_2$•H$_2$O*

Yield: 0.99 g (26.5%). Anal. Calcd for $CoC_{28}H_{38}N_4O_{10} \cdot H_2O$: C, 51.77; H, 6.16; N, 8.63. Found: C, 51.92; H, 6.31; N, 8.51. Selected IR data (KBr, ν cm^{-1}): 3450 $\nu(H_2O)$, 3074 ν(Ar–CH), 2938, 2866 ν(Alph.–CH), 1638 ν(C=N), 1488, 1459 ν(Ar–C=C), 1162, 653 $\nu(NO_3^-)$, 1287, 1245 ν(Ar–O), 1192, 1045, ν(R–O), 755 ν(substituted benzene), 553 ν(Co–O), 516 ν(Co–N). $\Lambda_M = 173\,\Omega^{-1}\,\text{mol}^{-1}\,\text{cm}^2$ (in DMF). UV-vis (λ_{max}, nm, in DMF): 238, 251, 260, 266, 311, 653. Mass spectra: 605 $[CoL^3](NO_3)_2\text{–}(OCH_2CH_2)]^+$. $\mu_{eff} = 4.18$ B.M.

3. Results and discussion

Reaction between 1,4-*bis*(2-carboxyaldehydephenoxy)butane, Ni(II) and Co(II) nitrate and amines in methanol, the [1 + 1] macrocycle Schiff-base complexes are formed as the major product. The macrocyclic complexes were characterized by elemental analysis, mass 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 H_2O, C_2H_5OH, CH_3OH, CH_2Cl_2, $CHCl_3$, Et_2O, $C_2H_5OOCCH_3$ and CH_3CN.

The characteristic infrared spectral data are given in the experimental section. Broad bands in the range 3336–3436 cm^{-1} for Ni(II) and 3450–3467 cm^{-1} for Co(II) complexes can be attributed to stretching vibrations of water ($\upsilon(H_2O)$) [32]. A strong band in the 1637–1652 cm^{-1} region is attributed to the υ(C=N) stretch, indicating coordination of the azomethine nitrogen to metal [33]. The spectra of all the Ni(II) and Co(II) metal complexes are dominated by bands between 2939–2802 cm^{-1} due to ν(Alph.–CH) groups. A new band in the 1195–1043 cm^{-1} region was assigned to ν(R–O) [34]. Also, infrared spectra of the Ni(II) and Co(II) metal complexes exhibit an intense band between 1163–1161 cm^{-1} along with a weak band between 654–622 cm^{-1}; assigned to ν(N–O) of uncoordinated nitrate [35]. The stretching vibrations ν(Ar–C=C) show very strong bands in the 1494–1489 and 1458–1456 cm^{-1} range. Conclusive evidence of the bonding is also shown by the observation that new bands in the IR spectra appear at 528–512 cm^{-1} and 500–473 cm^{-1} assigned to ν(Ni–O) and ν(Ni–N) and at 555–531 cm^{-1} and 516–501 cm^{-1} assigned to ν(Co–O) and ν(Co–N) stretching vibrations [36].

Electronic absorption spectral data of Ni(II) and Co(II) metal complexes in dimethylformamide (DMF) at room temperature are presented in the experimental section. Each Ni(II) and Co(II) metal complex shows several intense absorptions in the visible and ultraviolet region. In the electronic spectra of the Ni(II) and Co(II) metal complexes, the wide bands seem to be due to both the $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ and d–d transitions of C=N and charge transfer transitions arising from π electron interactions between the metal and ligand which involve either a metal-to-ligand or ligand-to-metal electron transfer [37, 38]. The absorption bands below 281 nm are practically identical and can be attributed to $\pi \rightarrow \pi^*$ transitions in the benzene ring and azomethine (–C=N) groups. The absorption bands observed within the 307–324 nm range are probably due to $n \rightarrow \pi^*$ transitions of imine groups [39]. The general character of these spectra is very similar to that of the corresponding complexes of unsymmetrically disubstituted phenoxy groups, probably due to metal-to-ligand charge transfer and ligand-to-metal

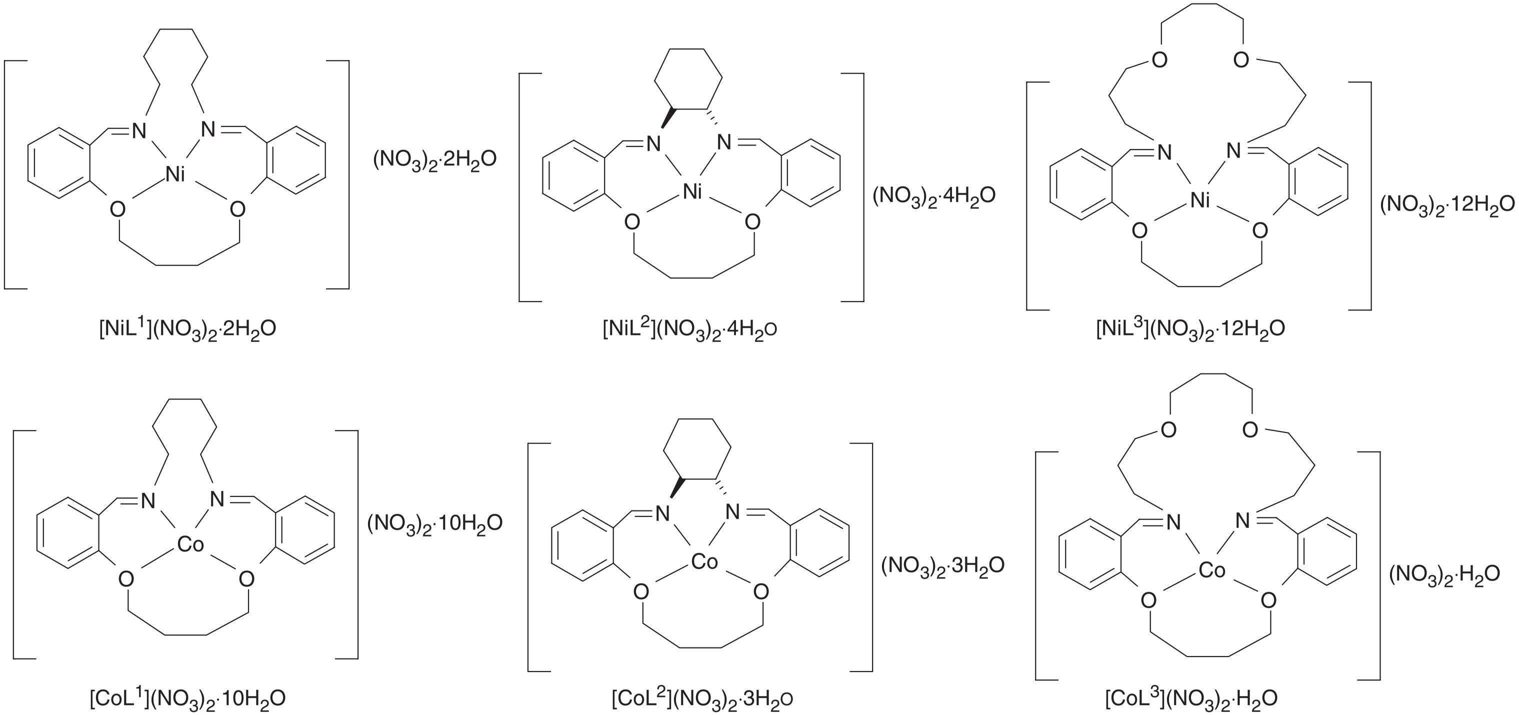

Figure 1. Suggested structures of the Ni(II) and Co(II) complexes.

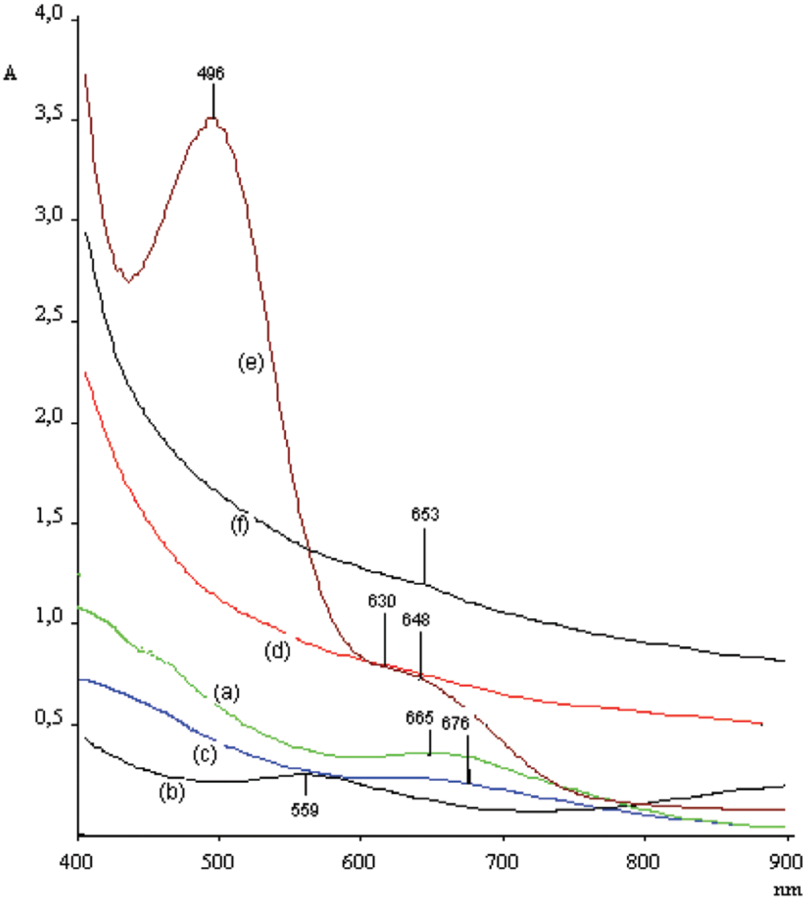

Figure 2. Vis spectra of $[NiL^1](NO_3)_2 \cdot 2H_2O$ (a), $[NiL^2][(NO_3)_2 \cdot 4H_2O$ (b), $[NiL^3](NO_3)_2 \cdot 12H_2O$ (c), $[CoL^1](NO_3)_2 \cdot 0H_2O$ (d), $[CoL^2](NO_3)_2 \cdot 3H_2O$ (e) and $[CoL^3](NO_3)_2 \cdot H_2O$ (f) in concentrated DMF solutions.

charge transfer transitions having similar energy differences [40]. The electronic spectra of the Ni(II) and Co(II) complexes shows a group of identical asymmetric bands in the range 559–670 nm, which are attributed to $d_{x^2-y^2} \rightarrow d_{xy}$ and $d_{x^2-y^2} \rightarrow d_{xz,yz}$ transitions, characteristic for tetragonal geometry [41]. The electronic absorption bands of the Ni(II) and Co(II) metal complexes in the visible region exhibit solvent dependent behavior. The observed red shifts in the low-energy d–d band of Ni(II) and Co(II) metal complexes in DMF can be interpreted in terms of weak ligand field strength [42]. The energy of the band assigned to d–d transitions provides a rough estimate of the ligand field strength, since one of the electronic transitions comprised in the band envelope is $d_{x^2-y^2} \rightarrow d_{xy}$ and the energy associated with this transition is 10Dq-C [43]. Also, the absorption band at 496 nm (in DMF) is assigned to M → L charge transfer (MLCT) or L → M charge transfer (LMCT) and $^1A_{1g} \rightarrow {}^1B_{1g}$ transitions for $[CoL^2](NO_3)_2 \cdot 3H_2O$ [44].

The metal–ligand mole ratio was found to be 1 : 1, according to elemental analysis. Since all of the Ni(II) and Co(II) complexes are paramagnetic, their NMR spectra could

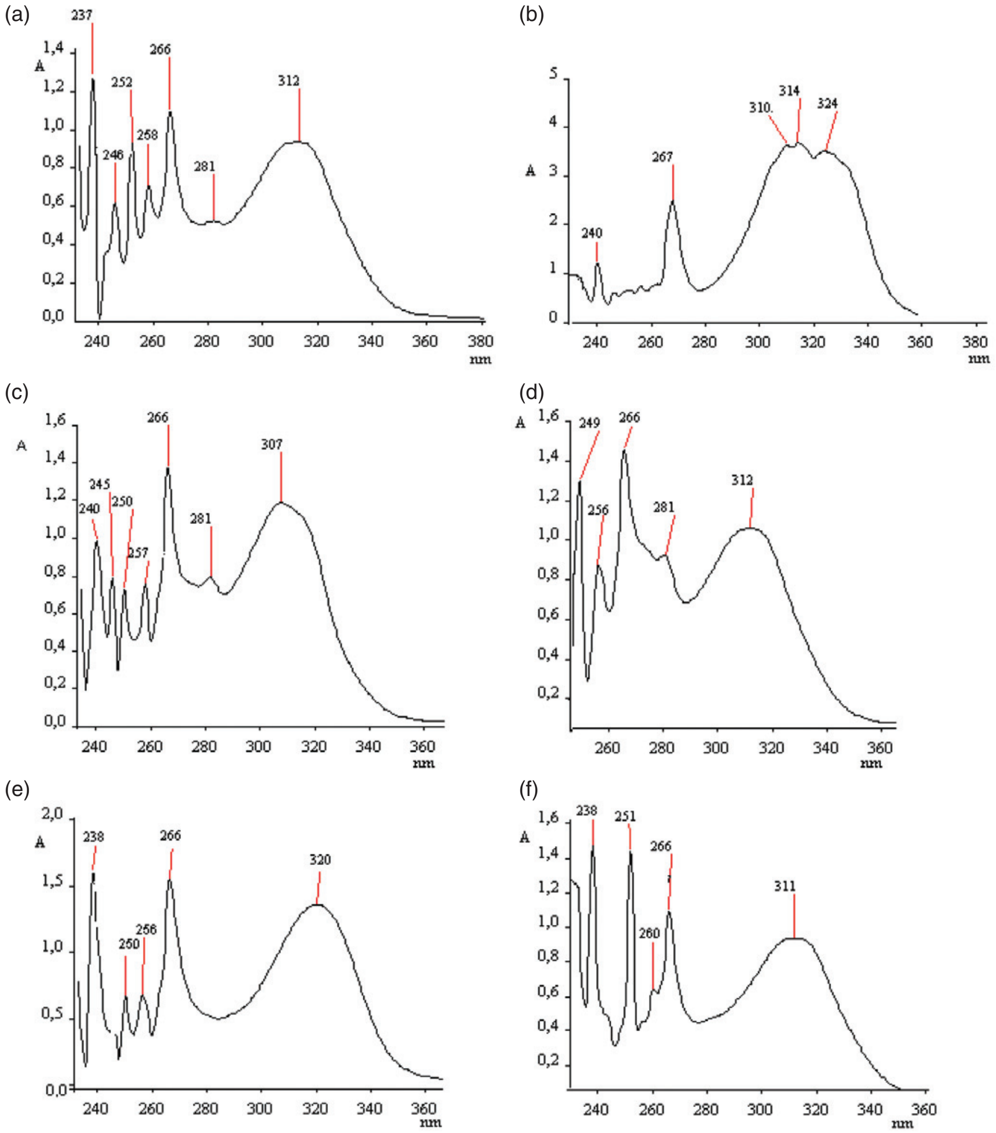

Figure 3. UV spectra of $[NiL^1](NO_3)_2 \cdot 2H_2O$ (a), $[NiL^2][(NO_3)_2 \cdot 4H_2O$ (b), $[NiL^3](NO_3)_2 \cdot 12H_2O$ (c), $[CoL^1](NO_3)_2 \cdot 10H_2O$ (d), $[CoL^2](NO_3)_2 \cdot 3H_2O$ (e) and $[CoL^3](NO_3)_2 \cdot H_2O$ (f) in dilute DMF solutions.

not be obtained. Magnetic susceptibility measurements provide sufficient data to characterize the Ni(II) and Co(II) metal complexes. The magnetic moments of the Ni(II) metal complexes carried out at room temperature range from 2.69–2.80 B.M, typical for mononuclear Ni(II) metal complexes with a $S = 1/2$ spin-state and do not indicate antiferromagnetic coupling of spins at this temperature [45]. The observed room-temperature magnetic moment values for the Co(II) complexes range from 3.98–4.27 B.M., close to the spin-only magnetic moments ($\mu = 3.87$ BM) for three unpaired electrons. This result and the absorption bands observed for the electronic spectra of

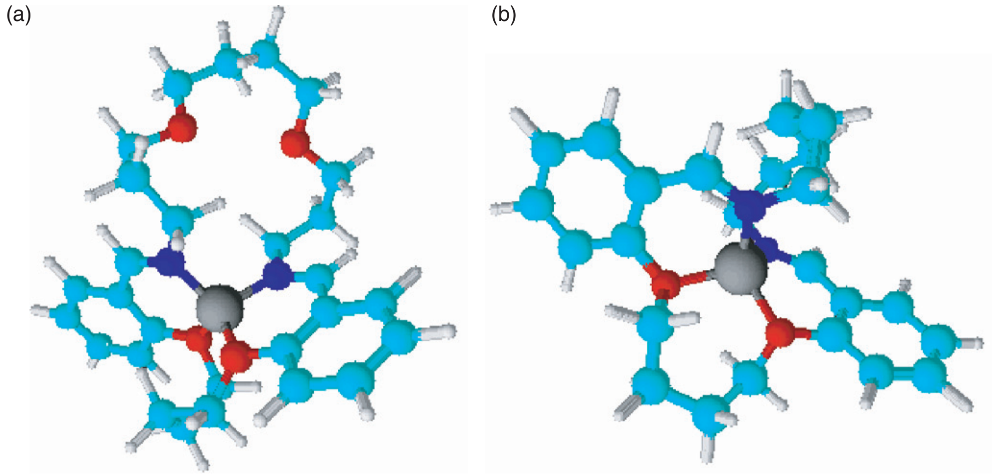

Figure 4. Rotational conformation of $[NiL^3](NO_3)_2 \cdot 12H_2O$ (a) and $[CoL^1](NO_3)_2 \cdot 10H_2O$ (b) metal complexes. The 3D viewer band model showing attachment of two nitrogen and two oxygen atom with complex.

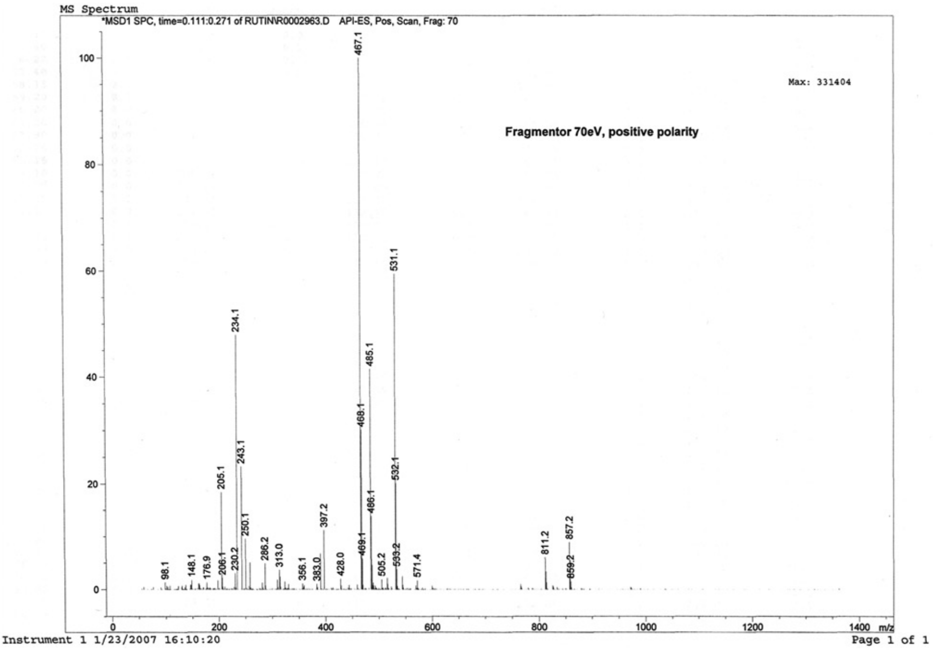

Figure 5. The mass spectra of $[NiL^3](NO_3)_2 \cdot 12H_2O$.

Ni(II) and Co(II) metal complexes support the tetrahedral geometry for Ni(II) and Co(II) metal complexes (figures 1–4).

The Ni(II) and Co(II) metal complexes are 2 : 1 electrolytes as shown by their molar conductivities (Λ_M) in DMF at 10^{-3} M, which are in the range 138–191 $\Omega^{-1} cm^2 mol^{-1}$ [46–49].

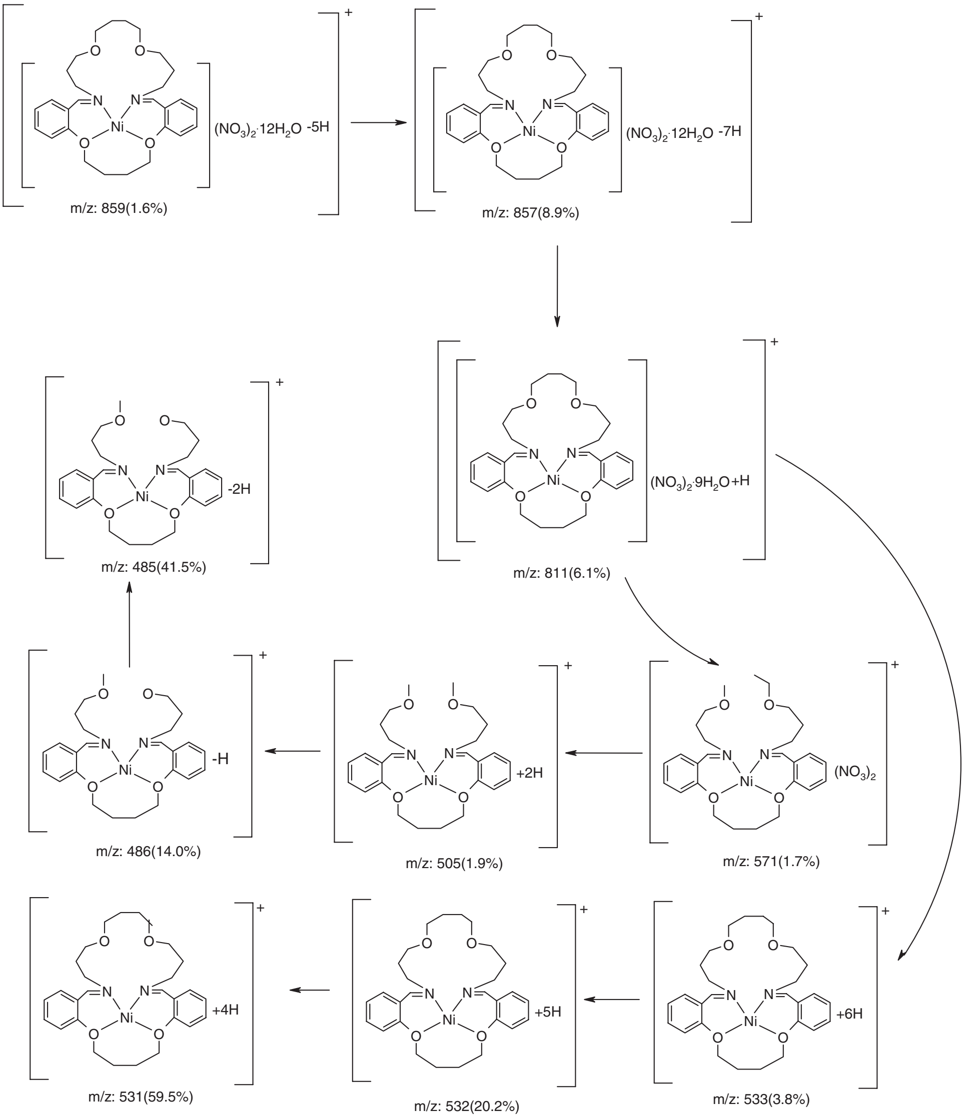

Figure 6. The fragments observed in the mass spectrum of the $[NiL^3](NO_3)_2 \cdot 12H_2O$.

The mass spectra of the complexes of nickel(II) and cobalt(II) peaks were attributable to the molecular ions (*m*/*z*): 597 $[[NiL^1](NO_3)_2 \cdot 2H_2O + H]^+$, 632 $[[NiL^2](NO_3)_2 \cdot 4H_2O]^+$, 859 $[[NiL^3](NO_3)_2 \cdot 12H_2O)–5H]^+$, 738 $[[CoL^1](NO_3)_2 \cdot 10H_2O–4H]^+$, 613 $[[CoL^2](NO_3)_2 \cdot 3H_2O–H]^+$, 649 $[[CoL^3](NO_3)_2–(OCH_2CH_2)]^+$ [50, 51]. The mass spectra of the L^3 and its nickel(II) complex, and the fragments observed in the mass spectrum of the complex, are shown in figures 5 and 6.

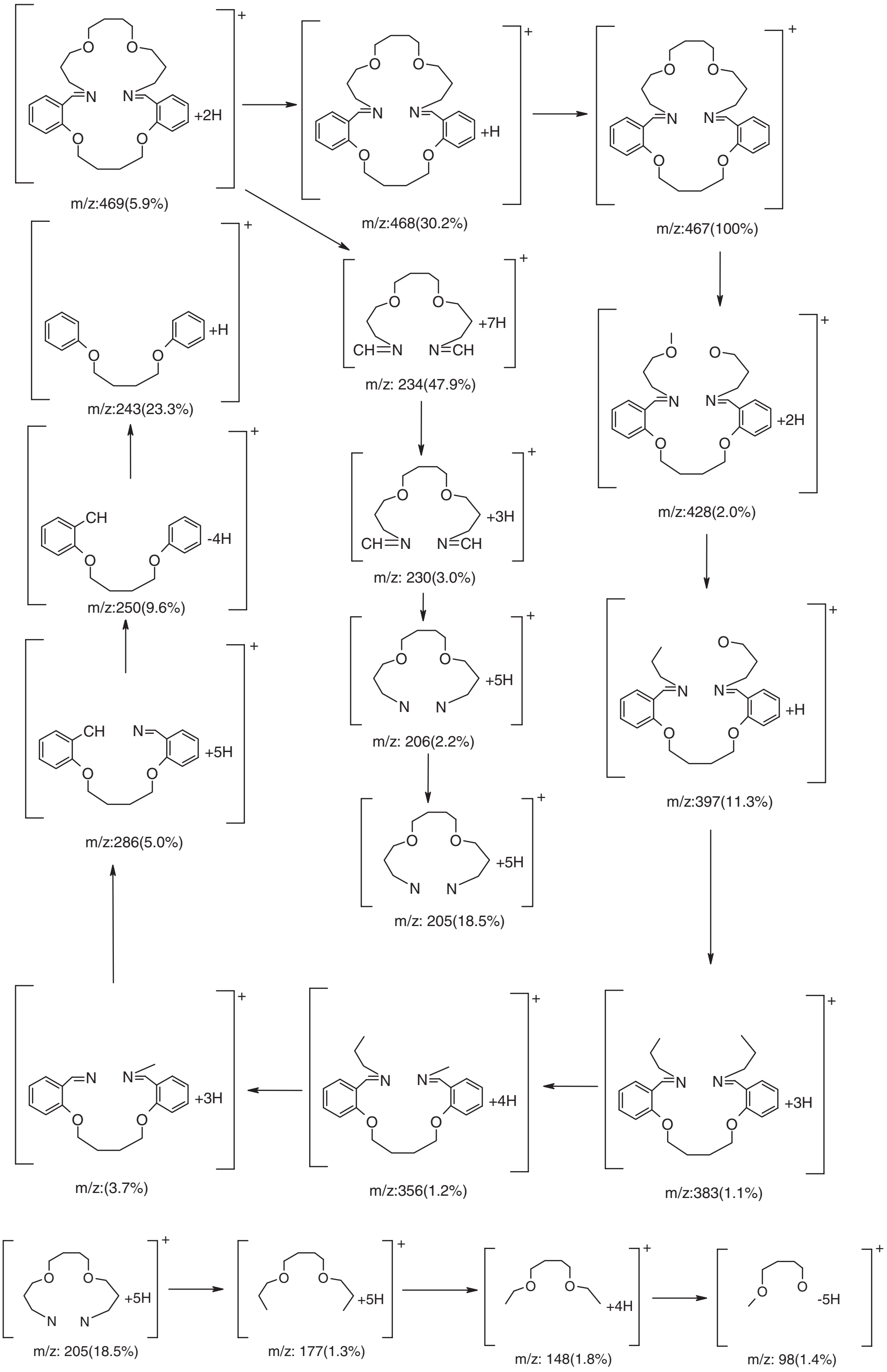

Figure 6. Continued.

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