Spectroscopic and Electrochemical Studies of Transition Metal Complexes with *N,N'*-Bis(2-aminothiophenol)-1,7-bis(2-formylphenyl)-1,4,7-trioxaheptane and Structure Effects on Extractability of Ligand towards some Divalent Cations

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Summary. La(III), Cu(II), Ni(II), and Zn(II) metal complexes with a novel quadridentate *Schiff* base derived from 1,7-bis(2-formylphenyl)-1,4,7-trioxaheptane and 2-aminothiophenol were synthesized and characterized by microanalytical data, elemental analysis, magnetic measurements, ^{1}H NMR, ^{13}C NMR, UV-Vis, IR, mass spectra, cyclic voltammetric and conductance measurements. The extractability of divalent cations was evaluated as a function of relationship between distribution ratio of the metal and *pH* or ligand concentration. The highest extraction percentage of Cu^{2+} and Ni^{2+} showed *pH* 7.0 and 6.4. It was concluded that the ligand can effectively be used in solvent extraction of copper(II) and nickel(II) from the aqueous phase to the organic phase.

Keywords. Thio *Schiff* base; Transition metal complexes; Extraction; Electrochemical studies.

Introduction

A large number of *Schiff* bases and their complexes have been studied because of their interesting and important properties, *e.g.*, their ability to reversibly bind oxygen [1], catalytic activity in hydrogenation of olefins [2] and transfer of amino group [3], photochromic properties [4], and complexing ability towards certain toxic metals [5]. Metal complexes of *Schiff* bases derived from substituted salicylalde-hydes and various amines have been widely investigated [6–14]. However, little attention has been given to *Schiff* bases, which include the ONS donor system [15, 16]. In addition, solvent extraction of metal chelate complexes has been used as a separation method for a long time. Utilizing an apparatus no more complicated than a separatory funnel, requiring several minutes at the most to perform, and applicable both to trace and macro levels of metals, these extraction procedures offer much to the analytical chemist [17]. The most widely used techniques for the separation and preconcentration of trace amounts are extraction [18], precipitation [19], and chelating resins [20]. Very often, both separation and preconcentration are required, and an advantage of solvent extraction is that both can be obtained in the same step [21]. Recovery of metals from an aqueous phase by solvent extraction is achieved by contacting the aqueous phase with an organic phase that contains a metal selective chelating agent dissolved in a diluent [22]. For extraction of metal ions, it is preferable that the chelating agent used has high distribution coefficient and *pH* dependence in the system chosen [23].

In the present work, we synthesized a new thio *Schiff* base by the reaction of 2-aminothiophenol and 1,7-bis(2-formylphenyl)-1,4,7-trioxaheptane. Then,

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its La(III), Cu(II), Ni(II), and Zn(II) complexes were synthesized using the template effect by reaction of 1,7-bis(2-formylphenyl)-1,4,7-trioxaheptane and 2-aminothiophenol with La(NO$_3$)$_3 \cdot$ 6H$_2$O, Cu(CH$_3$COO)$_2 \cdot$ H$_2$O, Ni(CH$_3$COO)$_2 \cdot$ 4H$_2$O, and Zn(CH$_3$COO)$_2 \cdot$ 2H$_2$O. Then the spectroscopic, magnetic, and electrochemical properties of all compounds were studied in detail. The new complexes with flexible structure and N and S donor atoms possibly offer the development of a novel extraction reagent having specific selectivity at various *pH* values. In addition, the electrochemical behavior of the Zn(II) complex has also been studied by cyclic voltammetry.

Results and Discussion

The ligand and complexes were synthesized (Schemes 1 and 2) and characterized. The ligand and its complexes were identified by elemental analysis, IR, ^{1}H, and ^{13}C NMR data, electronic spectra, magnetic susceptibility measurements, molar conductivity, mass spectra and cyclic voltammetry. The crystals were unsuitable for single-crystal X-ray structure determination.
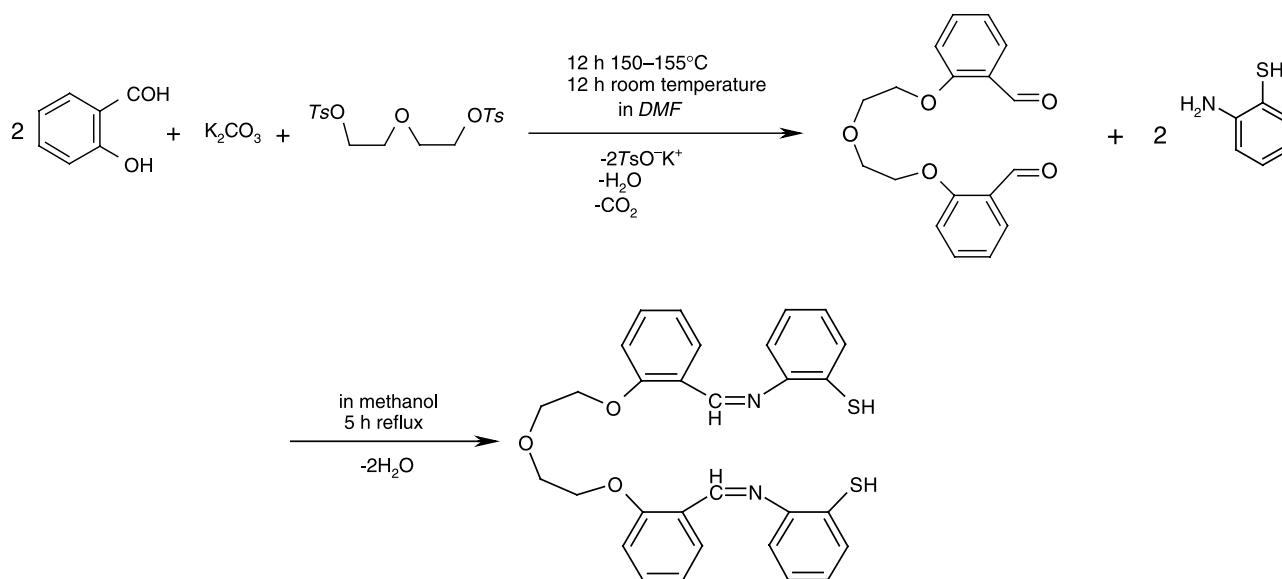
IR Spectra

The important features for the *Schiff* base and its complexes may be summarized as follows:

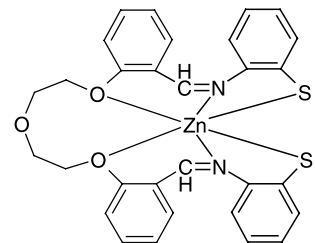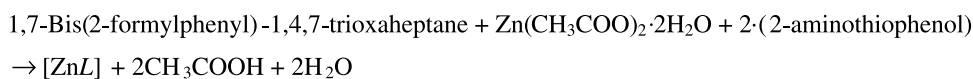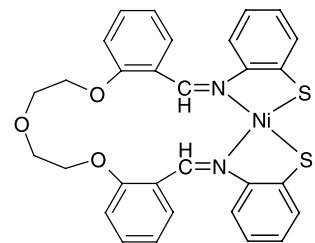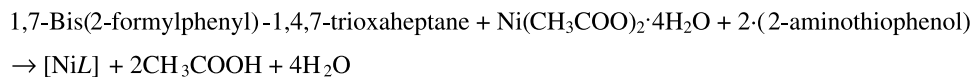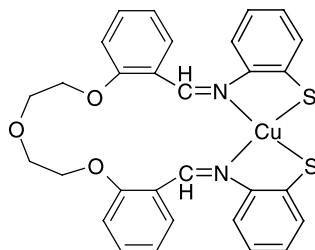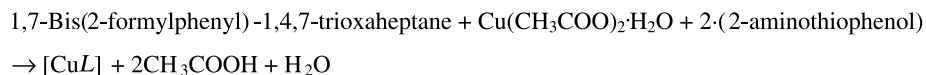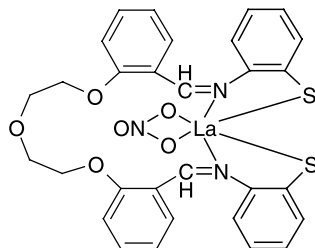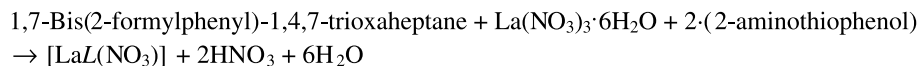The IR spectrum of the thio *Schiff* base ligand exhibited a strong sharp band at 3331 cm^{-1}. This band was previously assigned to be due to the stretching frequency of N$^+$H group, which is expected in these regions assigned to the stretching vibration of the intramolecular hydrogen bonded N $\cdots$ HS in the molecule.
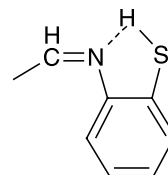
This band disappeared in the IR spectra of the complex. The bands at 752 and 696 cm^{-1} in the IR spectrum of the ligand are ascribed to the phenolic C–S [27, 28]. This band is found at *ca.* 754, 746, 727, 695, 694, 687, 668, 661, and 660 cm^{-1} in the IR spectra of the complexes. These changes suggest that the *o*-SH group of this *Schiff* base moiety has taken part in complex formation. The solid state IR spectra of the complexes compared with those of the ligand indicate that the C=N band 1599 cm^{-1} is shifted to lower values for complexes [6–14]. Conclusive evidence of the bonding is also shown by the observation that new bands in the spectra of the metal complexes appear at 475–458 cm^{-1} assigned to (*M*–N) stretching vibrations that are not observed in the spectra of the ligand [6–14]. The IR spectra of the Zn(II) complex clearly demonstrated that the COC and CCO stretching vibrations are altered compared to the ligand due to conformational changes. The C–O–C absorption is shifted to lower wave

Scheme 1

1,7-Bis(2-formylphenyl)-1,4,7-trioxaheptane + La(NO$_3$)$_3$·6H$_2$O + 2·(2-aminothiophenol)
→ [LaL(NO$_3$)] + 2HNO$_3$ + 6H$_2$O

1,7-Bis(2-formylphenyl)-1,4,7-trioxaheptane + Cu(CH$_3$COO)$_2$·H$_2$O + 2·(2-aminothiophenol)
→ [CuL] + 2CH$_3$COOH + H$_2$O

1,7-Bis(2-formylphenyl)-1,4,7-trioxaheptane + Ni(CH$_3$COO)$_2$·4H$_2$O + 2·(2-aminothiophenol)
→ [NiL] + 2CH$_3$COOH + 4H$_2$O

1,7-Bis(2-formylphenyl)-1,4,7-trioxaheptane + Zn(CH$_3$COO)$_2$·2H$_2$O + 2·(2-aminothiophenol)
→ [ZnL] + 2CH$_3$COOH + 2H$_2$O

Scheme 2

numbers in complexes providing another evidence of complexing [29, 30]. The La(III) complex shows six absorption bands near 1497, 1317, 1028, 923, 727, and 693 cm^{-1} assigned to $\bar{\nu}_4$, $\bar{\nu}_1$, $\bar{\nu}_2$, $\bar{\nu}_6$, $\bar{\nu}_3$, and $\bar{\nu}_5$ vibrations, respectively. The magnitudes of $\bar{\nu}_4$–$\bar{\nu}_1$ and $\bar{\nu}_3$–$\bar{\nu}_5$ are in the range of 210–220 and 41–47 cm^{-1}. This confirms the coordination of the nitrate group in a bidentate fashion [31, 32]. In addition, conclusive evidence of the bonding is also shown by the observation that new bands in the

spectra of the metal complexes appear at 1582, 1497 cm^{-1} assigned to (–ONO$_2$) stretching vibrations that are not observed in the spectra of the ligand [31, 32].

UV-Vis Studies

The electronic spectrum of the ligand (L) in C$_2$H$_5$OH shows absorption bands at 228 nm ($\varepsilon = 48720$), 297 nm ($\varepsilon = 17440$), and 322 nm ($\varepsilon = 23520$), in CHCl$_3$ shows absorption bands at 251 nm ($\varepsilon = 13500$), 286 nm ($\varepsilon = 21680$), and 323 nm ($\varepsilon = 13500$), and in *DMF* shows absorption bands at 295 nm ($\varepsilon = 27680$) and 321 nm ($\varepsilon = 38540$). 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 length compared to that of the ligand [33–35]. The bands are indicative of phenyl and other chromophore moieties present in the ligand. A moderately intensive band observed in the range of 320–325 nm is attributable to the n–π* transitions and the strong band observed in the range of 270–282 nm is due to the π–π* transitions [23] of the complexes. The Cu(II) complex shows an absorption band at 478 nm attributed to the $^2T_2g \rightarrow {}^2Eg$ (G) transition, which is compatible with these complexes having a square-planar structure [34]. The electronic spectrum of

the Ni(II) complex shows an absorption band at 479.00 nm attributed to the $^1A_1g \rightarrow {}^1B_1g$ transition, which is compatible with this complex having a square-planar structure [36] and according to a discussion based on group theory [37] (approximately, in D_{2h} symmetry), ligand field bands consist of a spin-forbidden transition $^1A_1g \rightarrow {}^3B_1g$ related to $d_{xy} \rightarrow d_{x2} - {}_{y2}$ orbital excitation at around 858 nm, a spin-allowed $^1A_1g \rightarrow {}^1B_1g$ transition related to $d_{xy} \rightarrow d_{x2} - {}_{y2}$ orbital excitation at around 478 [38]. The high absorption by the ligand as compared to the La(III) ions masks any splitting of the band and only slight wavelength and intensity variations are seen in the complex. The spectra of the La(III) complex is dominated by the ligand absorption bands [38].

^{1}H NMR and ^{13}C NMR

The NMR spectra of the Cu(II) and La(III) complexes could not be taken since the Cu(II) complex is paramagnetic and La(III) complex is little soluble in *DMSO*-d$_6$. The ^{1}H NMR and ^{13}C NMR spectral data of ligand and complexes are given in the Experimental. The ^{1}H NMR values of the CH$_2$OCH$_2$, CH$_2$OC$_6$H$_4$, and HC=N protons are changed in the complexes indicating that the metals are coordinated by the ligands. The ^{13}C NMR spectrum of the ligand is shown in Fig. 1.
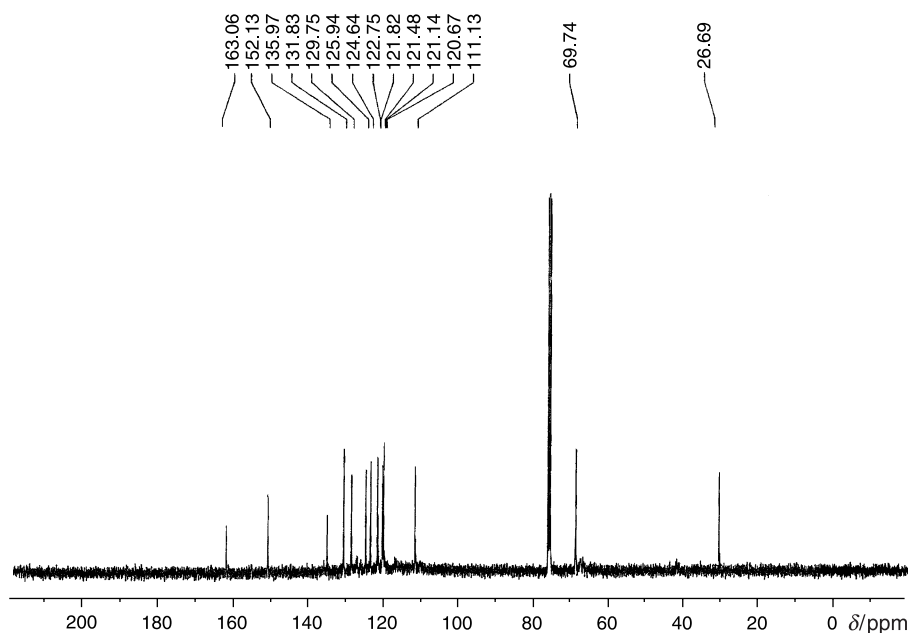

Fig. 1. ^{13}C NMR spectrum of *N,N'*-bis(2-aminothiophenol)-1,7-bis(2-formylpenyl)-1,4,7-trioxaheptane
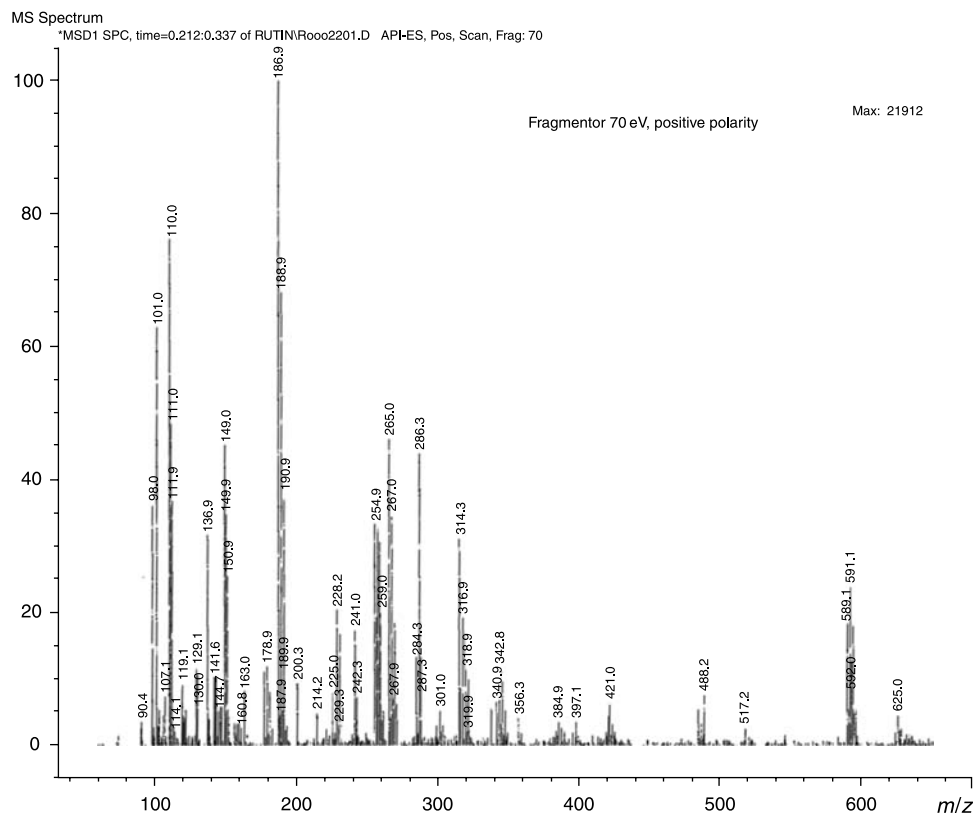
Fig. 2. The mass spectrum of the Zn(II) complex

Magnetic and Conductivity Studies

The Cu(II) complex is paramagnetic and its magnetic moment is $1.93\,\mu B$. Since the Cu(II) complex is paramagnetic [1–6], its ^1H NMR spectra could not be obtained. The Ni(II) and Zn(II) complex is diamagnetic. Their ^1H NMR spectra could be obtained. All complexes are nonelectrolytes [6–14].

Mass Spectra

The peaks of the mass spectra of the ligand and its metal complexes are attributable to the molecular ions: m/z: 527.1 $[L–H]^+$ (M_A: 528 g/mol), m/z: 553 $[[La(L)(NO_3)]–[O(CH_2)_2O(CH_2)_2O]–(NO_3)]^+$ (M_A: 727 g/mol), m/z: 523 $[Cu(L)–(CH_2)_2O(CH_2)_2 + 5H]^+$ (M_A: 590 g/mol), m/z: 592 $[Zn(L)]^+$ (M_A: 592 g/mol). The mass spectrum of the Zn(II) complex is shown in Fig. 2.

Extraction Studies

Distribution of the Metals

Equal volumes (10 cm^3) of chloroform containing 1.10^{-3} mol dm^{-3} of a ligand, an aqueous phase

containing 1.10^{-4} mol dm^{-3} of M^{2+} (M = Cu, Ni), 1.10^{-1} mol dm^{-3} of potassium nitrate, and 1.10^{-1} mol dm^{-3} of the buffer (acetic acid, acetate and sodium carbonate, bicarbonate) were introduced into a stoppered flask and shaken for 60 min at $25 \pm 0.1°C$. This period of shaking was enough to establish an equilibrium between the phases. The ionic strength of the aqueous phase was kept as $I = 0.1\,M$ by adding an appropriate amount of potassium nitrate. The two phases were separated by centrifugation and then, the *pH* of the aqueous phase after extraction was measured and metal concentrations were determined by AAS.

The percentage extraction (% E) of some divalent metals into chloroform with *Schiff* base were plotted as a function of the aqueous phase *pH* equilibrated with the organic phase in Fig. 4. The results are also expressed as distribution ratio (Table 1). The distribution ratio of divalent cation may be represented by Eq. (1).

$$D = \frac{[ML]_o}{[M^+]_w} \qquad (1)$$

As seen in Fig. 5, the effect of time on the degree of the extraction of Cu(II) and Ni(II) was studied at con-
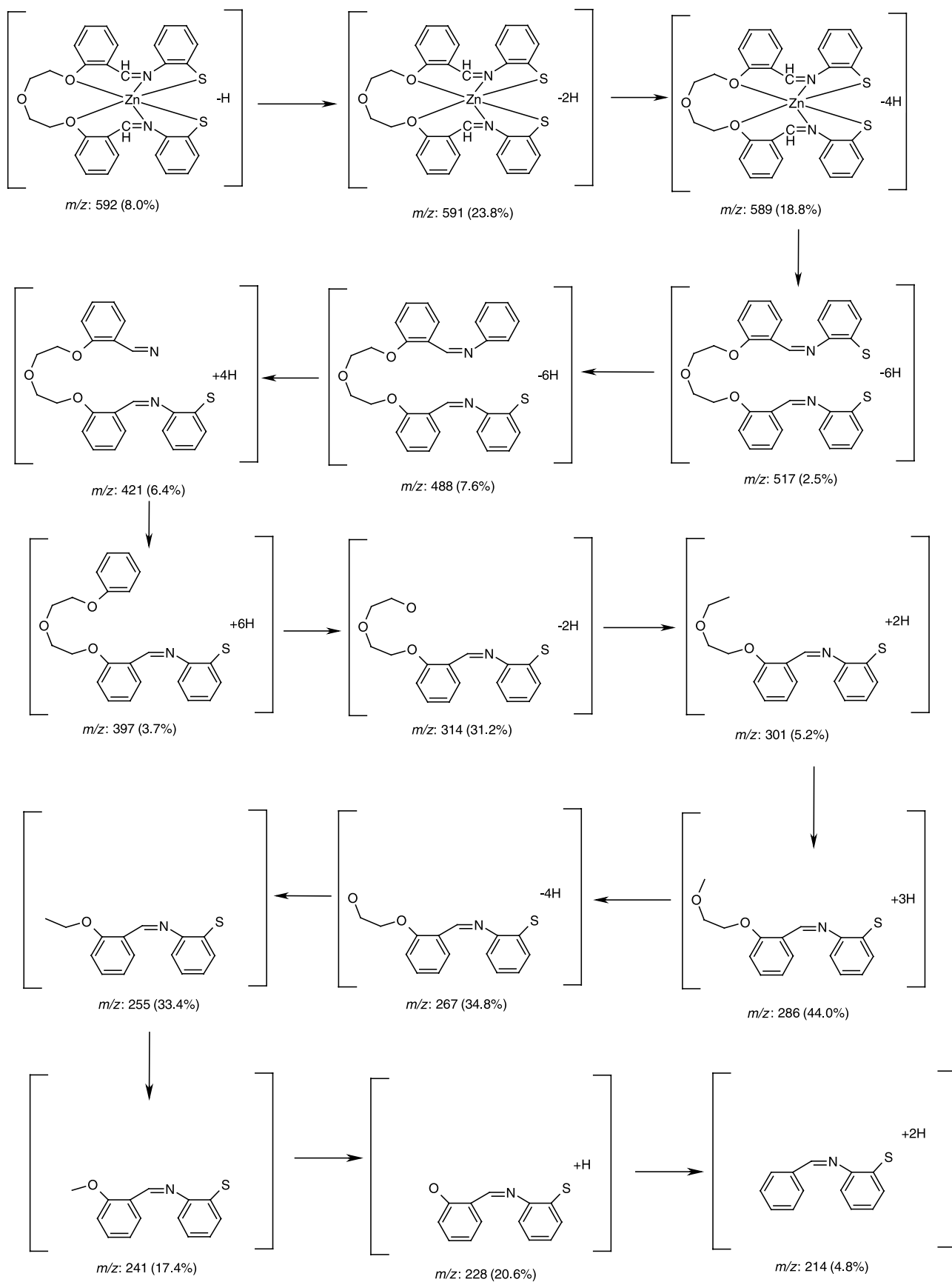
Fig. 3. The fragments observed in the mass spectrum of the Zn(II) complex

m/z: 592 (8.0%)

m/z: 591 (23.8%)

m/z: 589 (18.8%)

m/z: 421 (6.4%)

m/z: 488 (7.6%)

m/z: 517 (2.5%)

m/z: 397 (3.7%)

m/z: 314 (31.2%)

m/z: 301 (5.2%)

m/z: 255 (33.4%)

m/z: 267 (34.8%)

m/z: 286 (44.0%)

m/z: 241 (17.4%)

m/z: 228 (20.6%)

m/z: 214 (4.8%)

Fig. 4. The plot of % E *vs. pH* (Ni: ■, Cu: ◆)

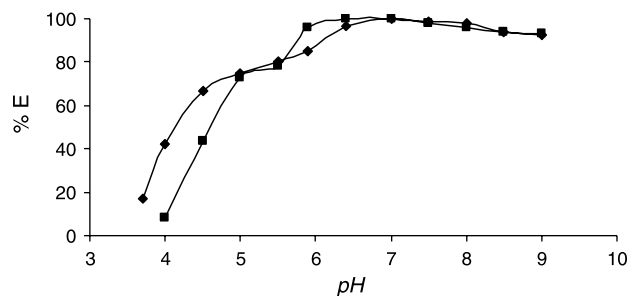**Table 1.** Distribution ratio of cation between the organic and aqueous phases

pH	Distribution ratio (D)[a]	
	Cu^{2+}	Ni^{2+}
3.7	0.21	0.0
4	0.74	0.08
4.5	1.98	0.77
5	3.00	2.67
5.5	4.15	3.62
5.9	7.06	21.67
6.4	26.84	1607
7	454	749
7.5	65.17	44.64
8	51.90	23.47
8.5	14.90	15.16
9	12.52	13.5

[a] Averages calculated for data obtained from three independent extraction experiments
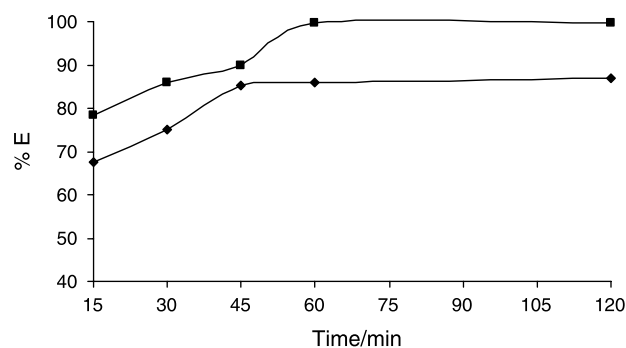

Fig. 5. The plot of % E *vs.* time (Ni: ■, Cu: ◆)

stant *pH* 7.0 and 6.4. Shaking time was determined as 45 and 60 min.

The extraction process may be represented by the equation:

$$M^{2+}_{w} + H_2L_o \longleftrightarrow ML_o + 2H^{+}_{w} \qquad (2)$$

where H_2L represents the extractant reagent and subscripts w and o denote the aqueous and organic phases.

In this case, extraction constant (K_{ex}) can be expressed as follows:

$$K_{ex} = \frac{[ML]_o[H^+]^2}{[M^{2+}][H_2L]_o} \qquad (3)$$

The values of log K_{ex} can be calculated by using the following equation:

$$\log K_{ex} = \log D - \log[H_2L]_o - 2pH \qquad (4)$$

According to Eq. (2), plots of log D against log $[H_2L]_o$ at constant *pH* 7 for Cu(II) and *pH* 6.4 for Ni(II) will give straight lines of slopes, one and intercept, log $K_{ex} + 2pH$. Hence, from the graphs (shown in Figs. 6 and 7) the extraction constants ($-\log K_{ex}$) have been calculated as 8.63 and 6.29. From the results, the extraction equilibrium was found as shown in Eq. (2). Both from quantitative evaluation of the extraction equilibrium data (Figs. 6 and 8) and *Job*'s method (Figs. 7 and 9) it has been deduced that the complexes extracted are the simple 1:1 chelates, [Cu*L*], [Ni*L*].
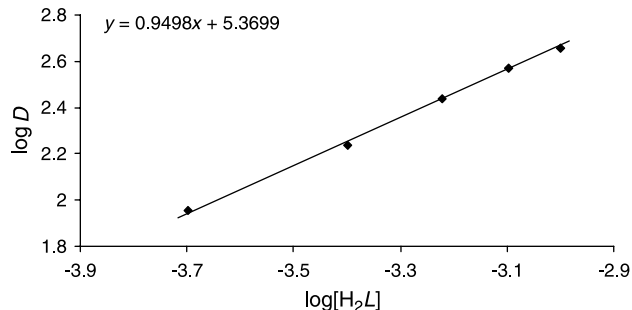

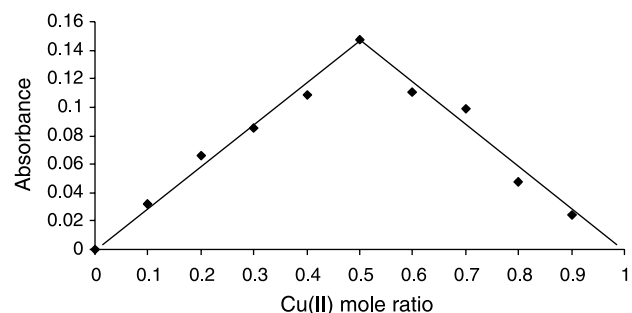**Fig. 6.** Graphical calculation of the extraction constant of Cu(II)

Fig. 7. The metal and ligand mole ratio (1:1) determined by *Job*'s method ($\lambda = 478$ nm)
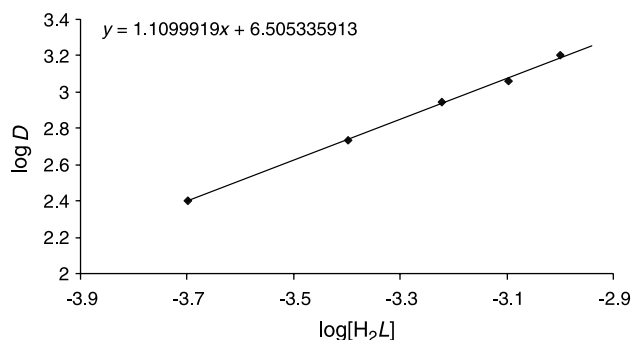
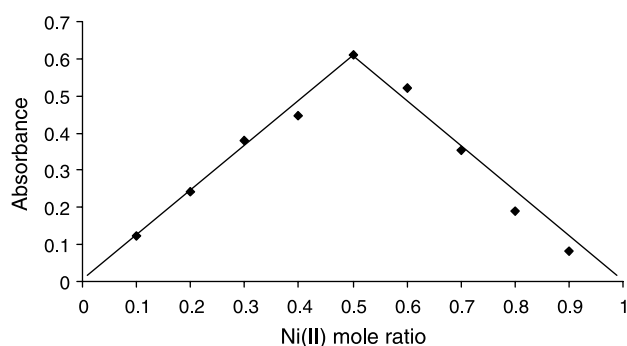**Fig. 8.** Graphical calculation of the extraction constant of Ni(II)

Fig. 9. The metal and ligand mole ratio (1:1) determined by *Job*'s method ($\lambda = 841$ nm)

Electrochemistry

The electrochemical behaviour of the new zinc complex was investigated using cyclic voltammetric (CV) technique in *DMSO* solution containing $0.1 M$
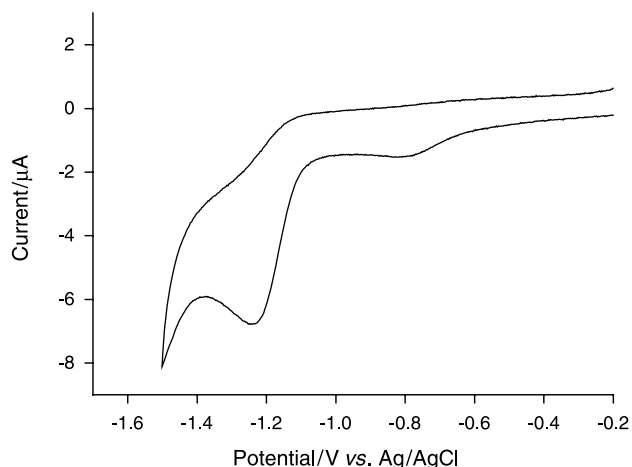

Fig. 10. Cyclic voltammogram of the Zn complex containing $0.1 M$ *TBAP* (cathodic scan). Scan rates $= 0.100 \, \mathrm{V \cdot s^{-1}}$
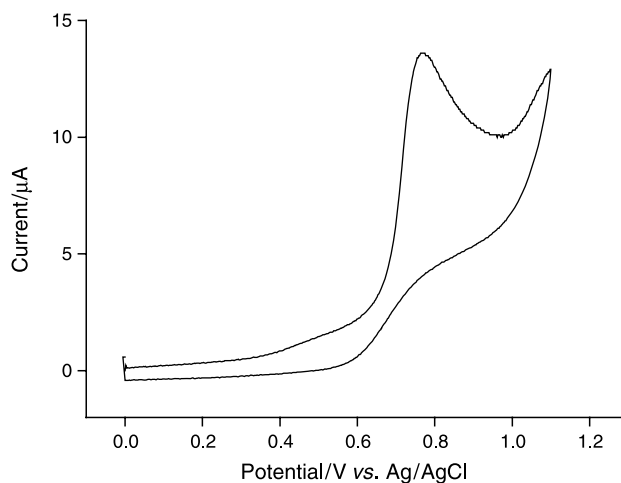

Fig. 11. Cyclic voltammogram of the Zn complex containing $0.1 M$ *TBAP* (anodic scan). Scan rates $= 0.100 \, \mathrm{V \cdot s^{-1}}$

TBAP. The Fig. 10 shows the CV of the Zn(II) complex which displays a cathodic wave without corresponding anodic wave and its cathodic peak potential (E_{pc}) was found to be -1.25 V *vs.* Ag/AgCl. As seen, the reduction process is irreversible and assigned to metal-based character since the ligand did not exhibit any process in the same scale upon cathodic scan. The complex also exhibited one irreversible oxidation peak without corresponding anodic wave (Fig. 11). The anodic peak potential corresponding to the oxidation wave is located at 0.767 V, which is assigned to the ligand-based process because the ligand exhibits the anodic wave at 0.746 V. Cathodic peak potential of the complex is anodically shifted by 0.021 V compared with that of the ligand. The nickel and copper complexes did not give any voltammetric response in the same experimental condition, probably due to highly unstable identity of their oxidized or reduced species in the time scale of the CV measurements.

The spectroelectrochemical behavior of the zinc complex was investigated using an *in situ* spectroelectrochemical technique including chronoamperometry and UV-Vis spectroscopy in *DMSO* solution containing $0.2 M$ *TBAP*. The UV-Vis spectral changes for the reduced complex were obtained in a thin-layer cell during applied potentials. The absorption spectra of the neutral complex and its electrochemically generated species are given in Fig. 12. The convenient applied potential value for *in situ* spectroelectrochemical experiment was determined for the reduction process by performing a CV measurement of the complex in the thin-layer cell.
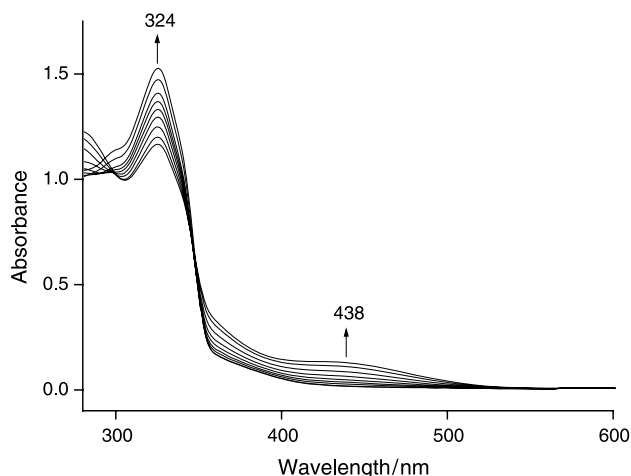
Fig. 12. Time-resolved UV-Vis spectral changes of the Zn complex during the reduction at $E_{app} = -1.45$ V in *DMSO* solution containing $0.2\,M$ *TBAP*

Figure 12 shows the changes of the electronic spectrum of the zinc complex during the reduction process in a thin-layer cell. The isosbestic points are observed at 350 confirming that the electrode reaction proceeds in a quantitative fashion and therefore the absence of any coupled chemistry [39–44]. The intensity of the band at 324 nm increased and a new broad band in low intensity formed at about 438 nm in the time scale of applied potential at $E_{app} = -1.45$ V (this process completed in about 300 s).

Experimental

Physical Measurements

Elemental analysis was carried out on a LECO CHNS model 932 elemental analyzer. The results agreed favorably with the calculated values. ^{1}H NMR and ^{13}C NMR spectra were recorded using a model Brucker Avance DPX-400 NMR spectrometer. IR spectra were recorded on a Perkin Elmer Spectrum RX1 FTIR spectrometer on KBr discs in the wavenumber range of 4000–400 cm^{-1}. The electronic spectra of the complexes in UV-Vis region were recorded in *DMF* solutions using a Shimadzu Model 160 UV-Vis spectrophotometer. Molar conductivity was measured with a WTW LF model 330 conductivity meter, using prepared solutions of the complex in *DMF:DMSO* (1:1). LC/MS-API-ES mass spectra were recorded using an Agilent model 1100 MSD mass spectrophotometer. Cyclic voltammograms were carried out using CV measurements with Princeton Applied Research Model 2263 potentiostat controlled by an external PC. A three electrode system (BAS model solid cell stand) was used for CV measurements in *DMSO* and consisted of a 2 mm sized platinum disc electrode as working electrode, a platinum wire counter

electrode, and an Ag/AgCl reference electrode. The reference electrode was separated from the bulk solution by a fritted-glass bridge filled with the solvent/supporting electrolyte mixture. The ferrocene/ferrocenium couple (Fc/Fc^+) was used as an internal standard but all potentials in the paper are referenced to the Ag/AgCl reference electrode. Solutions containing the complex were deoxygenated by a stream of high purity nitrogen for at least 5 min before running the experiment and the solution was protected from air by a blanket of nitrogen during the experiment. Controlled potential electrolysis (CPE) was performed with Princeton Applied Research Model 2263 potentiostat/galvanostat. A BAS model electrolysis cell with a fritted glass to separate the cathodic and anodic portions of the cell was used for bulk electrolysis. The sample and solvent were placed into the electrolysis cell under nitrogen. UV-Vis spectroelectrochemical experiments were performed with a home-built thin-layer cell that utilized a light transparent platinum gauze working electrode. Potentials were applied and monitored with a Princeton Applied Research Model 2263 potentiostat. Time- and potential-resolved UV-Vis spectra were recorded on Agilent Model 8453 diode array spectrophotometer. A Unicam model 929 atomic absorption spectrophotometer was used for the determination of the concentration of a metal in aqueous solution. A Toledo model *pH* meter equipped with a Toledo 413 combined glass electrode was used to determine the *pH* values. Magnetic moments were determined on a Sherwood Scientific magnetic moment balance (Model No: MK1) at room temperature (23°C) using Hg[Co(SCN)$_4$] as a calibrant: diamagnetic corrections were calculated from *Pascal*'s constants [24].

Materials

1,7-Bis(2-formylphenyl)-1,4,7-trioxaheptane was prepared by the literature method [25, 26]. All the other chemicals and solvents were of analytical grade and used as received.

Synthesis and Spectral Characterization of N,N′-Bis(2-aminothiophenol)-1,7-bis(2-formylphenyl)-1,4,7-trioxaheptane ($C_{30}H_{30}N_2O_3S_2$)

A solution of 2-aminothiophenol (20.00 mmol, 2.5 g) in 50 cm^3 absolute ethanol was added dropwise over 2 h to a stirred solution of 1,7-bis(2-formylphenyl)-1,4,7-trioxaheptane (10.00 mmol, 3.14 g) dissolved in 50 cm^3 warm absolute ethanol. A solid mass separated out on cooling, which was kept in a refrigerator for better crystallization. It was then filtered off and recrystallized from a mixture of absolute ethanol-*DMF*. Yield 3.43 g (65%), light yellow, mp 132–135°C; IR: $\bar{\nu} = 3331$ (N$^+$H), 3053 (Ar–CH), 2926, 2872 (Aliph–CH), 1599 (C=N), 1485, 1452 (Ar–C=C), 1290, 1250 (Ar–O), 1162, 1114, 1050 (R–O), 752, 696 (C–S) cm^{-1}; ^{13}C NMR: $\delta = 68.64$ (CH_2–OCH$_2$), 69.82 (CH_2–OC$_6$H$_4$), 163.03 (CH=N), 112.73, 121.17, 121.48, 122.61, 122.8, 124.61, 125.89, 129.72, 131.74, 136.09, 152.12, 156.42 (Ar–Cs) ppm; ^{1}H NMR: $\delta = 4.24$ (t, 4H, $J = 4$ Hz, CH_2–OCH$_2$), 4.4 (d, 4H, $J = 4$ Hz, CH_2–OC$_6$H$_4$), 7–8.1 (m, 16H, $J = 8$ Hz, Ar–H), 8.5 (s, CH=N) ppm; MS: $m/z = 527.1$ [L − H]$^+$ (M$_A$: 528 g/mol); UV-Vis (ε): $\lambda = 228$ (48270), 297 (17440), 322 (23520) nm (M^{-1} cm^{-1}) (in ethanol); $\lambda = 251$ (13500), 286

(21680), 323 (13500) nm (M^{-1} cm^{-1}) (in chloroform); $\lambda = 295$ (27680), 322 (38540) nm (M^{-1} cm^{-1}) (in *DMF*).

Synthesis of La(III), Cu(II), Ni(II), and Zn(II) Complexes

To a stirred solution of 1,7-bis(2-formylphenyl)-1,4,7-trioxa-heptane (1.5 mmol, 0.47 g) and 2-aminothiophenol (3 mmol, 0.38 g) in 40 cm^3 methanol was added dropwise metal acetate (1.5 mmol) in 40 cm^3 methanol. After the addition was completed, the stirring was continued for 2 h. A colored precipitation was filtered off, washed with CH_3COOH and diethyl ether, and then dried in air.

Spectral Characterization of La(III) Complex

($C_{30}H_{28}LaN_3O_6S_2$)

Yield 0.55 g (55%), dark yellow, mp 163–165°C; IR: $\bar{\nu} =$ 3058 (Ar–CH), 2923, 2866 (Aliph–CH), 1582 (C=N), 1497, 1446 (Ar–C=C), 1291, 1246, (Ar–O), 1143, 1115, 1051 (R–O), 751, 727, 694, 660 (C–S), 446 (La–N) cm^{-1}; MS: $m/z = 553$ [[La(*L*)(NO$_3$)]–[O(CH$_2$)$_2$O(CH$_2$)$_2$O]–(NO$_3$)]$^+$ (M$_A$: 727 g/mol); UV-Vis (ε): $\lambda = 298$ (27400), 323 (36280) nm (M^{-1} cm^{-1}); $\Lambda_M = 1.6$ $\Omega^{-1} \cdot$ mol$^{-1} \cdot$ cm^2; $\mu_{eff} =$ Dia.

Spectral Characterization of Cu(II) Complex

($C_{30}H_{28}CuN_2O_3S_2$)

Yield 0.73 g (82%), black, mp 201–202°C; IR: $\bar{\nu} = 3058$, (Ar–CH), 2938, 2873 (Aliph–CH), 1598, 1559 (C=N), 1482, 1452, (Ar–C=C), 1290, 1250 (Ar–O), 1160, 1116, 1055 (R–O), 754, 695, 668 (C–S), 475, 458 (Cu–N) cm^{-1}; MS: $m/z = 523$ [Cu(*L*)–(CH$_2$)$_2$O(CH$_2$)$_2$ + 5H]$^+$ (M$_A$: 590 g/mol); UV-Vis (ε): $\lambda = 277$ (1684), 321 (18020), 478 (3020) nm (M^{-1} cm^{-1}); $\Lambda_M = 6.8$ $\Omega^{-1} \cdot$ mol$^{-1} \cdot$ cm^2; $\mu_{eff} = 1.93$ μB.

Spectral Characterization of Ni(II) Complex

($C_{30}H_{28}N_2NiO_3S_2$)

Yield 0.66 g (75%), brown, mp 172–174°C; IR: $\bar{\nu} = 3072$ (Ar–CH), 2867 (Aliph–CH), 1596, 1582 (C=N), 1497, 1446, 1431 (Ar–C=C), 1291, 1257 (Ar–O), 1162, 1116, 1052 (R–O), 752, 727, 695, 661 (C–S), 456 (Ni–N) cm^{-1}; ^{1}H NMR: $\delta = 4.0$ (t, 4H, $J = 4$ Hz, CH_2–O–CH_2), 4.50 (t, 4H, $J = 5.2$ Hz, CH_2–OC$_6$H$_4$), 6.2–7.6 (m, 16H, $J = 8$ Hz, Ar–*H*), 8.17 (s, *H*C=N) ppm; MS: $m/z = 571$ [Ni(*L*)–(CH$_2$)]$^+$ (M$_A$: 587.4 g/mol); UV-Vis (ε): $\lambda = 275$ (25940), 841 (14380) nm (M^{-1} cm^{-1}); $\Lambda_M = 4.1$ $\Omega^{-1} \cdot$ mol$^{-1} \cdot$ cm^2; $\mu_{eff} =$ Dia.

Spectral Characterization of Zn(II) Complex

($C_{30}H_{28}N_2O_3S_2Zn$)

Yield 0.8 g (90%), orange, mp 108–110°C; IR: $\bar{\nu} = 3088$, 3038 (Ar–CH), 1589, 1573, 1549 (C=N), 1466, 1436 (Ar–C=C), 1297, 1261 (Ar–O), 1155, 1065 (R–O), 746, 724, 702, 687 (C–S) cm^{-1}; ^{13}C NMR: $\delta = 68.65$ (CH_2–OCH$_2$), 69.83 (CH_2–OC$_6$H$_4$), 163.42 (*C*H=N), 112.74, 121.16, 121.49, 122.62, 122.79, 124.60, 125.88, 129.73, 131.74, 136.08, 152.12, 156.42 (Ar–*C*s) ppm; ^{1}H NMR: $\delta = 4.2$ (t, 4H, $J = 4.8$ Hz, CH_2–O–CH$_2$), 4.4 (t, 4H, $J = 5.2$ Hz, CH_2–OC$_6$H$_4$), 7.0–8.1 (m, 16H, $J = 7.3$ Hz, Ar–*H*), 8.59 (s, 2H, *H*C=N) ppm; MS: $m/z = 592$ [Zn(*L*)]$^+$ (M$_A$: 594.07 g/mol); UV-Vis (ε): $\lambda = 324$ (30100) nm (M^{-1} cm^{-1}); $\Lambda = 0.7$ $\Omega^{-1} \cdot$ mol$^{-1} \cdot$ cm^2; $\mu_{eff} =$ Dia.

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