The Synthesis and Characterization of a Novel *vic*-Dioxime and its Mononuclear Complexes Bearing an 18-Membered N$_2$O$_2$S$_2$ Macrocycle and Their Characteristics as Extractants for Transition Metal Ions

HALİT KANTEKİN, ÜMMÜHAN OCAK, YAŞAR GÖK* and İRFAN ACAR
Department of Chemistry, Karadeniz Technical University, 61080-Trabzon, Turkey

Abstract

A new (E, E)-dioxime (**H$_2$L**) containing a diazadioxadithia macrocyclic moieties has been synthesized by reaction of an aromatic primary amine with cyanogendi-N-dioxide. The BF$_2^+$-capped Ni^{2+} mononuclear complex of this new oxime has been synthesized using a precursor hydrogen-bridged mononuclear Ni^{2+} complex. The solvent extraction of transition metal cations by (**3**) and (**6**) with picrate anion into chloroform has been studied at 25 °C and UV-visible spectroscopy. The extractability and selectivity of transition metal picrates, (Pb^{2+}, Ni^{2+}, Co^{2+}, Cd^{2+}, Zn^{2+}, Cu^{2+}, Ag$^+$) has been evaluated. The structures of new compounds are identified by using elemental analysis, ^{1}H and ^{13}C-NMR, IR and MS spectral data.

Introduction

The chemistry of transition metal complexes with dioxime ligands has been studied and has also been the subject of several reviews [1, 3]. The presence of mildly acidic hydroxyl groups and slightly basic nitrogen atoms cause vicinal dioximes to become amphoteric ligands which form corrin type square-planar, square-pyramidal and octa-hedral complexes with transition metal cations [4]. *vic*-Dioximes and their metal complexes are of current interest for their physicochemical properties, reactivity patterns and potential applications in many important chemical processes in the areas of medicine [5, 6], bioorganic systems, catalysis, electrochemical, electrooptical sensors and semiconducting properties [7]. The complexes prepared by *vic*-dioximes have been extensively used for various purposes owing to the high stability of this compound, including model compounds for vitamin B$_{12}$ or trace metal analysis [8].

Synthetic macrocycles have been known for over 75 years, although a real spate of publications in this area was observed in the late 1960s [9]. In that period, more than 5000 macrocyclic compounds were reported, and since then their number has increased markedly from year to year. The "hard" ether-oxygen containing macrocycles shows a binding preference toward "hard" alkali and alkaline earth metal cation, but the incorporation of "soft" sulfide or amine linkages shifts their preference towards "soft" heavy metal cations [10].

The incoporation of a *vic*-dioxime unit into the macrocycle provides an efficient binding site for transition metal cations by forming of an MN$_4$ core with two additional hydrogen bridges [11]. The transition metal complexes of mixed-donors macrocyclic ligands have been subjects of great interest. The successful design and synthesis of ligands capable of forming heteronuclear complexes have been receiving world-wide attention since obtaining special effects in magnetic, optical and electrical properties [12, 13]. Examples of heteronucleating ligands that could serve as polytopic receptor molecules for binding or cobinding of metal ions and molecular substrates include molecules that contain various functionalities appended to porphyrins, phthalocyanines, salen centers, macrocyclic tetraamines [14] and dithia-diaza centers [15]. The relevance of bimetallic compounds to bioinorganic systems has been one of the reasons for the increase in the amount of research on polynuclear compounds [16]. Recovery of valuable metal pollutants from air and water is very important. Therefore, compound (**6**) (Scheme 1) may be used for this purpose. For example, silver can be selectively removed from industrial wastewater by solvent extraction. The results of extraction experiment show high selective extraction of silver over the other transition metals.

In our previous studies we have investigated the synthesis and characterization of various transition metal complexes of (E, E)-dioxime [17]. Recently, solvent extraction properties of 23-membered macrocyclic ionophore attached with BF$_2^+$-capped cobalt (III) which was also synthesized in our laboratory [18]. In the present work, we have prepared an 18-membered macrocyclic a new *vic*-dioxime ligand, which contains two oxygen, two nitrogen and two sulfur binding sites. We synthesized hydrogen-bridged and BF$_2^+$-bridged nickel(II) mononuclear complexes of this new

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* Author for correspondence.

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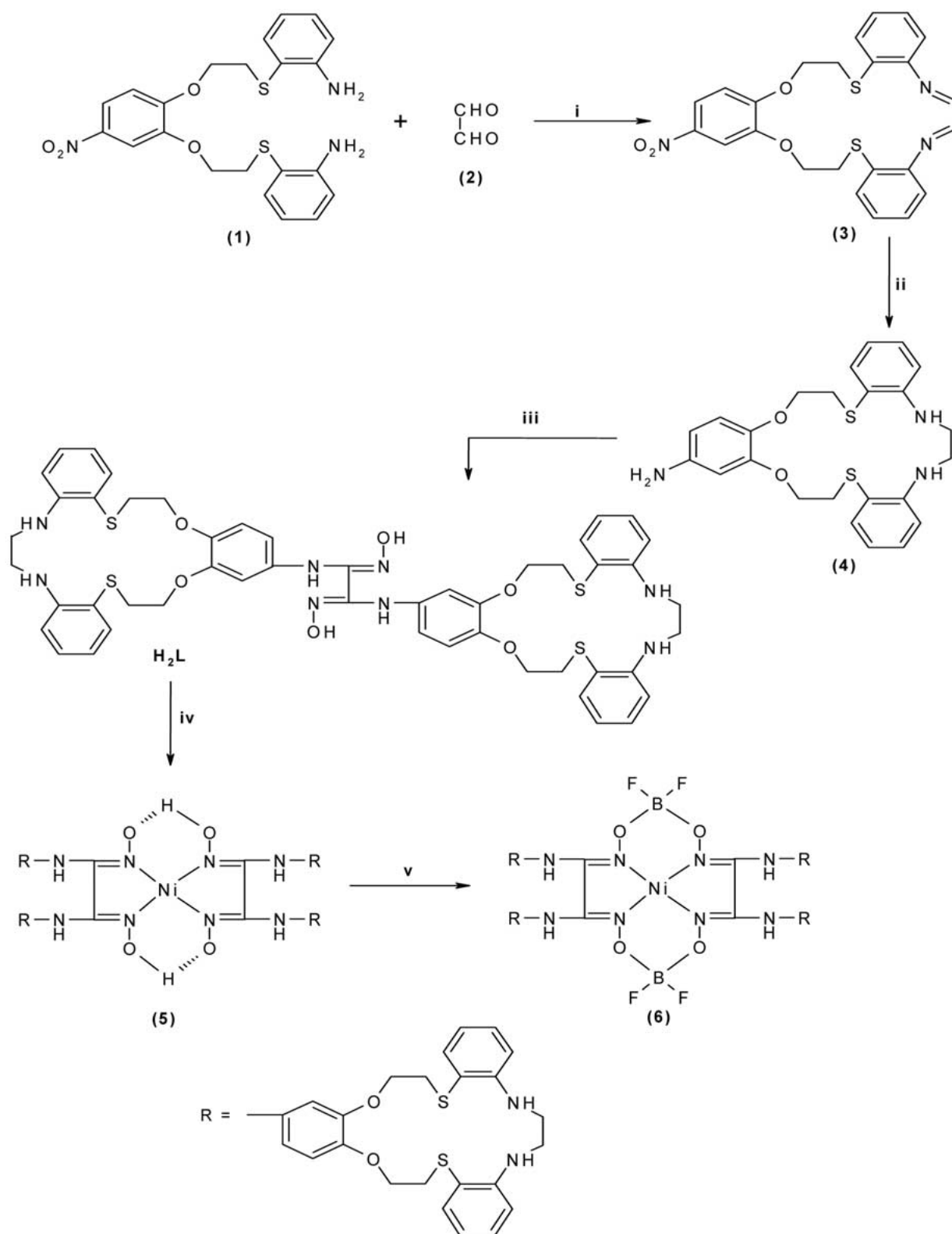
Scheme 1. Reagents and conditions: (i) in dry ethanol, under nitrogen atmosphere; (ii) 100% NH_2-NH-OH_2, 10% Pd/C, in *n*-buthanol at reflux temperature; (iii) cyanogen-di-N-oxide in CH_2Cl_2 at −10 °C; (iv) $NiCl_2 \cdot 6H_2O$ in EtOH at 60 °C; (v) $BF_3 \cdot Et_2O$ in dry acetonitrile under nitrogen atmosphere at reflux temperature.

(E, E)-dioxime and used compounds **(3)**, **(6)** in solvent extraction for some transition metal ions.

Experimental

^{1}H and ^{13}C-NMR spectra were recorded on a Varian Mercury 200 MHz spectrometer in DMSO-d$_6$, and chemical shifts are reported (δ) relative to Me$_4$Si as internal standard. Routine IR spectra were recorded on a Perkin-Elmer 1600 Fourier transform infrared spectrometer as KBr pellets. Mass spectra were measured on a Varian 711 and VG Zapspec spectrometer. Elemental analyses and metal contents of these compounds were determined by a Leco Elemental Analyser (CHNS 0932) and a Unicam 929 AA spectrophotometer. Melting points were measured on an Electrothermal apparatus and were uncorrected. (E, E)-dichloroglyoxime was prepared according to the reported procedure [19]. Commercially available pure solvents, dried and purified by conventional procedure [20] were used. For the two ligands (3, 6), a whole geometrical op-timization has been carried out by using semi-empirical AM1 [21] method and their stable conformations have been defined. According to the obtained results their cavity radii have been calculated. All computations were made with HYPERCHEM 6.2 programme on an HP Pentium-III 800 computer.

Synthesis of 2,3-(4′-nitrobenzo)-8,9: 14,15-dibenzo-7,16-dithia-1,4-dioxa-10,13-diazacyclooctadecane-10,12-diene **(3)**

A solution of 2,3:14,15-dibenzo-8,9-(4′-nitrobenzo)-4,13-dithia-7,10-dioxa-1,16-diazahexadecane **1** [22] (3.56 g, 7.79 mmol) was dissolved in dry ethanol (300 mL) and purged under nitrogen atmosphere in a Schenk system connected to a vacuum-line at 40 °C. This solution was cooled to room temperature and a solution of glyoxal **2** (0.53 g, 7.79 mmol) in dry ethanol (45 mL) was added dropwise to this solution under a nitrogen atmosphere for 30 min. at –5 °C. The reaction was monitored by using TLC [silica gel (petroleum ether/ethyl acetate) (2:1)] and continued for 8 h at 75 °C then the solvent was removed to (10 mL) under vacuum and the reaction mixture was stirred for 24 h at room temperature. Water was added (10 mL) to the reaction mixture, whereupon a yellow solid precipitated. The solid product was filtered off, washed with cold ethanol and diethyl ether then dried *in vacuo*. The pale yellow solid product (2.51 g, 67.29%) was obtained by recrystallization from ethanol, mp 114–115 °C (dec.). IR (KBr pellets, cm^{-1}): 3058 (Ar–H), 2924–2879 (C–H), 1638 (C=N), 1006 (N–O); ^{1}H-NMR (DMSO-d$_6$): (δ) 8.18 (s, 2 H, CH=N), 7.85–7.80 (d, H, Ar–H), 7.50 (s, H, Ar–H), 7.38–7.45 (d, H, Ar–H), 7.32–7.21 (d, 2 H, Ar–H), 7.18–7.10 (t, 2 H, Ar–H), 6.95 (d, 2 H, Ar–H), 6.72 (t, 2 H, Ar–H), 4.18–4.12 (t, 4 H, –OCH$_2$), 3.32–3.20 (d, 4 H, –NCH$_2$), 3.08–3.01 (t, 4 H, SCH$_2$); ^{13}C-NMR (DMSO-d$_6$): (δ) 161.18, 154.12, 146.05, 139.80, 131.16, 129.10, 127.05, 118.15, 117.85, 116.20, 112.05, 68.20, 31.40. MS (EI): m/z = 479 [M]$^+$.

Anal. Calcd. for C$_{24}$H$_{21}$N$_3$O$_4$S$_2$: C, 60.12; H, 4.38; N, 8.76. Found: C, 60.31; H, 4.20; N, 8.95.

2,3-(4′-Aminobenzo)-8,9:14,15-dibenzo-7,16-dithia-1,4-dioxa-10,13-diazacyclooctadecane **(4)**

The new Schiff base **3** (2.42 g, 5.05 mmol) was dissolved in *n*-butanol (150 mL) under a nitrogen atmosphere at 80 °C. Then the solution was cooled to 50 °C. The (10%) palladium/activated carbon (0.37 g) was added to this solution at the same temperature and allowed to stand at reflux temperature, and then 3.05 mL of hydrazine hydrate (100%) was added dropwise for 35 min. The reaction mixture was refluxed and stirred for 1.5 h. Then the hot solution was filtered and washed with *n*-butanol (10 mL). The pale yellow solution was concentrated to (25 mL) under reduced pressure and solution was placed in a refrigerator for 8 h at –5 °C. After filtration of the reaction mixture, the pale yellow solid was washed with cold ethanol, the ethyl ether and then dried *in vacuo*. The pale yellow product was crystallized from hot ethanol under a nitrogen atmosphere. The pale yellow solid (1.55 g, 67.68%) was obtained, mp 90–92 °C. IR (KBr pellets, cm^{-1}): 3449 (N–H), 3380–3355 (NH$_2$), 3052 (Ar–H), 2918–2848 (C–H), 1610 (N–H); ^{1}H-NMR (DMSO-d$_6$): (δ) 7.88–7.85 (d, H, Ar–H), 7.83–7.80 (d, H, Ar–H) 7.63 (s, H, Ar–H), 7.32–7.25 (d, H, Ar–H), 7.16 (d, 2 H, Ar–H), 7.04–6.95 (t, 2 H, Ar–H), 6.68–6.62 (d, 2 H, Ar–H), 6.45–6.48 (t, 2 H, Ar–H), 6.25 (s, 2 H, NH), 5.40 (s, 2 H, NH), 4.15–4.10 (t, 4H, –OCH$_2$), 3.42–3.28 (d, 4 H, –NCH$_2$), 3.13–3.08 (t, 4 H, –SCH$_2$); ^{13}C-NMR(DMSO-d$_6$): (δ) 153.65, 148.19, 146.28, 140.16, 135.30, 129.63, 118.10, 116.35, 114.80, 111.92, 108.30, 67.83, 47.57, 31.66. MS (EI): m/z = 453 [M]$^+$.

Anal. Calcd. for C$_{24}$H$_{27}$N$_3$O$_2$S$_2$: C, 63.57; H, 5.96.38; N, 9.27. Found: C, 63.69; H, 5.80; N, 9.06.

N,N′-bis[2,3-(4′-aminobenzo)-8,9;14,15-dibenzo)-7,16-dithia-1,4-dioxa-10,13-diazacyclooctadecane] iaminoglyoxime **(H$_2$L)**

A solution of cyanogendi-N-dioxide in dichloromethane (50 mL), prepared (E, E)-dichloroglyoxime (0.260, 1.65 mmol) in dichloromethane (50 mL) with an aqueous solution of Na$_2$CO$_3$ (0.5 M, 50 mL) in refrigerated bath at –10 °C, was added to a solution of 4 (1.5 g, 3.31 mmol) in dichloromethane (50 mL) at the same temperature. The reaction mixture was stirred at –10 °C for 12 h, and then evaporated to (15) mL under the reduced pressure. The reaction mixture was cooled to –15 °C in refrigerator overnight, giving a pale yellow solid. After filtration of the reaction mixture, the solid product was washed with cold ethanol, diethyl ether and dried *in vacuo*. The solid product was dissolved in ethanol (5 mL) and then purified by using column chromatography [silica gel (ethanol/chloroform) (3:1)]. The solid product (0.89 g, 54.26%) was obtained by crystallization from an ethanol-chloroform mixture (2:1), mp 165–167 °C (dec.). IR (KBr pellets, cm^{-1}): 3344 (N–H), 3258 (O–H), 3055 (Ar–H), 2980–2878 (C–H), 1640 (C=N), 1608 (NH$_2$), 941 (N–O); ^{1}H-NMR (DMSO-d$_6$): (δ) 10.42 (s, 2 H, OH),

8.35 (s, 2 H, NH), 7.45 (s, 2 H, Ar–H), 7.20–7.12 (d, 2 H, Ar–H), 6.80–6.72 (d, 2 H, Ar–H), 6.50–6.45 (m, 16 H, Ar–H), 5.58 (s, 4 H, NH), 4.02–3.77 (t, 8 H, –OCH$_2$), 3.30–3.18 (t, 8 H, HNCH$_2$), 3.10–2.93 (t, 8 H, –SCH$_2$); ^{13}C-NMR (DMSO-d$_6$): (δ) 149.58, 147.61, 143.17, 142.70, 135.35, 129.50, 116.08, 114.76, 114.26, 112.09, 67.63, 48.05, 32.67. MS (FAB positive): m/z = 991 [M + 1]$^+$.

Anal. Calcd. for C$_{50}$H$_{54}$N$_8$O$_6$S$_4$: C, 60.60; H, 5.45; N, 11.31. Found: C, 60.43; H, 5.67; N, 11.09.

Synthesis of the nickel(II) complex **[Ni(HL)$_2$] (5)**

A solution of NiCl$_2$·6H$_2$O (0.049 g, 0.207 mmol) in ethanol (25 mL) was added to a hot solution of **H$_2$L** (0.41 g, 0.414 mmol) in ethanol (50 mL) and was continuously stirred. The color of the solution turned immediately into reddish brown and a decrease in pH was observed. Therefore, the pH of the mixture was adjusted to about 4.50 by addition of KOH (0.1 M). The reaction mixture was kept at 60 °C on a water bath for 2 h. Then it was brought to room temperature and the brown solid product was filtered off. The brown solid product (0.251 g, 59.76%) was washed with water, ethanol and diethyl ether and dried *in vacuo*. mp 255–258 °C (dec). IR (KBr pellets, cm^{-1}): 3409 (N–H), 3062 (Ar–H), 2920–2847 (C-H), 1685 (O...H–O), 1640 (C=N) 1611 (N–H), 1013 (N–O); ^{1}H-NMR (DMSO-d$_6$): (δ) 16.45 (s, 2 H, O...H–O), 8.56 (s, 2 H, NH), 7.62 (s, 2 H, Ar–H), 7.23–7.14 (d, 2 H, Ar–H), 6.80–6.75 (d, 2 H, Ar–H), 6.51–6.45 (m, 16 H, Ar–H), 5.56 (s, 4 H, NH), 4.12–3.77 (t, 16 H, –OCH$_2$), 3.32–3.10 (t, 16H, HNCH$_2$), 3.01–2.94 (t, 16 H, –SCH$_2$); ^{13}C-NMR (DMSO-d$_6$): (δ) 150.97, 148.83, 142.14, 139.47, 136.42, 133.92, 128.47, 127.68, 122.12, 119.57, 67.63, 47.90, 32.67. MS (FAB positive): m/z = 2037 [M + 1]$^+$.

Anal. Calcd. for [C$_{100}$H$_{106}$N$_{16}$O$_{12}$S$_8$Ni]: C, 58.91; H, 5.20; N, 10.99; Ni, 2.88. Found: C, 59.12; H, 5.34; N, 10.72; Ni, 2.74.

Synthesis of the nickel(II) complex **[Ni(LBF$_2$)] (6)**

The suspension of **5** (0.200 g, 0.098 mmol) in freshly distilled acetonitrile (20 mL) was brought to the reflux temperature under a nitrogen atmosphere. Boron trifluoride diethyl ether complex (0.049 mL, 0.0196 mmol) in acetonitrile (1.5 mL) was slowly added to suspension. The reaction mixture was completely dissolved and turned into dark red within 15 min. After the color changed, the mixture was refluxed 1 h further and solvent was removed to dryness under reduced pressure. Then the residue was disolved in acetonitrile (5 mL) and evaporated to dryness. The last step was repeated twice and the reaction mixture was allowed to stand –18 °C in a refrigerator for 10 h. The dark brown product (0.12 g, 57.42%) was filtered off, washed with cold acetonitrile and diethyl ether and dried *in vacuo*, mp 208–210 °C. IR (KBr pellets, cm^{-1}): 3437 (N–H), 3068 (Ar–H), 2926–2878 (C–H), 1645 (C=N), 1611 (N–H), 1016 (N–O); ^{1}H-NMR (DMSO-d$_6$): (δ) 9.40 (s, 2 H, NH), 7.85 (s, 2 H, Ar–H), 7.48–7.30 (d, 2 H, Ar–H), 7.25 (d, 2 H, Ar–H), 6.80–6.45 (m, 16 H, Ar–H), 5.68 (s, 4 H, NH) 4.18–3.78 (t, 8 H,

OCH$_2$), 3.35–3.10 (t, 8 H, HNCH$_2$), 3.08–2.96 (t, 8 H, –SCH$_2$). MS (FAB positive): m/z = 2131 [M + 1]$^+$.

Anal. Calcd. for C$_{100}$H$_{104}$N$_{16}$O$_{12}$S$_8$B$_2$F$_4$Ni: C, 56.27; H, 4.87; N, 10.50; Ni, 2.75. Found: C, 56.10; H, 5.03; N, 10.75; Ni, 2.59.

Solvent extraction

Chloroform, picric acid, AgNO$_3$, Pb(NO$_3$)$_2$, Cd(NO$_3$)$_2$, Cu(NO$_3$)$_2$, Zn(NO$_3$)$_2$, Ni(NO$_3$)$_2$, Co(NO$_3$)$_2$ were analytical grade reagents. Chloroform was washed three times with distilled water before use in order to prevent volume changes of the phases during extraction.

A chloroform solution (10 mL) of ligand and an aqueous solution (10 mL) containing 2.5×10^{-5} M picric acid and 1×10^{-2} M metal nitrate were shaken at 25 °C ±0.1 for 1 h. This period of shaking was enough to establish equilibrium between the two phases. The phases were then left for 2 h to separate and clarify. The range of the ligand was from 7.5×10^{-6} M to 1.2×10^{-4} M. The concentration of picrate ion re-maining in the aqueous phase was then determined spectrophotometrically at 355 nm. In blank experiments, for the metal cations no detectable extraction was found in the absence of crown ether. The extractability was determined based on the absorbance of picrate ion in the aqueous solutions. The extractability was calculated from Equation (1),

$$E(\%) = [(A_0 - A)/A_0] \times 100, \qquad (1)$$

where A_0 is the absorbance in the absence of ligand. A denotes the absorbance in the aqueous phase after extraction. The spectrophotometric measurements were made with unicam model UV2 UV-visible spectrophotometer. Grant model SS 30 type shaker with thermostat was used.

Results and discussion

Compound **(3)** was synthesized by reaction of 2,3:14,15-dibenzo-8,9-(4′-nitrobenzo)-4,13-dithia-7,10-dioxa-1,16-diazahexadecane **(1)** [22] with glyoxal **(2)** in dry ethanol under nitrogen atmosphere under high dilution conditions [23]. In the ^{1}H-NMR spec-trum of **(3)**, there is a singlet at $\delta = 8.18$ ppm for the protons of azomethine groups indicating the formation of a Schiff base. The absence of primary aromatic amine groups belonging to compound **(1)** supports the purposed structure. The proton-decoupled ^{13}C-NMR spectrum for schiff base **(3)** is in accordance with the proposed structure. The chemical shift observed at $\delta = 161.18$ ppm corresponds to azomethine carbons. In the IR spectrum of this compound, the stretching vibrations at 1638 cm^{-1}, confirms the presence of imine groups and the absence of carbonyl and aromatic primary amine groups of the starting metarials. The result of the mass spectral data at m/z = 479 confirms the formation of desired compound.

The aromatic primary amine **(4)** was obtained by reduction of **(3)** in butanole using 10% palladium/activated charcoal and hydrazine hydrate (100%) at 125 °C [24]. In

the ^{1}H-NMR spectrum of (**4**), there are singlets at $\delta = 5.40$ and 6.25 ppm belonging to secondary and primary aromatic protons, respectively. These protons can be easily identified by deuterium exchange. The proton-decoupled ^{13}H-NMR spectrum of (**4**), displayed a new resonance at $\delta = 47.57$ ppm indicating formation of methylene carbon. Formation of methylene groups, secondary and primary aromatic amine groups support the formation of the desired compound. In the IR stretching and bending vibrations belonging to secondary and primary aromatic amine groups are observed 3449, 3380–3355 and 1610 cm^{-1}, respectively. The mass spectra data at m/z = 453 indicates the formation of (**4**).

(E, E)-Dioxime containing an 18-membered $N_2O_2S_2$ macrocyclic [**H$_2$L**] was synthesized according to the reported procedure [25] which involves the reaction of (**4**) with cyanogendi-N-dioxide in dichloromethane at −10 °C for 12 h (Scheme 1). In the ^{1}H-NMR spectrum of **H$_2$L**, the singlet at $\delta = 6.25$ ppm belonging to precursor compound (**4**) disappeared and new chemical shifts at $\delta = 8.12$ ppm and $\delta = 10.42$ were observed, which could be assigned to NH which is connected to oxime group and = N–OH protons, respectively. The deuterium exchange properties of these protons also showed the formation of the target compound. The resonance was observed at 142.70 ppm, in the ^{13}C-NMR spectrum of this new (E, E)-dioxime belonging to azomethine carbon atoms [15]. The equivalent carbon and proton resonance related to hydrox-imino groups can be attributed to the oxime groups which are in the (E, E)-form [26]. In the IR spectrum of **H$_2$L**, the new characterized absorptions belonging to NH, OH and C=N groups are observed 3344, 3258, 1640 cm^{-1} respectively, which are in agree-ment with the desired (E, E)-dioxime. This was also supported by the presence of the characteristic molecular ion peak at m/z = 991 [M + 1]$^+$ in the mass spectrum obtained using the FAB technique.

The Ni(II) hydrogen bridged complex (**5**) was synthesized by reaction of H$_2$L with NiCl$_2$.6H$_2$O. The mononuclear Ni(II) hydrogen bridged complex has a metal:ligand ratio of 1:2 according to the elemental analysis data. In this mononuclear complex, the metal is coordinated by the N,N′-atoms of the dioxime (Scheme 1). The ^{1}H-NMR spectrum of (**5**) provides the most useful evidence for desired the square-planar-Ni(II) complex. The disappearance of chemical shift at $\delta = 10.42$ ppm belonging to = NOH group and the existence of intra-molecular H-bridge protons observed at lower field, at $\delta = 16.60$ ppm indicate the formation of (**5**) [15]. The disappearance of the O–H stretching, vibrations and the shift of C=N resonance to lower frequency in the IR spectrum of [Ni(HL)$_2$] (**5**) can be attributed to N,N′-chelation [27]. The weak band assigned to the intramolecular hydrogen bonded (O–H$\cdots$O) bending vibrations was observed at 1685 cm^{-1}, which confirmed the formation of a complexation reaction. Upon coordination to Ni(II), the ligand resonances shift slightly; however their number is unchanged. The FAB mass spectrum of 5 exhibits an intense peak at m/z = 2037 [M + 1]$^+$, which is in accord with the proposed structure.

The template synthesis of the macrocyclic nickel(II) complex (**6**) was prepared by adding an equivalent amount of BF$_3$·Et$_2$O to an acetonitrile suspension of the hydro-gen-bonded precursor (**5**). The binding protons in proton-linked complex were replaced by BF$_2^+$ groups. In the ^{1}H-NMR spectrum of (**5**), the chemical shifts of O–H$\cdots$O protons belonging to proton-linked precursor disappear after the formation by BF$_2$-bridging macrocyclic complex (**6**). The NH protons belonging to hydroxyimino and an 18-membered macrocyclic ring were observed at $\delta = 9.45$ and $\delta = 8.56$ ppm, respectively. These signals can be identified by D$_2$O exchange. The IR spectrum of this complex exhibits upward shifts in the stretching vibrations of the C=N groups due to the strong electron-withdrawing effects of BF$_2^+$ groups incorporated in the macrocycles [28]. The result of the mass spectrum of this compound (**6**) at m/z = 2131 [M+1]$^+$ and elemental analysis data are in accordance with proposed structure.

Extraction of transition metal picrates

Binding abilities of compound (**6**) and of the monocyclic model compound (**3**) toward transition metal cations were evaluated by a picrate extraction method. Aqueous solutions of Pb^{2+}, Ni^{2+}, Co^{2+}, Cd^{2+}, Zn^{2+}, Cu^{2+} and Ag$^+$ picrates were extracted from water within to chloroform solutions of (**3**) and (**6**). Table 1 shows data concerning the percentage of the transition metal picrate extracted from aqueous phase.

As can be seen in Table 1, the extractability of transition metal picrates differs in Ag$^+$ $\gg$ Pb^{2+} (Cu^{2+} > Cd^{2+} > Co^{2+} > Zn^{2+} > Ni^{2+} order. However, it is seen that ligands are selective for the Ag$^+$ cation, and that it does not show the same characteristic for all transition metal cations other than the Ag$^+$ cation. While the Ag$^+$ extraction in the ligand of imine form (**3**) is 65.4%, it reaches 83% in the ligand of amine form (**6**) that has four macrocyclic units in the same molecule. Compound **6** is able to form polynuclear complexes with extracted metal ions. However, formation of such complexes with M^{2+} metal ions, due to electrostatic interaction seems to be less probable then in case of the 1$^+$ charged silver ions.

Considering that macrocycle in amine form (**6**), theoretically, having four times more cavity than macrocycle imine form (**3**), it could be understood that this compound (**6**) has a lower extraction ability than expected. Quantum mechanical calculations via semi-empirical AM1 [21] method indicated the distance of S–S and N–O as 5.23 and 6.46 Åin the amine form of macrocycle (**6**), whereas these values were calculated as 5.36 and 6.30 Åin the imine form of macrocycle (**3**). These results indicate that the cavity in the amine form (**6**) is more elliptic than the imine form (**3**) which seems cycler. It seems certain that such a formation effects complexation ability.

The hybridization of the donor atoms may effect the macrocyclic hole size. Relative to the corresponding macrocycle **6** containing sp^3-amine donor atoms, introduction of sp^2-imine donors into the macrocyclic ligand **3** leads to a reduction of the cavity hole size largerly. On the other hand, with sp^2 hybridization there is a prospect of metal-ligand p-bond formation in certain case, this will further shorten the metal-imine bond. Once again, the two effect are in op-

Table 1. Transition metal picrate extractions for monocyclic model compound (3) and BF_2^+-capped nickel(II) mononuclear complex (6) into chloroform[a]

Metal ion	Extractability[a,b] (%)		Selectivity[c] Ag^+/M^{2+}	
	(3)	(6)	(3)	(6)
Ag^+	65.4	83.0		
Pb^{2+}	8.2	10.4	21.29	41.87
Cd^{2+}	4.4	5.3	41.19	86.73
Zn^{2+}	1.9	2.8	99.73	167.48
Cu^{2+}	4.8	7.2	37.15	62.26
Co^{2+}	3.1	5.5	59.21	83.74
Ni^{2+}	0.8	2.0	236.8	242.85

[a]Temperature: $25 \pm 0.1\,°C$; aqueous phase (10 ml); $[pic^-] = 2.5 \times 10^{-5}$ M, organic phase (10 ml chloroform); $[L] = 1.25 \times 10^{-4}$ M.
[b]Defined as percent picrate extracted into the organic phase.
[c]Defined as D_{Ag}^+/D_M^{2+}, where D_{Ag}^+ and D_M^{2+} represent the distribution ratio of Ag^+ ion and M^{2+} ion, respectively.

position. The unsaturation in the macrocyclic ring may have major steric and electronic consequences for the nature of the ring. This property will result in loss of flexibility with a corresponding restriction of the number of possible modes of coordination. Further, loss of flexibility tends to be reflected in an enhanced "macrocyclic effect" [29].

To characterize the extraction ability, the dependence of the distribution ratio D of the cation between the two phases upon compound (3) concentration was examined. The general extraction equilibrium is assumed to be given by Equation (2),

$$M^{n+} + nPic_{aq}^- + x[L]_{org} \rightleftharpoons [M(Pic)_n (L)_x]_{org} . \quad (2)$$
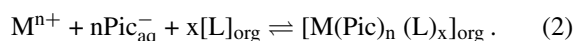
The overall extraction equilibrium constant is expressed as Equation (3),

$$K_{ex} = \frac{[M(Pic)_n(L)_x]}{[M^{n+}][Pic^-]^n[L]^x} . \quad (3)$$

The distribution ratio D would be defined by Equation (4),

$$D = \frac{[M(Pic^-)_n(L)_x]}{[(M^{n+})]} . \quad (4)$$

It follows that

$$D = K_{ex}[Pic^-]^n[L]^x, \quad (5)$$

$$Log\ D = \log K_{ex} + n \log[Pic^-] + \times \log[L]. \quad (6)$$

Figure 1 shows the extraction into chloroform at different concentrations of the ligand for Ag^+. A linear relationship between log D versus log[L] is observed. The slope of line is equal to 0.97 suggesting that the ligand forms a 1:1 complex with Ag^+. From both Equation (6) and the result shown in Figure 1, log $K_{ex} = 12.94$ for the extraction of silver (I) with compound (3) was calculated.
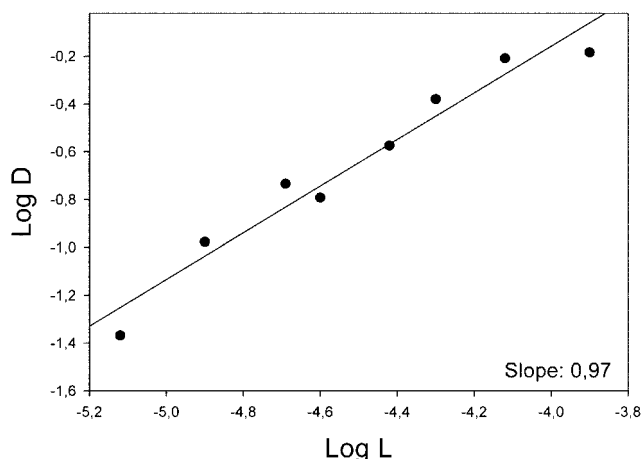

Figure 1. Plots of log D versus log[L] for Ag^+ compound (3).

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