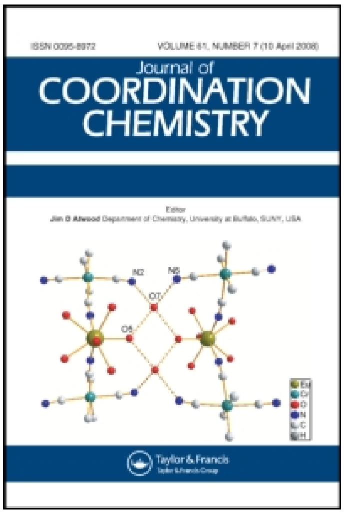

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SYNTHESIS AND COMPLEXATION OF A NOVEL SOLUBLE *VIC*-DIOXIME

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SYNTHESIS AND COMPLEXATION OF A NOVEL SOLUBLE *VIC*-DIOXIME

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A new soluble *vic*-dioxime, 1,4-bis(2-methoxyethyl-2,3-bis(hydroxyimino)-5,6-diphenylpiperazine (LH_2) has been synthesized as a mixture of isomers from dicyan di-*N*-oxide and 1,2-diphenyl-1,2-bis(2′-methoxyethylamino)ethane, **1**, which has been prepared through the reduction of the condensation product of benzaldehyde and 2-methoxyethylamine with the aluminium amalgam. LH_2 gives *N*,*N*-coordinated planar metal complexes with Co^{II}, Ni^{II}, Cu^{II} and Pd^{II}. Oxidation of $(LH)_2Co$ in the presence of a base such as py or triphenylphoshine leads to octahedral complexes $(LH)_2Co(B)Cl$. The uranyl complex of LH_2 has a 1 : 1 metal–ligand ratio and a binuclear structure with μ-hydroxo bridges.

Keywords: Oximes; *vic*-dioximes; copper(II); Ni(II); Co(II); uranyl; Pd(II)

INTRODUCTION

vic-Dioximates have been proven to be efficient chelating agents by extensive studies reporting various derivatives in the last decade.[1] Among the three isomers, namely *anti*, *amphi* and *syn*, the first one is more liable to form *N*,*N*-coordinated planar complexes with d^8 metal ions; here, two hydrogen bridges among the OH groups of oximes especially enhance the stability of the complexes.[2] Although the number of chiral dioximato-ligands is rather few, they have been successfully utilized in asymmetric reactions such as enantioselective cyclopropanation which is catalyzed by bis(camphorquinone α-dioximato)cobalt(II).[3,4] In addition to nopinoquinone dioximes, camphorquinone dioximes are the most frequently studied chiral bicyclic ligands, the geometrical isomers of which are shown to be

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* Corresponding author.

affected by the bite angle which in turn influences the electronic state of the metal ion.[5,6]

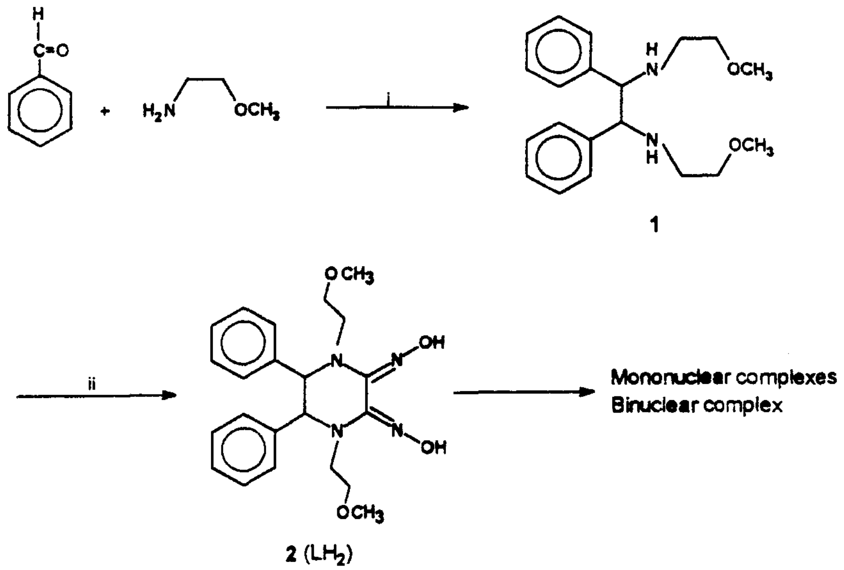
Our previous work in this area has focussed on the reaction of amines or thiols with *anti*-dichloroglyoxime or cyanogen di-*N*-oxide to yield various substituted diamino- or dithioglyoxime derivatives.[7–12] In the case of *anti*-monochloroglyoxime, asymmetric vicinal dioximes have been obtained.[13–17] When starting compounds with macrocyclic groups have been utilized, vicinal dioximes incorporating macrocyclic groups capable of binding transition and alkali metal ions simultaneously have been achieved.[18–25]

In the present work we report the synthesis of a novel soluble *vic*-dioxime ligand carrying optically active centres and its complexes with Cu(II), Ni(II), Co(II), Co(III), Pd(II) and $U(VI)O_2$.

RESULT AND DISCUSSION

The work of Schlenk *et al.* reporting in two successive papers the reduction of Schiff bases with aluminium amalgam to give dimeric structures, is the only source which gives a number of examples for these reactions.[26–28] As a starting point, we chose benzaldehyde and 2-methoxyethylamine. Without isolation of the condensation product, the mixture was treated with aluminium amalgam at room temperature to obtain a dimer, 1,2-diphenyl-1,2-bis(2′-methoxyethylamino)ethane (**1**). Condensation of **1** and dicyan di-*N*-oxide,[29] which was prepared by treating a suspension of *anti*-dichloroglyoxime in CH_2Cl_2 with 1 N aqueous Na_2CO_3 at −10°C, gave a novel *vic*-dioxime ligand, 1,4-bis(2-methoxyethyl)-2,3-bis(hydroxyimino)-5,6-diphenyl piperazine (LH_2) as a mixture of isomers (Scheme 1). Our efforts to detect and isolate the pure isomers by chromatography were not successful. Elemental analysis of **1**,**2** (LH_2) and the complexes were satisfactory in all cases.

The molecular ion peak observed at $m/z = 412$ by the electron impact technique closely follows the expected value for $C_{22}H_{28}N_4O_4$. The ^{1}H NMR spectrum in DMSO is rather complex as expected while this 6-membered heterocyclic *vic*-dioxime contains two asymmetric centres and the saturated piperazine ring is not planar (Table I). Consequently, there are three peaks for N–OH groups at 11.13, 11.05 and 10.02 ppm which disappear on deuterium exchange (Table II). For a symmetrical *vic*-dioxime in the *anti*-form only a single peak is expected.[18,19] Although these three values might correspond to a mixture of *anti*- and *amphi*-forms, which brings an additional two peaks for the latter,[5,6] this possibility is removed by the fact that



SCHEME 1 Synthetic route to *vic*-dioxime **2** (LH_2) and its metal complexes; (i) Diethylether, Al/Hg; (ii) Dichloroglyoxime, 1N Na_2CO_3, CH_2Cl_2.

TABLE I Mass spectroscopy data *m*/*z* (%)

1[a]	329.2[$(M+1)^+$(6)], 178.0(39), 165.1(100), 132(48), 118(66), 105.1(76), 91.0(69), 77.0(36), 59.0(57)
2(LH_2)[b]	412(M^+, 8), 395(100), 349(31), 337(40), 189(31), 180(47), 164(33), 91(53)
$(LH)_2Ni$[b]	881.3(M^+, 100), 865(39), 637(60), 500.1(15), 397.2(34)
$(LH)_2Cu$[b]	886.5(M^+, 100), 875(16), 789.3(11), 457.2(11), 397.2(27)

[a] EI. [b] FAB.

the free ligand obtained by demetallation of the orange Ni(II) complex, known to be a product of the *anti*-form, still gives these three peaks. A similar splitting is also observed for protons at tertiary carbon atoms; in **1**, there is a singlet at 3.74 ppm for the protons attached to tertiary carbons and this peak is not split indicating the equal chemical environment around each carbon (Table II). After cyclization to LH_2, these protons show two doublets around 5.08 and 4.64 ppm and a singlet at 4.74 ppm (Table II). These chemical shifts can be attributed to the *cis* and *trans* position, with respect to each other, of the protons at tertiary carbons.

In the IR spectrum of LH_2, characteristic absorptions for the oxime groups are easily recognized at 3250 (ν_{OH}),1650–1608 ($\nu_{C=N}$) and 970 cm^{-1} (ν_{N-O}). They closely follow the values for similar compounds (Table III).[7–25]

TABLE II ^{1}H-NMR data (δ) for **1**, **2**(LH_2) and the complexes in DMSO

Compounds	*O–H···O*	*N–OH*	*Ar–H*	*C–H*	*O–CH$_2$*	*O–CH$_3$*	*N–CH$_2$*	*N–H*
1			7.20 (m, 10H)	3.74 (s, 2H)	3.20 (t, 4H)	3.01 (s, 6H)	2.35 (t, 4H)	1.84 (s, 2H)[a]
2(LH_2)		11.13 (s) 11.05 (s) (2H)[a] 10.02 (s)	6.92 (m, 10H)	5.08(d) 4.74 (s) (2H) 4.64 (d)	3.35 (m, 14H)			
$(LH)_2Ni$	17.44 (s, 2H)[a]		7.02 (m, 20H)	4.88 (s) 4.65 (t) (4H) 4.60 (t)		3.31 (m, 28H)		
$(LH)_2CoPyCl$	18.32 (s, 2H)[a]		7.56 (m, 25H)	4.90 (d, 4H)		3.22 (m, 28H)		
$(LH)_2(UO_2)_2(OH)_2$		11.09 (s, 2H)[a]	6.96 (m, 20H)	4.92 (d, 4H)		3.49 (m, 28H)		

[a] D_2O exchangeable.

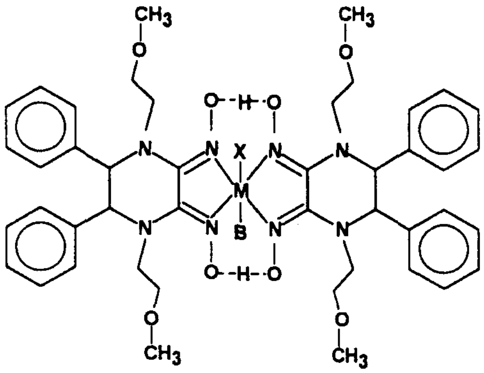
TABLE III Characteristic IR bands (cm^{-1}) for **1**, **2** $(LH)_2$ and the complexes (KBr pellets)

Compounds	*ν(N–H)*	*ν(O–H)*	*ν(CH Arom.)*	*ν(CH–Aliph.)*	*δ(O–H···O)*	*ν(C=N)oks* *ν(C=N)Py*	*ν(Ar-skel vib)*	*ν(CH_2–O–CH_3)*	*ν(N–O)*	*Other*
1	3330		3067–3033	2933–2883			1500–1433	1100		
2 (LH_2)		3250	3030–3017	2917–2867		1650–1608	1550–1500	1117–1050	970	
$(LH)_2Ni$			3066–3025	2925–2883	1750	1616–1567	1517–1450	1117–1067	1000	
$(LH)_2Cu$			3067–3033	2925–2883	1740	1617–1567	1517–1450	1117–1050	1000	
$(LH)_2Pd$			3067–3033	2933–2883	1710	1600–1550	1500–1450	1117–1050	1000	
$(LH)_2Co$			3050–3025	2925–2883	1750	1616–1566	1500–1450	1117–1041	1000	
$(LH)_2CoPyCl$			3067–3033	2933–2883	1700	1617–1600–1575	1500–1450	1117–1067	1000	
$(LH)_2CoTPPCl$			3067–3033	2933–2883	1740	1616–1567	1500–1450	1117–1067	1000	
$(LH)_2(UO_2)_2(OH)_2$		3260	3067–3033	2937–2900		1650–1617	1550–1467	1117–1050	1000	917 (O = U = O)

Complexation of LH_2 with some transition metal ions and the uranyl cation gave products with metal–ligand of 1 : 2 or 2 : 2. In the case of Co(II), Ni(II), Cu(II) and Pd(II), a planar *N*,*N*-coordination sphere around the metal ion with an additional two hydrogen bridges as in the case of well-known dimethylgloxime complexes can be proposed (Figure 1). For the large uranyl cation elemental analysis correspond to 2 : 2 metal–ligand ratio with two μ-hydroxo bridges as encountered in our earlier work (Figure 2). Trivalent octahedral cobalt complexes of LH_2 were prepared by oxidation of $(LH_2)Co$ in solution by bubbling air through it in the presence of a base such as pyridine or triphenylphosphine.

The orange-red crystalline $(LH_2)Ni$ complex gives a molecular ion peak at 881.3 (*m*/*z*) as expected (Table I). The hydrogen bridges are observed as a single deuterium exchangeable peak at 17.44 ppm as encountered in similar compounds (Table II). A singlet at 4.88 ppm and two neighbouring triplets at 4.65 and 4.60 ppm can be assigned to protons on tertiary carbons indicating the asymmetry in ligand isomers. A similar spectrum for diamagnetic $(LH)_2Co(py)Cl$ confirms the proposed structures with chemical shifts for hydrogen bridges at 18.32 ppm and CH-protons around 4.90 ppm.

IR spectra of all mononuclear complexes $(LH_2)M$ where M=Co(II), Cu(II) and Pd(II) are very similar to those of LH_2 except for the disappearence of the OH stretching frequencies. Weak bands around 1700 cm^{-1} indicate OH· · ·O bridges, while the shift of C=N vibrations to lower wavenumbers is



	$(LH)_2Ni$	$(LH)_2Cu$	$(LH)_2Pd$	$(LH)_2Co$	$(LH)_2CoPyCl$	$(LH)_2Co(TPP)Cl$
M	Ni	Cu	Pd	Co	Co	Co
B	—	—	—	—	Py	TPP
X	—	—	—	—	Cl	Cl

FIGURE 1 Mononuclear complexes of **2** (LH_2).

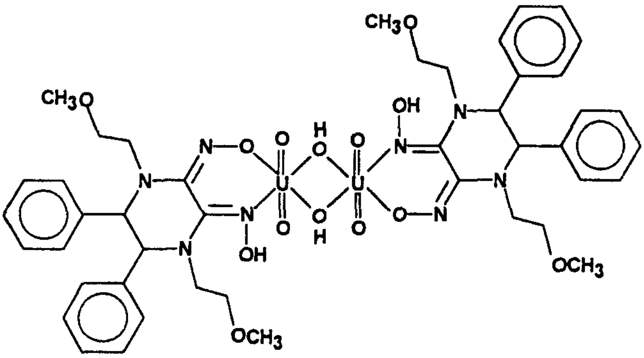


FIGURE 2 Binuclear uranyl complex of **2** (LH_2).

TABLE IV Electronic spectroscopy data for **1**, **2** (LH_2) and the complexes in dichloromethane

Compound	λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})
LH_2	305(10500)(sh)
$(LH)_2Ni$	381(15050), 445(2560)(sh)
$(LH)_2Cu$	382(7500)(sh), 470(2460)(sh)
$(LH)_2Co$	382(7500)(sh), 470(4554)(sh)
$(LH)_2Pd$	370(7300)(sh), 495(2300)(sh)
$(LH)_2Co(py)Cl$	385(3799)(sh), 487(944)(sh)
$(LH)_2Co(TPP)Cl$	368(3799)(sh), 512(1884)(sh)
$(LH)_2(UO_2)_2(OH)_2$	345(15000)(sh), 445(2628)(sh)

sh: shoulder

a consequence of *N*,*N*-chelation in *vicinal* dioxime complexes (Table III). In the case of the uranyl complex, OH-stretching vibrations of the oxime groups still appear as a broad band. A strong band around 910 cm^{-1} is characteristic for the O=U=O stretch.

A common feature of the complexes of LH_2 is their extensive solubility in common organic solvents such as ethanol, methanol, chloroform, dichloromethane. The electronic spectra of the complexes give intense charge transfer absorptions near 400 nm, but d → d transitions could not be detected (Table IV).

EXPERIMENTAL

Routine IR spectra were recorded on a Mattison 1000 FTIR spectrophotometer using KBr pellets, and electronic spectra on a Unicam UV2 spectrophotometer. Elemental analysis was performed by the Instrumental Analysis Laboratory of TÜBİTAK Marmara Research Centre. Proton NMR spectra were recorded on a Bruker 200 MHz spectrometer using $SiMe_4$ as reference. *anti*-Dichloroglyoxime was synthesized according to the reported procedure.[32,33]

1,2-diphenyl-1,2 bis(2′-methoxyethylamino)ethane, 1

Benzaldehyde (10.60 g, 0.1 mol) and 2-methoxyethylamine (7.50 g, 0.1 mol) were mixed and heated on a water-bath for an hour. The mixture was brought to room temperature and a mixture of aluminium amalgam (7.00 g) in 400 cm^3 of diethylether and then 7.5 cm^3 of water were slowly added. After the reaction mixture was kept at room temperature with stirring for 24 h, precipitated $Al(OH)_3$ was eliminated by filtration. The solid was washed with diethylether (3 x 100 cm^3) and the combined filtrates evaporated. The yellow oily residue was recrystallized from THF/hexane (5 : 1) to obtain a white crystalline compound. It was filtered and dried *in vacuo*. Yield 4.80 g (29.23%); m.p. 72°C. This compound is soluble in methanol, ethanol, dichloromethane, chloroform, THF and hexane.

1,4-bis(2′-methoxyethyl)-2,3-bis(hydroxyimino)-5,6 diphenyl piperazine, 2 $(LH)_2$

Compound **1** (0.985 g, 3 mmol) was dissolved in dichloromethane (50 cm^3) and stirred at −5°C. To this solution was added a solution of dicyan di-*N*-oxide in dichloromethane (40 cm^3) which was prepared from 0.688 g (4.3 mmol) of *anti*-dichloroglyoxime and 1 N Na_2CO_3 (100 cm^3). The reaction was continued for 3 h. The yellow solution was evaporated and the residue treated with refluxing hexane four times and filtered to remove any unreacted starting materials. The creamy product was recrystallized from acetone/water (2 : 1) to obtain the product as white crystals. It was filtered, washed with hexane and dried *in vaccuo*. Yield: 0.620 g (50.11%); m.p.: 150–151°C. This compound is soluble in methanol, ethanol, dichloromethane, chloroform and THF.

Mononuclear Complexes

$(LH)_2Ni$ To a solution of LH_2 (0.206 g, 0.5 mmol) in ethanol (50 cm^3) was added a solution of $NiCl_2 \cdot 6H_2O$ (0.059 g, 0.25 mmol) in ethanol (20 cm^3) at 70°C. The colour of the solution turned orange and the pH dropped to 3.2. The reaction mixture was kept stirring at 70°C for 2 h. Then it was bought

to room temperature and the orange crystalline complex precipitated. The product was filtered, washed with water, ethanol and diethyl ether and dried *in vacuo*. Yield: 0.110 g (49.88%); m.p. > 250°C.

$(LH)_2Co$ To a solution of LH_2 (0.206 g, 0.5 mmol) in ethanol (40 cm^3) was added a solution of $CoCl_2 \cdot 6H_2O$ (0.059 g, 0.25 mmol) in ethanol (10 cm^3) at 70°C. The colour of the solution turned brown and the pH dropped to 2.09. The pH was raised to 4.70 by addition of 0.1 M KOH in ethanol. The mixture was heated for 2 h at the same temperature. After the volume of the reaction mixture was reduced to 10 cm^3 on a rotary evaporator, the brown compound precipitated. The product was filtered, washed successively with water and hexane and dried *in vacuo*. Yield: 0.081 g (36.7%); m.p. = 170°C.

$(LH)_2Cu$ This pale brown complex was prepared following the same procedure as described for the preparation of $(LH_2)Co$, starting from LH_2 (0.206 g, 0.5 mmol) and $CuCl_2 \cdot 2H_2O$ (0.043 g, 0.25 mmol). Yield: 0.120 g (54%); m.p. 210°C (dec).

$(LH)_2Pd$ This brown complex was prepared following the same procedure as described for the preparation of $(LH)_2Co$, starting from LH_2 (0.412 g, 1 mmol) and Na_2PdCl_4 solution obtained from $PdCl_2$ (0.089 g, 0.5 mmol) and NaCl (0.059 g, 1 mmol) in ethanol (50 cm^3) Yield: 0.130 g (55.92%); m.p. 205°C.

$(LH)_2$ Co BCl To a solution of LH_2 (0.206 g, 0.5 mmol) in ethanol was added a solution of $CoCl_2 \cdot 6H_2O$ (0.059 g, 0.25 mmol) in ethanol (10 cm^3) and base component (B) [2 mmol triphenylphosphine (0.540 g) or pyridine (0.158 g, 0.16 ml)] at 70°C. Air was bubbled through the reaction mixture for 4 h. After the volume of the reaction mixture was reduced to 10 cm^3, a brown complex precipitated. It was filtered, washed first with water and then with hexane and dried *in vacuo*. For $(LH)_2Co(TPP)Cl$: Yield 0.120 g (40.69%); m.p. = 165°C. For $(LH_2)Co(py)Cl$: Yield 0.110 g (44.16%); m.p. = 175°C.

Binuclear Uranyl Complex

$(LH)_2(UO_2)_2(OH)_2$ To a solution of LH_2 (0.206 g, 0.5 mmol) in ethanol (40 cm^3) was added a solution of $UO_2(AcO)_2 \cdot 2H_2O$ (0.212 g, 0.5 mmol) in ethanol (30 cm^3) at 70°C. The colour of the solution turned orange-red and the pH came to 6.30. The mixture was heated for 2 h at the same temperature. After the volume of the reaction mixture was reduced to 10 cm^3 by rotary evaporation, the orange compound precipitated. The product was filtered, washed with water and hexane and dried *in vacuo*. Yield: 0.160 g

(55.27%) m.p. 150°C. The mononuclear and binuclear complexes are soluble in ethanol, methanol, dichloromethane and chloroform.

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