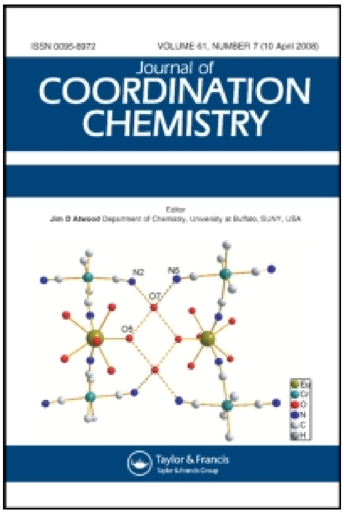


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

SYNTHESIS AND COMPLEXATION OF A NEW SEVEN MEMBERED HETEROCYCLIC *VIC*-DIOXIME

Sebnur Merey[a]; Özer Bekroğlu[a]
[a] Department of Chemistry, Technical University of Instanbul, Istanbul, Turkey

To cite this Article Merey, Sebnur and Bekroğlu, Özer(1996) 'SYNTHESIS AND COMPLEXATION OF A NEW SEVEN MEMBERED HETEROCYCLIC *VIC*-DIOXIME', Journal of Coordination Chemistry, 40: 3, 177 — 192

To link to this Article: DOI: 10.1080/00958979608024343

URL: http://dx.doi.org/10.1080/00958979608024343

J. Coord. Chem., 1996, Vol. 40, pp. 177–192
Reprints available directly from the publisher
Photocopying permitted by license only

SYNTHESIS AND COMPLEXATION OF A NEW SEVEN MEMBERED HETEROCYCLIC *VIC*-DIOXIME

SEBNUR MEREY and ÖZER BEKÂROĞLU*

Department of Chemistry, Technical University of Instanbul, 80626, Maslak, Istanbul, Turkey

(Received 22 January 1996)

A new seven membered heterocyclic ligand, 2,3-*bis* (hydroxyimino)-1,4-*bis* (2'-hydroxybenzyl)-1,4-diaza-cycloheptane, containing two phenolate-type pendant arms and two oxime groups, has been prepared. Mononuclear, tetranuclear, homo- and hetero- pentanuclear metal complexes of this ligand have been synthesized with Cu (II), Ni (II) and U (VI) O_2. The structures of the newly synthesized ligand and its complexes have been investigated. Protonation constants of the ligand and overall formation constants have been measured by potentiometric techniques.

Keywords: *vic*-dioximes; heterocycles; complexation; cyclic voltammetry; protonation constants

INTRODUCTION

The coordination chemistry of *vic*-dioximates is an intensive area of study and numerous transition–metal complexes of these ligands have been investigated.[1-2] The successful design and synthesis of ligands capable of forming multinuclear complexes are of great interest for obtaining special magnetic, optical and electrical properties. For these purposes, the ligands need to carry multidonor groups to be able to bind more to than one metal ion simultaneously.

In previous papers, we have shown that a quite useful approach to hetero-polynuclear compounds is to carry out the complexation reaction in a stepwise fashion which requires coordination of ligands containing at least two different donor sites of comparable coordination capability.[3]

---

*Author for correspondence.

Both *E,E*-dichloroglyoxime and cyanogen di-*N*-oxide have been used to prepare *vic*-dioxime derivatives.[4–5] The addition reaction of either of these two reactants with diamino compounds gives acyclic, heterocyclic or macrocyclic dioximes. We have long had an interest in the chemical behaviour of complexes containing a planar MN_4 core structure and additional donor sites.[6–7] While phthalocyanines or *vic*-dioximes have formed the central co-ordination site, crown ethers,[8–9] monoazacrown ethers,[10] cyclopentadienyl groups,[11] tetrathiamacrocycles[12] or tetraazamacrocyles[13] have been used to bind alkali or transition metal ions.

In the present paper, a new *vic*-dioxime ligand with two additional phenolic pendant arms has been synthesized with the aim of obtaining mono-, as well as, multinuclear complexes.

EXPERIMENTAL

Routine IR spectra were recorded on a Mattson 1000 FTIR spectrometer using KBr pellets and electronic spectra on a Varian DMS 90 spectrophotometer. ^1H NMR spectra were recorded on a Bruker 200 MHz spectrometer. Mass spectra were recorded on a VG Zabspec GC-MS spectrometer with fast atom bombardment. DSC measurements were carried out with Rigaku 8230B calorimeter. The metal contents of the complexes were determined using a Perkin Elmer Zeemen 3030 atomic absorption spectrophotometer with solutions prepared by decomposing the compounds in *aqua regia* and subsequent digestion in concentrated HCl.

Cyclic voltammograms were performed using an analytical cyclic voltammetry instrument (EG and G PARC Model 273), controlled by an external computer. A three electrode system with a saturated calomel reference electrode and a platinum wire counter electrode was used. The working electrode was a platinum plate. Voltammograms were recorded on X—Y recorder (RE 0091). Triplydistilled water and spectrosol grade DMSO, dried over 4Å molecular sieves, were used in the voltammetric experiments. Tetrabutylammonium perchlorate (0.1 M) was the supporting electrolyte in DMSO. Solutions were purged with nitrogen prior to each voltammetric measurement. Coulometric measurements were carried out at constant potentials corresponding to the CV peak potentials of the species.

Potentiometric titrations were carried out using a Metrohm E-415 dosimate and a Metrohm E-415 pH meter. A Metrohm 6.0204.000 combined glass electrode was used for pH and emf measurements. Ionic strength was kept constant at 0.1 M KCl. All titration solutions were prepared in a total volume of 20 cm^3 and thermostated at 25°C±0.1°C. The following solutions were prepared to obtain the pH titration curves: solution A: HCl (2.5 cm^3, 0.1 M), KCl (10 cm^3, 0.1 M), solution of H_4L in ethanol (2.5 cm^3, 0.01 M), ethanol (5 cm^3); solutions B—D: HCl (2.5 cm^3, 0.1 M), KCl

(10 cm^3, 0.1 M), solution of H_4L in ethanol (2.5 cm^3, 0.01 M), solution of metal salt in ethanol (2.5 cm^3, 0.01 M), ethanol (2.5 cm^3). The solutions were titrated with 0.1 M NaOH.

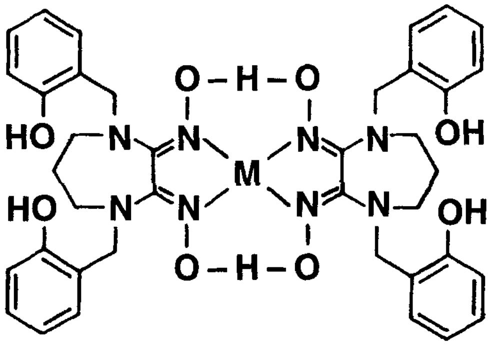
2, 6-Diaza-1, 7-*bis*(2′-hydroxyphenyl)heptane,[14–15] and *E,E*-dichloroglyoxime[16] were prepared according to reported procedures.

1,3-Bis(hydroxyimino)-1,4-bis(2′-hydroxybenzyl)-1,4-diaza-cycloheptane (H_4L)

A solution of *E,E*-dichloroglyoxime (0.55 g, 3.5 mmol) in ethanol (45 cm^3) was added dropwise to a solution of 2,6-diaza-1,7-*bis*(2′-hydroxyphenyl) heptane (1.0g, 3.5 mmol) in dichloromethane (80 cm^3) which also contained sodium hydrogen carbonate (1.47 g, 17.5 mmol) in excess at room temperature. After the reaction mixture was stirred at this for 4h, it was filtered. The filtrate was concentrated to *ca* 40 cm^3 and white crystals of the product formed as the filtrate cooled. The precipitate was filtered off, washed with water and ethanol and then diethylether and dried under vacuum (P_2O_5). This compound is soluble in hot ethanol, acetone, tetrahydrofurane, dioxane, DMF and DMSO. Yield: 0.77 g (60 %); m.p. 188°C; λ_{max}/nm (DMF) 276 (ε/m^{-1} cm^{-1} 2100).

Mononuclear nickel(II) or copper(II) complexes (1a or 1b)

When a solution of $NiCl_2.6H_2O$ (0.048 g, 0.21 mmol) or $CuCl_2.2H_2O$ (0.034 g, 0.2 mmol) in ethanol (12 cm^3) was added to a solution H_4L (0.15 g, 0.4 mmol) in hot ethanol



Complex	M
1a	Ni^{II}
1b	Cu^{II}

FIGURE 1 Mononuclear complexes **1a** and **1b**.

(25 cm^3) at 70°C, the colour of the solution became red and the pH dropped to 2.51, 0.1M KOH solution in ethanol was used to raise the pH to about 4.7 when precipitation of complex started. The mixture was heated on a water-bath for another 2 h during which time the precipitation was completed. The yellow Ni(II) or the pale green Cu(II) complex was filtered off, washed with water and ethanol and then diethylether and dried in vacuum at room temp. The complexes are soluble in tetrahydrofurane, DMF and DMSO.

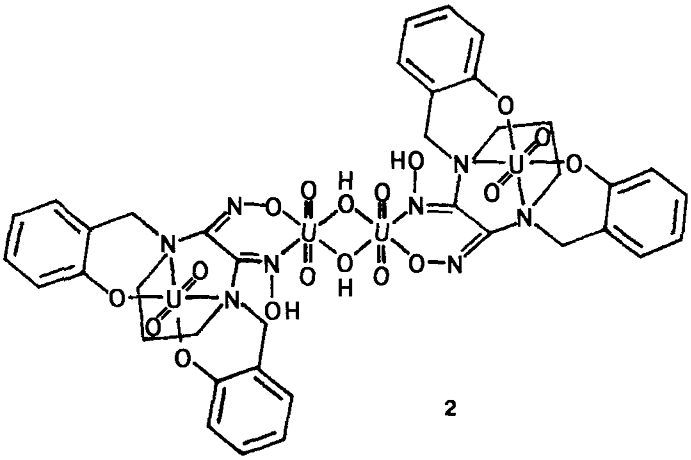
1a: Yield: 0.14 g (87%); λ_{max}/nm (DMF): 275 and 381 (ε /$m^{-1}cm^{-1}$: 14530 and 14550). **1b**: Yield: 0.14 (86%); λ_{max}/nm (DMF): 277 and 302 (ε /$m^{-1}cm^{-1}$: 60700 and 9700).

Tetranuclear uranyl (VI) O_2 complex (2)

To a solution of $\mathbf{H_4L}$ (0.1 g, 0.27 mmol) in hot ethanol (30 cm^3) was added a solution of $UO_2(AcO)_2.2H_2O$ (0.229 g, 0.54 mmol) in ethanol (30 cm^3) at 70°C. The colour of the solution turned red and the pH dropped to 4.4. When the pH was raised to 5.8 by addition of 0.1 M KOH solution in ethanol, precipitation of a reddish-orange complex started. The mixture was heated for two hours in order to complete precipitation. Product was filtered off, washed with ethanol and diethylether and dried. Yield: 0.22 g (88%;λ_{max}/nm (DMF): 284 (ε/$m^{-1}cm^{-1}$: 38920).

Homopentanuclear copper(II) complex (3)

To a solution of **1b** (0.1 g, 0.125 mmol) in tetrahydrofuran (15 cm^3) was added a solution of 1,10-phenanthroline (0.049 g, 0.25 mmol) in tetrahydrofuran (7 cm^3) and a solution of



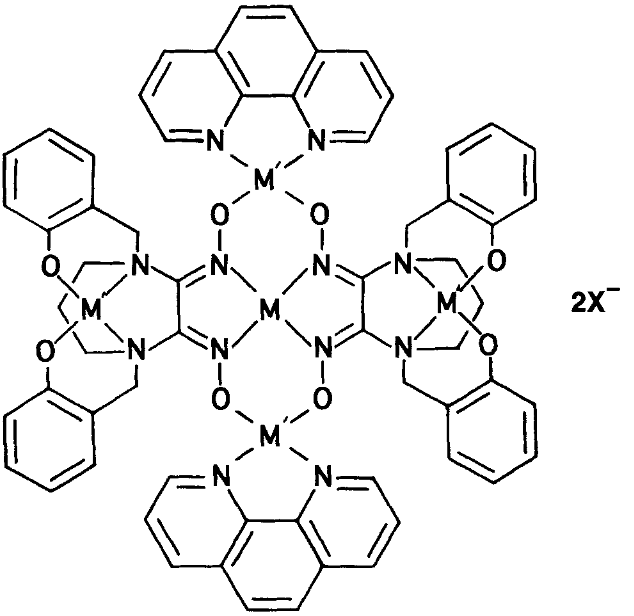
2

FIGURE 2 Tetranuclear U(VI)O_2 complex **2**.

Cu $(NO_3)_2.3H_2O$ (0.090 g, 0.5 mmol) in tetrahydrofurane (5 cm^3). The mixture was stirred and heated at reflux. After 5h, the volume of the reaction mixture was reduced to 10 cm^3 on a rotary evaporator and diethylether was slowly added with continuous stirring to the precipitated complex. The precipitate was filtered off, washed with water, hot and cold tetrahydrofuran and diethylether and dried in vacuum (P_2O_5). The brown-green complex is soluble in DMF and DMSO. Yield: 0.077 g (40%); λ_{max}/nm (DMF): 277, 302, 380 and 482 (ε/$m^{-1}cm^{-1}$: 43100, 39000, 14500 and 700).

Heteropentanuclear nickel(II) and copper(II) complex (4)

The dark green complex was synthesized in a similar manner to 3 by starting with **1a** (0.079 g, 0.099 mmol), $Cu(NO_3)_2.3H_2O$ (0.071 g, 0.396 mmol) and 1, 10-phenanthroline (0.039 g, 0.198 mmol). It is soluble in DMF and DMSO. Yield: 0.072 g (47%); λ_{max}/nm (DMF): 275, 380 and 460 (ε/$m^{-1}cm^{-1}$ 40860, 30900 and 5200).



Complex	M	M′	X
3	Cu^{II}	Cu^{II}	NO_3
4	Ni^{II}	Cu^{II}	NO_3
5	Ni^{II}	$U^{VI}O_2$	AcO

FIGURE 3 Pentanuclear complexes 3, 4 and 5.

Heteropentanuclear nickel(II) and uranyl(VI)O_2 complex (5)

1a (0.1 g, 0.125 mmol) was dissolved in tetrahydrafuran (50 cm^3) with heating and stirring. A solution of 1,10-phenanthroline (0.049 g, 0.25 mmol) in tetrahydrofuran (20 cm^3) and a solution of $UO_2(AcO)_2.2H_2O$ (0.212 g, 0.5 mmol) in tetrahydrofuran (5 cm^3) was added to **1a**. The mixture was heated on a water-bath for 10 min, when precipitation of the complex started. After heating for another hour, the complex had precipitated completely. The orange precipitate was filtered off, washed first with water, then with hot and cold tetrahydrofuran and diethylether and dried in vacuum (P_2O_5). Yield: 0.260 g (88 %); λ_{max}/nm (DMF): 277 and 380 (ε/$m^{-1}cm^{-1}$ 40730 and 20500).

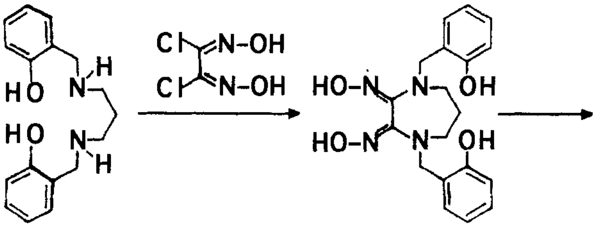
RESULTS AND DISCUSSION

A new *vic*-dioxime ligand, 2, 3-*bis*(hydroxyimino) - 1, 4-*bis*(2′ - hydroxybenzyl) - 1,4 diazacycloheptane, **H_4L**, has been prepared by a one-step reaction of *E, E* dichloroglyoxime (DCGO) with 2,6-diaza-1,7-*bis*(2′-hydroxyphenyl) heptane [14-15](Scheme). Excess of $NaHCO_3$ was added to the reaction mixture in order to neutralize HCl formed. Since the order of relative reactivity for the groups in the reaction with DCGO has been given as NH > SH > OH, DCGO preferred to react with NH instead of OH functions; a 7-membered heterocycle formed as a consequence of 1:1 condensation of the two reactants. Physical data and elemental analyses for **H_4L** and its metal derivatives are listed in Table I.

TABLE I Analytical data[a] for **H_4L** and its complexes

		Analysis (%)				
Compound	*Formula*	*C*	*H*	*N*	*M*	*M′*
H_4L	$C_{19}H_{22}N_4O_4$	61.46	6.06	14.92		
		(61.62)	(5.94)	(15.13)		
1a	$C_{38}H_{42}N_8O_8Ni$	57.17	5.19	14.26	7.17	
		(57.24)	(5.27)	(14.06)	(7.37)	
1b	$C_{38}H_{42}N_8O_8Cu$	56.47	5.16	13.76	7.79	
		(56.89)	(5.24)	(13.97)	(7.92)	
2	$C_{38}H_{40}N_8O_{18}U_4$	24.96	2.47	5.84	51.22	
		(24.67)	(2.16)	(6.06)	(51.52)	
3	$C_{62}H_{52}N_{14}O_{14}Cu_5$	48.74	3.47	12.91	20.10	
		(48.52)	(3.39)	(12.78)	(20.70)	
4	$C_{62}H_{52}N_{14}O_{14}NiCu_4$	48.77	3.39	12.60	3.23	16.26
		(49.67)	(3.40)	(12.82)	(3.84)	(16.62)
5	$C_{66}H_{58}N_{12}O_{20}NiU_4$	34.02	2.67	6.99	2.37	40.11
		(33.72)	(2.47)	(7.15)	(2.50)	(40.53)

[a]Required values are given in parentheses.



1a
1b
2
3
4
5

H_4L

SCHEME Synthesis of the *vic*-dioxime H_4L and its metal complexes.

In the IR spectrum of $\mathbf{H_4L}$, characteristic OH, C=N and NO streching vibrations have been observed at 3260, 1630 and 1040 cm^{-1}, respectively (Table II). These values are in agreement with those previously reported.[6, 8, 12] The broad band at 2500–2700 cm^{-1} in the spectrum of 2, 6-diaza-1, 7-*bis*(2′-hydroxyphenyl) heptane indicating the formation of hydrogen bonds between OH and NH groups[14] disappeared after its reaction with DCGO. In the ^{1}H NMR spectrum of $\mathbf{H_4L}$ (Table III), two protons which disappear on deuterium exchange were recorded around $\delta = 9.72$ and 9.0, the former corresponding to phenolic OH groups and the latter to oxime groups; a single chemical shift for oxime protons at such a low field indicates an *E,E*-structure for the *vic*-dioxime moiety.[17] No chemical shifts attributable to secondary amine groups were present.

This hexadentate ligand has two phenolic OH groups and two aza functions in the heterocyclic ring in addition to two oxime groups. Consequently, all or some of these donor groups can participate in complex formation, according to reaction conditions.

When the chloride salts of Ni(II) and Cu(II) were used in 1:2 (metal:ligand) ratio and the pH of the mixtures have raised to *ca* 4.7, mononuclear metal complexes **1a** and **1b** were obtained. In these square planar complexes four donor nitrogen

TABLE II IR data[a] (cm^{-1}) for **H4L** and its complexes

Compound	*OH*	*OH...O*	*C=N*	*OH*	*NO*	*Others*
$\mathbf{H_4L}$	3260		1630	1375	1040	
1a	3260	1710	1590	1375	1040	
1b	3380	1710	1590	1375	1040	
2	3230		1590	1360	1035	895(O=U=O)
3			1600–1580		1050	1380(NO_3)
4			1600–1580		1050	1380(NO_3)
5			1600–1580		1050	900(O=U=O) 1575(asym) (AcO) 1430 (sym)

[a] (KBr pellets).

TABLE III ^{1}H NMR data for $\mathbf{H_4L}$ and its complexes (in DMSO-d_6)

Fragment	H_4L	*1a*	2^a	5^b
CCH_2C	1.58(p,2H)	1.56 (p, 4H)	1.83 (p, 4H)	1.36(p,4H)
NCH_2C	3.14(t,4H)	2.94(t,8H)	2.59 (t, 8H)	2.86(t,8H)
$ArCH_2N$	4.30(s,4H)	4.53(s,8H)	3.86 (s,8H)	4.47(s,8H)
Aromatic	6.60–7.20 (m,8H)	6.70–7.20(m,16H)	6.44–7.35^c (m, 16H)	6.49–7.37^c(m,16H)
NOH^d	9.00(s,2H)		10.58(s,2H)	
$ArOH^d$	9.72(s,2H)	9.75(s,4H)		
O... HO^d		16.28(s,2H)		
phen				7.75 (q,4H) 7.97 (s, 4H) 8.49 (d, 4H) 9.08(s, 4H)

[a] The peak for μ–OH is at δ = 4.44 ppm. [b]The peak for acetate protons is at δ = 2.07 ppm .[c]Broad. [d]Disappears on deuterium exchange.

atoms of two *vic*-dioxime molecules coordinate with a metal ion and two hydrogen bridges bonds formed. In the IR spectrum of these mononuclear complexes, intramolecular hydrogen-bridged OH protons were observed at 1710 cm^{-1}. By comparison of the spectrum with that of the free ligand, a small shift to lower frequency (1590 cm^{-1}) is observed for the C$=$N vibration, consistent with *N,N*-chelate coordination.[6,8,18] As expected for a d^8 configuration in square planar field, complex **1a** is diamagnetic according to the NMR spectrum. In the ^{1}H NMR spectrum of **1a** the proton of the intramolecular hydrogen bond was found at lower field ($\delta = 16.28$). Phenolic OH protons which disappear on deuterium exchange were not much affected upon complex formation.

The tetranuclear U(VI)O_2 complex **2** was obtained by starting with any ratio of the ligand and the metal salt. In this complex, one uranyl ion is linked to phenolic and to aza groups of each ligand molecule, while the third and the fourth uranyl ion are coordinated through one nitrogen and one oxygen of each dioxime group in the two ligand molecules. In the IR spectrum of **2**, OH streching appear at 3230 cm^{-1}. The strong band at 895 cm^{-1} is the characteristic asymmetric streching mode of the O$=$U$=$O group.[6] The ^{1}H NMR spectrum of **2** shows a single chemical shift for the deuterium-exchangeable N—OH group ($\delta = 10.58$). There is also another deuterium-exchangeable signal at 4.44 ppm which can be assigned to μ-hydroxo groups coordinated to uranyl ions. These chemical shifts are in agreement with those previously reported for the binuclear complex with μ-hydroxo-bridges.[6,8,19] No chemical shifts attributable to phenolic OH groups were present.

All the pentanuclear complexes **3**, **4** and **5** have been synthesized by the reaction of an appropriate metal salt with mononuclear complexes **1a** or **1b** as the bridging ligand and 1,10-phenanthroline (*phen*) as an end-cap ligand at 4:1:2 mol ratio in tetrahydrofuran. In these complexes, while the second and third metal ions are coordinated with phenolic OH and aza groups,[20] other ions are coordinated to oxygens of the oximates and to nitrogens of the phenanthroline.[21] It is known that the oximate group (=N—O—) can function as a bridge between two metal ions through the imino nitrogen and the deprotonated oxygen to afford bi- and trinuclear complexes.[22] These types of complexes with double oximate bridges in a *cis* arrangement may be obtained by the use of glyoximate ligands. The metal-*bis*(glyoximate) dianion functions as a bridge between two metal (II) ions through its deprotonated oximate oxygens.

In the IR spectra of the pentanuclear complexes with phen, **3**, **4** and **5**, characteristic bands originating from phen are observed at 3030, 1515, 1460, 1100 and 720 cm^{-1}. The C=N bands due to the oxime groups and phen are observed as a combined band at 1600–1580 cm^{-1}. These complexes show no IR band attributable to OH...O vibration in the region 1600–2000 cm^{-1}, indicating that all dioxime oxygens are deprotonated. Additionally, the IR spectra of **3** and **4** indicate a single absorption at 1380 cm^{-1}, typical of uncoordinated nitrate anions. In the IR spectrum of **5** uncoordinated acetate ions give rise two bands: an asymmetric streching band at 1575 cm^{-1} and a symmetrical band at 1430 cm^{-1}. The former band is stronger and more characteristic.[23] The uranyl group band is at 900 cm^{-1}.

NMR measurements are precluded owing to the paramagnetic nature of complexes **3** and **4**. The characteristic features of the ^1H NMR spectrum of the diamagnetic $U(VI)O_2$ complex **5** are the disappearence of the phenolic OH protons and intramolecular hydrogen-bridged OH protons after pentanuclear complex formation. Protons of the acetate anions are observed at 2.07 ppm as a singlet and phen peaks are at 7.75, 7.97, 8.49 and 9.08 ppm. The mass spectra of the complexes **1a** and **1b** confirm mononuclear complexation by molecular ion peaks M^+ at m/z 796 for **1a** and $(M+1)^+$ at m/z 804 for **1b** (fast atom bombardment technique). However, no satisfactory spectra could be obtained for the pentanuclear complexes. All attempts to obtain single crystals of the complexes were unsuccessful, because of the low solubility of the compounds.

Free $\mathbf{H_4L}$ has an absorption maximum at 276 nm in the UV region. The electronic spectra of all the transition metal complexes in DMF are very similar to that of $\mathbf{H_4L}$ except for the high intensity charge transfer absorptions around 400 nm. The general character of these spectra is very similar to that of corresponding complexes of symmetrically disubstituted dioximate ligands[6,8,17] and the similarity is probably a consequence of the fact that for charge transfer transitions the electrons involved are not greatly altered by chelation of different transition metal ions.[17] Only in the cases of **3** and **4**, are strong absorptions seen around 482 and 460 nm, respectively. The glyoximate-bridged trinuclear Cu(II) complexes are characterized by an intense absorption at 476 nm and the higher energy transition around 480-460 nm, which is absent in the free ligand and other complexes,[22] can be assigned to a *phen*-to-Cu(II) charge-transfer transition.

Although thermal decompositions of **1a** and **4** are observed as sharp peaks at 239°C and 215 °C, respectively; those for all the other complexes are found to be above 300°C.

Electrochemical Measurements

A typical voltammogram of **H_4L** in DMSO is shown in Figure 4. Two one-electron reduction waves were observed for this species; these waves are *quasi*-reversible at all sweep rates studied.

Cyclic voltammograms of mononuclear **1a**, tetranuclear **2** and pentanuclear **5** complexes are shown in Figures 5, 6 and 7, respectively. A one-electron reduction peak at –1.190 V and two one-electron oxidation peaks at -0.580 V and +0.220 V were observed for **1a**. In the Ni (II) species the only reduction wave in the cathodic region and the oxidation peak at –0.580 V appear approximately in the same region as the species **H_4L**. These waves may be attributed to reductions in the ligand. The oxidation wave at +0.220 V may be metal-centred and attributed to the Ni(II) / Ni(III) couple.[24-26] In the voltammogram of complex **2**, three one-electron reduction waves and two one-electron oxidation waves appeared. The reduction peak at –0.570 V and oxidation peak at –0.080 V may be attributed to U(VI)O_2 centred reactions.[27]

In the cyclic voltammograms of the complex **2** and **5**, the reduction peaks around –0.700 V and –1.200 V are the same as in the voltammogram of **H_4L**. The cyclic voltammogram of the pentanuclear complex **5** showed three one-electron reduction peaks at –0.620 V, –0.780 V and –1.220 V successively. One of the two oxidation peaks (at –1.145 V) involves two electrons, is reversible in character at all sweep rates studied and may be attributed to phenanthroline ring oxidation.[28]

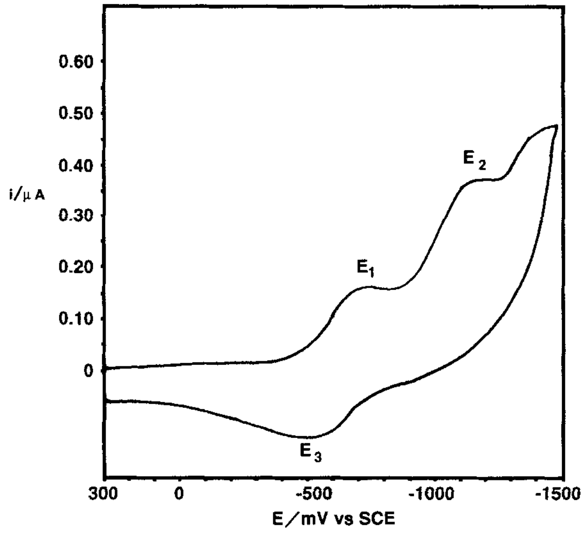


FIGURE 4 Cyclic voltammogram of H_4L in DMSO.

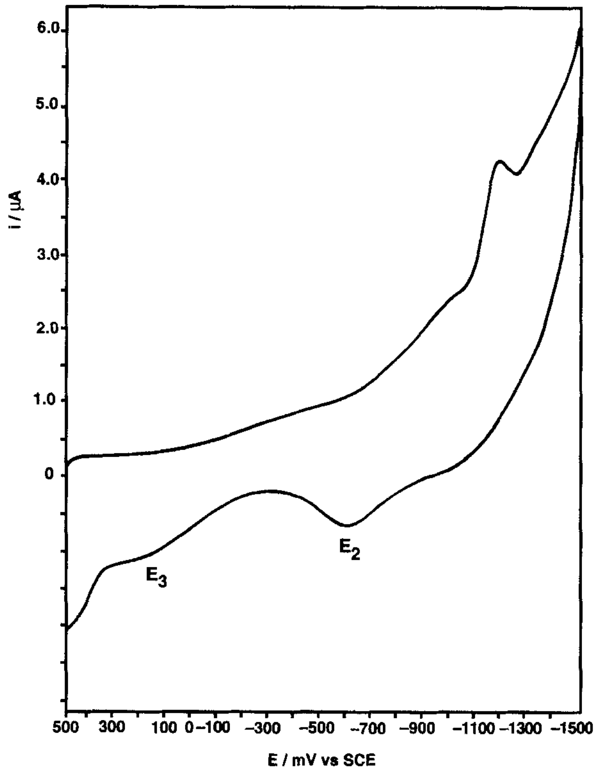


FIGURE 5 Cyclic voltammogram of 1a in DMSO.

For **1** and its complexes **1a, 2** and **5**, the heterogenous electron transfer rate is relatively slow, so that separation between cathodic and anodic peaks varies with the sweep rate. Variation of Ep with sweep rate changed from the *quasi*-reversible case to the charge transfer rate-determining case within the sweep rates studied (Table IV). One of the principal tests for electrochemical reversibility rests on the magnitude of the slope in the plot of Ep or Ep/2 *vs* log v.[29-30] Slopes (ΔC) between the limits of 0 and 30 mV per decade are indicative of reversible electron transfer and provide information about the order of subsequent chemical reactions. If the ratio of anodic to cathodic peak currents is unity and independent of the switching potential, the absence of coupled chemical reactions is demonstrated. In these complexes, the ratio of anodic to cathodic peak currents differs from unity and depends on the switching potential, thus indicating the presence of coupled chemical reactions.

The diffusion coefficients associated with these species in the cyclic voltammograms were calculated by using the Randles-Sevcik equation (Table IV).

According to α_n values calculated, the number of electrons transfered is one except for the oxidation peak of species **5** (n = 2 for peak 4). When the transfer coefficient deviates from 0.5, cyclic voltammograms become asymmetric as shown in Figures 4,5,6 and 7. Thus when α_n is around 0.75, the cathodic peak is sharper then the anodic peak as expected from the Butler-Volmer equation.[31] For the tetranuclear and pentanuclear uranyl species, cyclic voltammograms revealed that peaks 1 and 5 were related to each other. The diffusion coefficient of reduction peak 1 is about 4 times smaller than that of oxidation peak 5. Thus it may be attributed to a metal-based redox reaction.

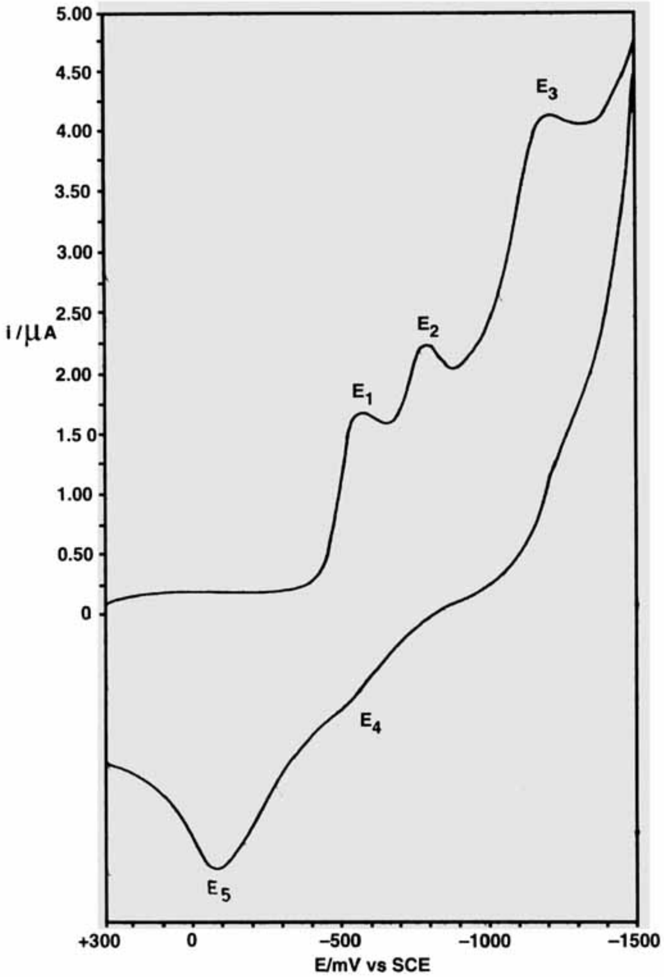


FIGURE 6 Cyclic voltammogram of 2 in DMSO.

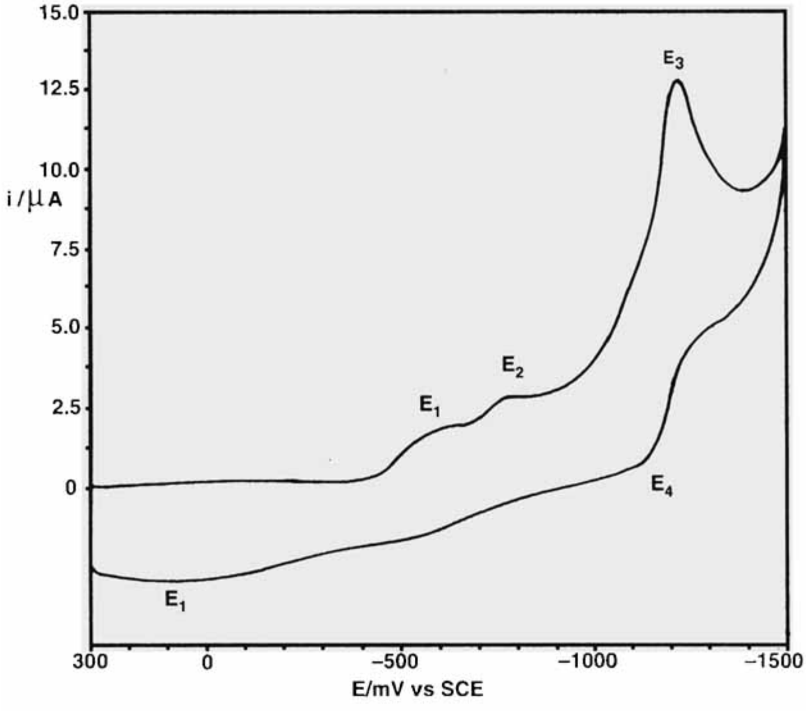


FIGURE 7 Cyclic voltammogram of **5** in DMSO.

TABLE IV Current functions and diffusion coefficients for **H_4L**, **1a**, **2** and **5** species in DMSO with 0,1 M TBAP as supporting electrolyte (v = 0.05 Vs – 1)

Compound	*Peak No*	*$\Delta C^a/v$*	*E_p/v*	*n*	*$\alpha_n{}^b$*	*$I^c{}_p/\mu A$*	*$10^{12}D/m^2s^{-1}$*
H_4L	1	0.0329	−0.7700	1	0.8960	0.1400	0.0066
(5×10^{-4}M)	2	0.0515	−1.2300	1	0.5720	0.3050	0.0487
	3	0.0711	−0.5400	1	0.4150	0.4500	0.0015
1a	1	0.0330	−1.1900	1	0.8940	5.1000	9.5500
(5×10^{-3}M)	2	0.1020	−0.5800	1	0.2890	0.7000	0.5050
	3	0.1360	+0.2200	1	0.2170	1.8500	4,7070
2	1	3.0380	−0.5700	1	0.7750	1.4250	0.7850
(5×10^{-4}M)	2	0.0505	−0.7900	1	0.5830	1.4750	1.1160
	3	0.0994	−1.2000	1	0.2970	2.9500	8.7730
	4	0.0532	−0.5100	1	0.5540	0.5250	0.1490
	5	0.0843	−0.0800	1	0.3490	1.8250	2.8550
5	1	0.0413	−0.6200	1	0.7130	1.7500	1.2870
(4×10^{-6} M)	2	0.0393	−0.7800	1	0.7500	1.3750	0.7550
	3	0.0422	−1.2200	1	0.6990	12.3750	65.6100
	4	0.0165	−0.1450	2	0.7800	2.8750	0.3798
	5	0.0653	+0.0900	1	0.4520	2.6250	4.5690

[a] ΔC = Ep/log v. [b] $\Delta C = 0.0295/\alpha_n$; hence α can be obtained. [c] $I_p = 2.98\times10^5 n\alpha_n{}^{1/2}CAD^{1/2}v^{1/2}$. [c] $I_p = 2.69\times10^5 n^{3/2} CAD^{1/2}v^{1/2}$; hence D can be obtained when α_n is known for v = 0.05 Vs^{-1}. [c] $I_p = 2.99\times10^5 n\alpha_n{}^{1/2}CAD^{1/2}v^{1/2}$.

Diffusion coefficients decrease with charge. This a reflection of two effects. As the charge increases, the size of the solvation shell increases, and with increasing charge outer-sphere solvent molecules are also oriented about the ion. Thus a large aggregate with its solvation sheath moves through solution more slowly.[31] In the case of these compounds, in anodic regions, diffusion coefficients appear to be smaller than those in cathodic regions.

Potentiometric Measurements

The *vic*-dioxime ligand may be represented by the conventional symbolic formula **H_4L** explicitly showing the presence of four ionizable protons. In the absence of metal ions, depending on the pH, there are five possible forms ligand could take: H_4L, H_3L^-, H_2L^{2-}, HL^{3-} and L^{4-}, on titration with a strong base in the pH range 2.0-12.0. The values for the protonation constant for **H_4L** are $\log K_1 = 10.80$, $\log K_2 = 9.75$, $\log K_3 = 7.92$ and $\log K_4 = 4.34$.

The assignments of the two protons to the oxime groups and the two protons to the phenolic groups in **H_4L** can be made on the basis of comparable values obtained for each of them and by anology with known values for related compound.[32-34] Titration data obtained for **H_4L** in the presence of Cu(II), Ni(II) and $U(VI)O_2$ ions were processed by the program TITFIT with respect to protonated, neutral and hydroxo complexes.[35]

Results are collected in Table V and a species distribution diagram is shown in Figure 8. Precipitation of complexes prevented the collection of titration data attributable to the species ML_2 and others. The stability order of overall formation constants of the complexes is as Cu(II) > Ni(II) > $U(VI)O_2$.

TABLE V Protonation and overall formation constants for H_4L and its complexes

Metal ion	*Species*	*log β ($\pm$ 0.1)*
H^+	HL^{3-}	10.8
	H_2L^{2-}	20.6
	H_3L^-	28.5
	H_4L	32.8
Ni^{2+}	ML	16.2
	MLH	23.4
	MLH_2	29.5
Cu^{2+}	ML	16.7
	MLH	23.5
	MLH_2	26.4
UO_2^{2+}	ML	15.7
	MLH	22.8
	ML_2H	34.2
	ML(OH)	1.0

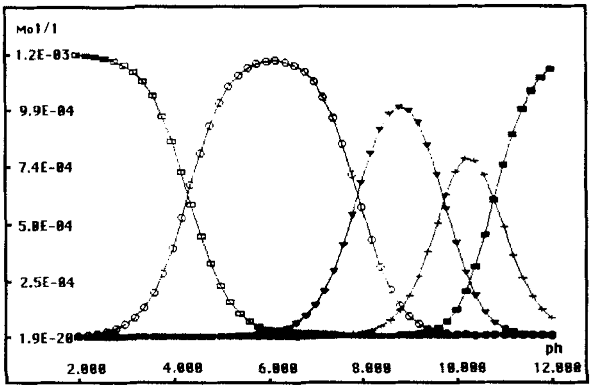


FIGURE 8 Species distribution diagram for 0.01 M **H_4L** at 0.1 M ionic strength and 25°C (+ +, HL^{3-}; ▼▼, H_2L^{2-}; **OO** H_3L^{1-}; □□, H_4L).

Acknowledgments

This work was supported by the Research Fund of the Technical University of Istanbul. We are grateful to Professor N. Tan for cyclic voltammetry measurements.

References

[1] A. Chakravorty, *Coord. Chem. Rev.*, **13**, 1 (1974).
[2] R.C. Mehrotra, *Comprehensive Coordination Chemistry*, G. Wilkinson, R.D. Gillard and J.A. McCleverty, Eds., (Pergamon Press, New York, 1988), **Vol. 2**, p. 269.
[3] M. Koçak, A. Cihan, A.I. Okur and Ö. Bekaroğlu, *J. Chem. Soc., Chem. Commun.*, 577 (1991); A. Gürek, V. Ahsen, A. Gül and Ö. Bekaroglu, *J. Chem. Soc., Dalton Trans.*, 3367 (1991).
[4] C. Grundmann, V. Mini, J.M. Dean and H.D. Frommeld, *Liebigs Ann. Chem.*, **687**, 191 (1965).
[5] Y. Gök and Ö. Bekaroğlu, *Synth. React. Inorg. Metal-Org. Chem .*, **11**, 621 (1981); S. Serinand and Ö. Bekaroğlu, *Z. Anorg. Allg. Chem.*, **496**, 197 (1983); G. Irez and Ö. Bekaroğlu, *Synth. React. Inorg. Metal-Org. Chem.*, **13**, 781 (1983).
[6] A. Gül and Ö. Bekaroğlu, *J. Chem. Soc., Dalton Trans .*, 2537 (1983).
[7] A.R. Koray, V. Ahsen and Ö. Bekaroğlu, *J. Chem. Soc., Chem. Commun .*, *932 (1986).*
[8] V. Ahsen, F. Gökçeli and Ö. Bekaroğlu, *J. Chem. Soc., Dalton Trans.*, 1827 (1987).
[9] V. Ahsen, E. Yilmazer, M. Ertas and Ö. Bekaroğlu, *J. Chem. Soc., Dalton Trans.*, 401 (1988).
[10] V. Ahsen, E. Musluoglu, A. Gürek, A. Gül, Ö. Bekaroğlu and M. Zehnder, *Helv. Chim. Acta*, **73**, 174 (1990).
[11] M. Ertas, V. Ahsen, A. Gül and Ö. Bekaroğlu, *J. Orgamomet. Chem.*, **335**, 105 (1987).
[12] V. Ahsen, A. Gürek, A. Gül and Ö. Bekaroğlu, *J. Chem. Soc., Dalton Trans.*, 5 (1990).
[13] A. Gürek, V. Ahsen, A. Gül and Ö. Bekaroğlu, *J. Chem. Soc., Dalton Trans.*, 3367 (1991).
[14] P.C.H. Mitchell and D.A. Parker, *J. Chem. Soc., Dalton Trans.*, **17**, 1828 (1972).
[15] A. Neves, S.M.D. Erthal, I. Vencato, A.S. Ceccato, Y.P. Mascarenhas, O.R. Nascimento, M. Hörner and A.A. Batista, *Inorg. Chem.*, **31**, 4749 (1992).
[16] G. Ponzio and F. Baldrocco, *Gazz. Chim. Ital.*, **60**, 415 (1930).
[17] I. Gürol, V. Ahsen and Ö. Bekaroğlu, *J. Chem. Soc., Dalton Trans.*, 2283 (1992).
[18] A. Nakamuro, A. Konishi and S. Otsuka, *J. Chem. Soc., Dalton Trans.*, 488 (1979).
[19] A. Gül, A.I. Okur, A. Cihan, N. Tan and Ö. Bekaroğlu, *J. Chem. Research*, (*S*), 90 (1986); (*M*) 881 (1986).

[20] D.M. Rudkevich, W. Verboom, Z. Brzozka, M.J. Palys, W.P.R.V. Stauthamer, G.J. van Hummel, S.M. Franken, S. Harkema, J.F.J. Engbersen and D.N. Reinhoudt, *J. Am. Chem. Soc.*, **116**, 4341 (1994).

[21] E. Hamuryudan and Ö. Bekaroğlu, *Chem. Ber.*, **127**, 2483 (1994).

[22] H. Okawa, M. Koikawa, S. Kida, D. Luneau and H. Oshio, *J. Chem. Soc., Dalton Trans.*, 469 (1990).

[23] K, Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, (Wiley, New York, 1978), 3rd Ed., p. 213.

[24] M,A. Bambenek and R.T. Pflaum, *Inorganic Chemistry*, **2**, 289 (1963).

[25] A.G. Lappin and M.C.M. Laranjeira, *J. Chem. Soc. Dalton Trans.*, 1861 (1982).

[26] J.A. Bertrand, E. Grovenstein, Lu Pang-chia Jr. and D. VanDerveer, *J. Am. Chem. Soc.*, **98**, 7836 (1976).

[27] J.B. Gandhi and N.D. Kulkarni, *J. Chem. Research* (*S*), 488 (1994).

[28] N. Tan, E. Hamuryudan and Ö. Bekaroğlu, *Bull. Electrochem. India,* in press.

[29] R.S. Nicholson and I. Shain, *Anal. Chem.*, **36**, 706 (1964).

[30] J,M. Saveant and D. Tessler, *J. Phys. Chem.*, **82**, 1723 (1978).

[31] P.H. Rieger, *Electrochemistry*, (Prentice-Hall International, New York, 1987).

[32] U. Avciata, A.E. Bozdoğan, M. Koçak, A. Gül and Ö. Bekaroğlu, *J. Coord. Chem.*, **35**, 319 (1995).

[33] S. Can and Ö. Bekaroğlu, *J. Chem. Soc. Dalton Trans.*, 2831 (1988).

[34] T. Hirotsu, S. Katoh, and K. Sugasaka, *J. Chem. Soc. Dalton Trans.*, 1609 (1986).

[35] A.D. Zuberbühler and T.A. Kaden, *Talanta*, **29**, 201 (1982).