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Synthesis and Complexation of a New *vic*-Dioxime Ligand

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Summary. A new *vic*-dioxime ligand, N,N′-*bis*-(8-salicylideneimino-1-naphthyl)-diaminoglyoxime, has been synthesized from *anti*-dichloroglyoxime and 1-amino-8-salicylideneiminonaphthalene which has been prepared *via* the condensation product of 1,8-diaminonaphthalene and salicylaldehyde. The *vic*-dioxime ligand forms trinuclear complexes with Cu(II), Ni(II), Co(II), and Pd(II). The uranyl complex of this ligand has a 2:1 metal-ligand ratio and a binuclear structure with μ-hydroxo bridges.

Keywords. *Schiff* base; *vic*-Dioxime; Complexation.

Introduction

Metal complexes of vicinal dioximes have been widely investigated as analytical reagents [1] and models for biological systems [2], such as vitamin B_{12}. The columnar stacking of the compounds is thought to be the reason for their semiconducting properties [3] and their behaviour in macrocyclization reactions [4]. The exceptional stability and unique electronic properties of these complexes can be attributed to their planar structure which is stabilized by hydrogen bonding [5]. Another rapidly emerging area of chemical interest in recent years is the synthesis of heterobi- or -trinucleating ligands and the coordination chemistry of heteronuclear complexes of such ligands [6].

The coordination chemistry of *Schiff* bases derived from *o*-diamines and salicylaldehyde has been the subject of many studies, and the oxygen-carrying properties of some of these complexes are of considerable current interest due to the obvious implications to complicated biological systems [7,8].

We have long been interested in the chemical behaviour of complexes containing a planar MN_4 core structure and additional donor sites with phthalocyanines or *vic*-dioximes with the central coordination moiety and crown ethers [9,10], N_2O_2 macrocycles [11–13], seven-membered heterocyclic ligands [14], and S_2O_2 groups [15] as peripheral groups. In the present paper the synthesis of a new *vic*-dioxime ligand containing two naphthalene groups with the aim of obtaining tri- and tetranuclear complexes is presented.

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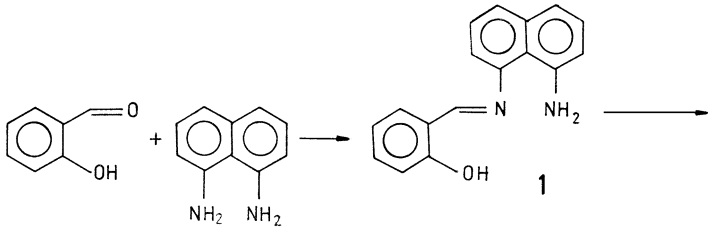
Results and Discussion

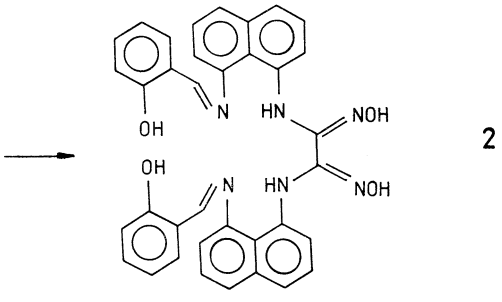
The condensation reaction of 1,8-diaminonaphthalene and salicylaldehyde was carried out in absolute ethanol at 60–65°C, and the new *Schiff* base ligand 1-amino-8-salicylideneimino-naphthalene (**1**) was isolated as yellow needles in good yield. A new *vic*-dioxime ligand, N,N′-*bis*-(8-salicylideneimino-1-naphthyl) diaminoglyoxime (**2**) was then prepared by a one-step reaction of *E,E*-dichloroglyoxime (*DCGO*) and **1.** Excess of $NaHCO_3$ was added to the reaction mixture in order to neutralize the HCl formed. The synthetic process for the formation of the *Schiff* base and the vicinaldioxime is shown in Scheme 1.

The elemental analyses of **1, 2,** and its metal derivatives were found to agree with their constitutions. In the IR spectrum of **1**, stretching vibrations for NH_2 were observed at 3300–3350 cm^{-1}. The band due to the C=N stretching was observed at 1650 cm^{-1}. The O–H, C=N, and N–O vibrations which belong to **2** are observed at 3200, 1650, and 950 cm^{-1}.

In the ^1H NMR spectrum of **1**, a singlet at $\delta = 5.65$ ppm for the aromatic amine protons is observed. After its reaction to **2**, this singlet disappears, and a new signal is observed at $\delta = 10.17$ ppm which can be assigned to the NH protons in the neighbourhood of the two oxime groups. On the other hand, a resonance at $\delta = 11.4$ ppm was found after the reaction with *E,E*-dichloroglyoxime indicating that the new OH protons belong to the oxime groups. The N–OH and NH protons were also identified by D_2O exchange.

Trinuclear complexes were obtained with Cu(II) (**3**), Ni(II) (**4**), Co(II) (**5**), and Pd(II) (**6**). For each ligand, one metal ion is coordinated to two aza and two oxa atoms of each ligand, whereas the third metal ion is coordinated by the N,N′ atoms





Scheme 1

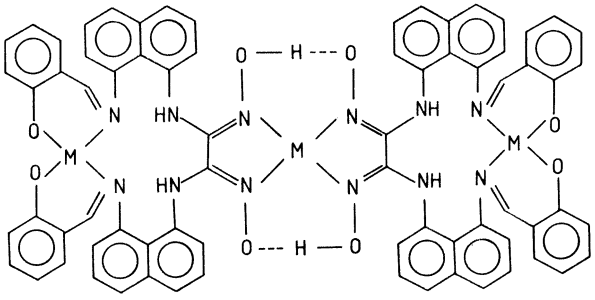


Fig. 1. Formula of compunds **3–6** (M = Cu, Ni, Co, Pd, respectively)

of each oxime group in the two ligand molecules (Fig. 1). The IR spectra of all trinuclear complexes were very similar to those of **2** except for the disappearance of the OH stretching frequencies. Weak bands around 1700 cm^{-1} indicate O–H···H bridges, whereas the shift of the C=N vibrations to lower wavenumbers is a consequence of N,N′-chelation in vicinal dioxime complexes.

In the NMR spectrum of the nickel complex **4**, the hydrogen bridging protons were observed as a single deuterium exchangeable peak at 16.7 ppm as encountered in similar compounds [9,11]. The signals from the NH protons of the Ni and Pd complexes **4** and **6** appeared at 10.3 and 10.25 ppm and disappeared upon addition of D_2O, indicating that one metal ion in each ligand was coordinated two aza and two oxa atoms of each ligand. No signals attributable to OH groups in the trinuclear complexes were present.

The tetranuclear uranyl complex **7** was obtained by starting with any ratio of the ligand and the metal salt. In this complex, one uranyl ion is linked to the phenolic OH and to the aza groups of each ligand, whereas the third and the fourth uranyl ions are coordinated through one nitrogen and one oxygen atom of each dioxime group in the two ligand molecules [14] (Fig. 2). The IR spectrum was also consistent with this

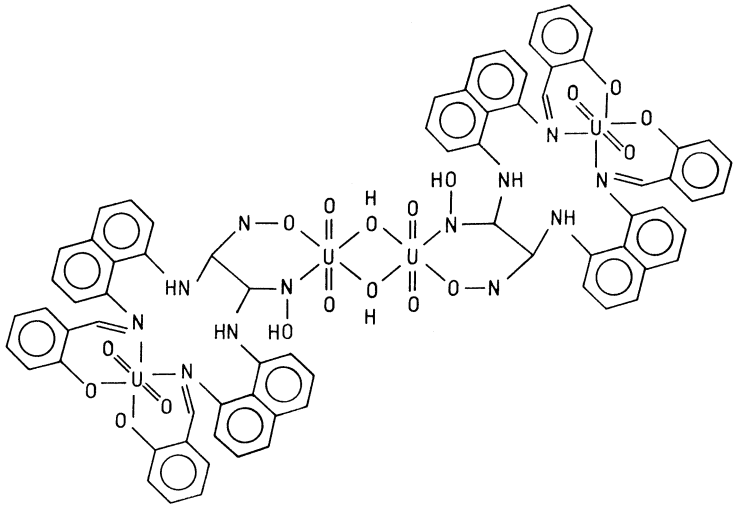


Fig. 2. Formula of compound **7**

structure. A strong band around 900 cm^{-1} is characteristic for ν(O=U=O) vibrations. The ^1H NMR spectrum of **7** showed two signals for the N-OH protons at $\delta = 11.37$ and 11.15 ppm and for the NH protons at $\delta = 9.41$ and 9.14 ppm. This can be attributed to the magnetic anisotropy of the uranyl ion as discussed in relation to carboxylate and amine complexes [16]. The uranyl ion enhances the chemical shift difference between non-equivalent protons. This effect is similar to increasing the NMR observing frequency by a few orders of magnitude [17].

The electronic spectra of all complexes showed an intense absorption around 400 nm which was assigned to charge-transfer transitions. However, d-d transitions could not be detected.

Experimental

IR spectra were recorded on a Mattison 1000 FTIR spectrophotometer using KBr pellets; the electronic absorption spectra were obtained on a Unicam UV2 spectrophotometer. Elemental analysis was performed by the Instrumental Analysis Laboratory of the Tubitak Marmara Research Centre. The results were in satisfactory agreement with the calculated values (C, H, N, metal). Proton NMR spectra were recorded on a Bruker 200 MHz spectrometer. *anti*-Dichloroglyoxime was prepared according to Refs. [18,19]. All other reagents and solvents were obtained from commercial suppliers.

1-Amino-8-salicylideneiminonaphthalene (**1**; $C_{17}H_{12}N_2O$)

A solution of 0.75 g 1,8-diaminonaphthalene (4.7 mmol) in 10 cm^3 absolute ethanol was added dropwise to a solution of 0.99 cm^3 salicylaldehyde (9.4 mmol) in 15 cm^3 absolute ethanol under an N_2 atmosphere at 60–65°C. The reaction mixture was stirred for 2 h at the same temperature, and a pale yellow precipitate was obtained which was filtered off, washed with H_2O and cold ethanol, and dried with cold diethyl ether.

Yield: 0.725 g (59%); m.p.: 186°C; IR (KBr): $\nu = 3350$–3300 (ν_{N-H}), 3250 (ν_{OH}), 3060–3035 ($\nu_{CH\text{-}arom}$), 1650 ($\nu_{C=N}$) cm^{-1}; ^1H NMR (*DMSO*-d_6, δ, 200 MHz): 13.30 (s, OH, D-exchangeable), 8.70 (s, CH=N), 7.60-6.41 (m, $10H_{arom}$), 5.65 (s, NH_2, D-exchangeable) ppm.

N,N′-Bis-(8-salicylideneimino-1-naphthyl)-diaminoglyoxime (**2**; $C_{36}H_{28}N_6O_4$)

A solution of 0.136 g *anti*-dichloroglyoxime (0.86 mmol) in 6 cm^3 absolute ethanol was added dropwise to a solution of 0.45 g **1** (1.7 mmol) in 35 cm^3 absolute ethanol which also contained 0.8 g sodium hydrogen carbonate (9.5 mmol) at 30–35°C. After the reaction mixture was stirred at this temperature for 24 h it was filtered. The filtrate was poured into 300 cm^3 ice-water. The dark yellow precipitate was filtered off and washed with H_2O and cold ethanol. The crude product was chromatographed on silica gel (eluted with $CHCl_3$: $CH_3OH = 20{:}1$). The compound is soluble in common solvents (*e.g.* methanol, aceton) up to concentrations of 4.1×10^{-2} mol dm^{-3}.

Yield: 0.180 g (35%); m.p.: 116–119°C; IR (KBr): $\nu = 3350$ (ν_{N-H}), 3200 (ν_{OH}), 3050–3020 ($\nu_{CH\text{-}arom}$), 1650 ($\nu_{C=N}$), 950 (ν_{N-O}) cm^{-1}; ^1H NMR (*DMSO*-d_6, δ, 200 MHz): 12.05 (s, OH, D-exchangeable), 11.40 (s, N–OH, D-exchangeable), 10.17 (s, N–H, D-exchangeable), 9.11 (s, CH=N), 7.60-6.41 (m, $20H_{arom}$) ppm.

Bis-(salicylideneiminato-copper-1-naphthyl)-diaminoglyoximato-copper) (**3**; $C_{72}H_{50}N_{12}O_8Cu_3$)

To a solution of 0.24 g **2** (0.39 mmol) in 20 cm^3 ethanol was added a solution of 98 mg $CuCl_2 \cdot 2H_2O$ (0.58 mmol) in 10 cm^3 ethanol. The mixture was heated on a water bath at 30–40°C for 3 h; during

this time the colour of the solution turned dark, and the brown-green complex was precipitated. The product was filtered off, washed with water, ethanol, and diethyl ether, and dried *in vacuo*.

Yield: 0.17 g (62%); m.p.: >250°C; MS (FAB): $m/z = 1401.5$ [M+1]; IR (KBr): $\nu = 3375$ (ν_{N-H}), 3055–3025 ($\nu_{CH\text{-}arom}$), 1720 ($\nu_{O-H\cdots O}$), 1610 ($\nu_{C=N}$), 960 (ν_{N-O}) cm^{-1}.

Bis-(salicylideneiminato-nickel-1-naphthyl)-diaminoglyoximato-nickel (**4**; $C_{72}H_{50}N_{12}O_8Ni_3$)

The reddish brown complex was prepared following the same procedure as described for the preparation of **3** starting from 0.24 g **2** (0.39 mmol) and 0.138 g $NiCl_2 \cdot 2H_2O$ (0.58 mmol).

Yield: 0.110 g (40%); m.p.: >250°C; IR (KBr): $\nu = 3300$ (ν_{N-H}), 3050-3025 ($\nu_{CH\text{-}arom}$), 1750 ($\nu_{O-H\cdots O}$), 1600 ($\nu_{C=N}$), 960 (ν_{N-O}) cm^{-1}; ^1H NMR (*DMSO*-d_6, δ, 200 MHz): 16.73 (s, O–H···O, D-exchangeable), 10.30 (s, N–H, D-exchangeable), 9.03 (s, CH=N), 7.82-6.23 (m, $40H_{arom}$) ppm.

Bis-(salicylideneiminato-cobalt-1-naphthyl)-diaminoglyoximato-cobalt (**5**; $C_{72}H_{50}N_{12}O_8Co_3$)

The dark brown complex was prepared following the same procedure as described for the preparation of **3** starting from 0.24 g **2** (0.39 mmol) and 0.138 g $CoCl_2 \cdot 6H_2O$ (0.58 mmol).

Yield: 0.180 g (66%); m.p.: >250°C; IR (KBr): $\nu = 3350$ (ν_{N-H}), 3060-3027 ($\nu_{CH\text{-}arom}$), 1700 ($\nu_{O-H\cdots O}$), 1605 ($\nu_{C=N}$), 960 (ν_{N-O}) cm^{-1}.

Bis-(salicylideneiminato-palladium-1-naphthyl)-diaminoglyoximato-palladium
(**6**; $C_{72}H_{50}N_{12}O_8Pd_3$)

A mixture of 0.102 g $PdCl_2$ (0.57 mmol) and 66 mg NaCl (1.14 mmol) was dissolved in 40 cm^3 ethanol. The solution was stirred at 70°C until the $PdCl_2$ was dissolved completely. A solution of 0.240 g **2** (0.38 mmol) in 209 cm^3 ethanol was added to this Na_2PdCl_4 solution, and the procedure described above for **3**–**5** was followed.

Yield: 0.170 g (56%); m.p.: >250°C; IR (KBr): $\nu = 3370$ (ν_{N-H}), 3062-3031 ($\nu_{CH\text{-}arom}$), 1730 ($\nu_{O-H\cdots O}$), 1600 ($\nu_{C=N}$), 960 (ν_{N-O}) cm^{-1}; ^1H NMR (*DMSO*-d_6, δ, 200 MHz): 10.25 (s, N–H, D-exchangeable), 9.01 (s, CH=N), 8.07-6.04 (m, $40H_{arom}$) ppm.

Bis-(salicylideneiminato-uranyl-1-naphthyl)-diaminoglyoximato-μ-hydroxo-diuranyl
(**7**; $C_{72}H_{52}N_{12}O_{18}U_4$)

To a solution of 0.120 g **2** (0.19 mmol) in 20 cm^3 hot ethanol a solution of 0.161 g $UO_2(AcO)_2 \cdot 2H_2O$ (0.38 mmol) in 10 cm^3 ethanol was added. The mixture was heated on a water bath for 1 h at 50–60°C. The color of the solution became dark, and the brown complex precipitated. The precipitate was filtered off, washed with hot and cold ethanol and diethyl ether, and dried *in vacuo*.

Yield: 0.072 g (31%); m.p.: >250°C; IR (KBr): $\nu = 3350$ ($\nu_{N\text{-}H}$), 3061-3033 ($\nu_{CH\text{-}arom}$), 1640 ($\nu_{C=N}$), 900 ($\nu_{O=U=O}$) cm^{-1}; ^1H NMR (*DMSO*-d_6, δ, 200 MHz): 11.37-11.15 (s, N-OH, D-exchangeable), 9.41–9.14 (s, N-H, D-exchangeable), 9.20 (s, CH=N), 8.12-6.57 (m, $40H_{arom}$), 3.65 (s, μ-OH, D-exchangeable)ppm.

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