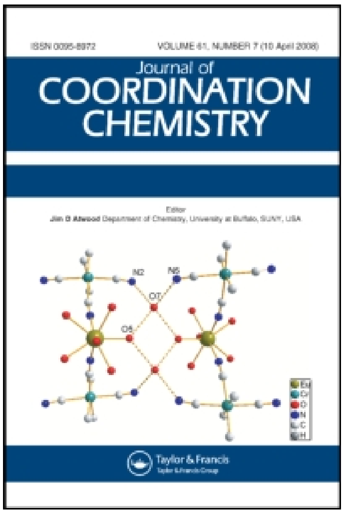

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THE SYNTHESIS AND CHARACTERIZATION OF A NOVEL *vic*-DIOXIME AND ITS MONO AND TRINUCLEAR COMPLEXES CARRYING A TRIOXADITHIA MACROCYCLE

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A new vicinal dioxime, 1,15-*bis*(hydroxyimino)-2,14-dithia-5,8,11-trioxacyclopentadecane (H_2L) was synthesized by the reaction of (*E*, *E*)-dichloroglyoxime (**1**) with 1,11-dithio-3,6,9-trioxaundecane (**2**). Mononuclear copper(II) complexes with a metal/ligand ratio of 1/2 were prepared. The two ligands coordinate to copper(II) through the deprotonated oximate oxygens which then afford the trinuclear structure bridged by the oximate groups with 1,10-phenanthroline or 2,2′-dipyridyl as the end-cap ligand.

Keywords: (*E*, *E*)-dioxime; dithiatrioxamacrocycle; trinuclear complexes; copper(II)

INTRODUCTION

Crown ethers have played an important role in host–guest complexation phenomena since the discovery of their complexes with metal ions.[1] At the same time, considerable attention has been devoted to the development of new ionophores to achieve selective complexation of metal ions. The design of selective crown ethers is of great importance with respect to the separation and recovery of metal ions.[2] Crown ethers in which some or all of the oxygen atoms are replaced by sulfur atoms, thiacrown ethers, are known to show great affinity for softer metal ions than alkali and alkaline earth metal ions.[3] Replacement of oxygen by sulfur causes a decrease in cavity size of crown ether cavity. Although thioethers have moderately low σ-donor and

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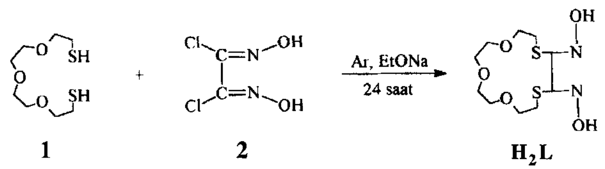
* Corresponding author.

π-acceptor abilities, bonding analogy between thioether and phosphine ligands suggest that transition metal complexes utilizing SR_2 donor ligands might mimic or complement those carrying PR_3.[4] Dithiocrown ethers show fairly selectivity for ions such as Hg^{2+} due to the relationship between the rates of transport, complexation ability and chain length.

Study of the exchange interaction between metal centres through extended bridges has been one of the most active research fields in magnetism.[5] The fundamental understanding of the factors that govern magnetic properties, the design of new materials which can fulfil specific task and the biological relevance of the exchange-coupled polynuclear systems are at the origin of the interest in this phenomenon.[6] One of the best strategies to design and prepare polynuclear compounds is the use of mononuclear complexes as ligands which contain potential donor groups for another metal ions.[7] A convenient example is represented by copper(II) oximato complexes. Complexes of these group compounds have played a relevant role in molecular magnetism because of the remarkable efficiency of the oxamidate bridge (=N–O–H · · O–N=) to transmit electronic effects between metal ions. Recently, we reported trinuclear copper(II) complexes of the general formula **$[Cu(dioxim)_2\{CuL\}_2]X_2$** [L = 1,10-phenanthroline (phen) or 2,2′-dipyridyl (bpy); X = NO_3^-] where $Cu(dioxim)_2{}^{2-}$ functions as a bridge to combine two **CuL^{2+}** moieties through its deprotonated oximate oxygens to afford a trinuclear skeleton.[8] A vast amount of fascinating chemistry with this type of oxime ligand has accumulated for first row transition metals with fundamental bearing on structure, magnetism, stability and reactivity of molecules, analytical chemistry and biochemical models.[9] We describe herein the synthesis of a novel (*E*, *E*)-dioxime and its mono or trinuclear copper(II) complexes.

RESULTS AND DISCUSSION

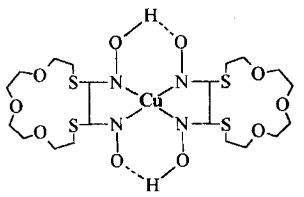
The preparation of the dithiatrioxa macrocyclic moiety from dichloroglyoxime (**1**) and 1,11-dithio-3,6,9-trioxaundecane (**2**) requires direct condensation to form the ring product in favour of polymers. In an attempt to achieve this goal, many different macrocyclization procedures have been developed. The high dilution technique is convenient as it requires simultaneous addition of **1** and **2** to a large volume of solvent over an extended period of time. 1,15-*Bis*(hydroxyimino)-1,14-dithia-5,8,11-trioxacyclopentadecane (**H_2L**) was prepared by the reaction of 1,11-dithio-3,6,9-trioxaundecane (**2**) with (*E*, *E*)-dichloroglyoxime (**1**) during 24 h at room temperature in dry ethanol in the presence of equivalent amounts of sodium ethoxide by using high dilution techniques under an argon atmosphere (Scheme 1).



SCHEME 1

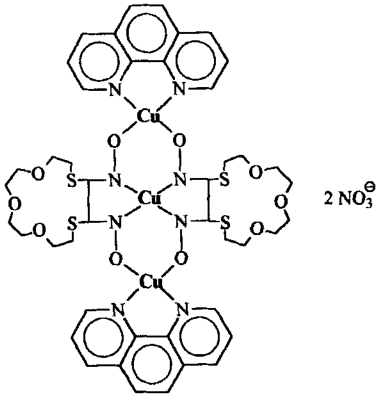
The novel vicinal dioxime (H_2L) was characterized by ^1H NMR, IR and MS spectroscopy and elemental analysis (see Experimental Section). The EI mass spectrum of H_2L exhibits a strong parent ion at $m/z = 310$, which accords with the proposed structure. The ^1H NMR spectrum of H_2L displayed a singlet at $\delta = 7.85$ ppm for the =N–OH protons which further confirms the (E,E) configuration of the dioxime subunit; such a shift is similar to that observed for other (E,E)-dioximes.[10] Multiplets at $\delta =$ 3.60–3.87 and 2.80–3.04 ppm are due to $-OCH_2$ and SCH_2, respectively.[11] IR has been utilized to establish the nature of ligand structure. Stretching vibrations at 3260 and 1645 cm^{-1} are assigned to the oxime (O–H) and azomethine (C=N) groups, respectively. The medium-strong band at 1015 cm^{-1} is assignable to the N–O stretch and the absence of S–H stretching is notable.

When ligand (H_2L) was heated to 60°C in ethanol with equivalent amount of $CuCl_2 \cdot 6H_2O$ **[Cu(HL)₂]** was isolated in 30.4% yield. The fast atom bombardment mass spectrum (FAB positive) of this complex exhibit a molecular ion peak at $m/z = 681$ $[M+1]^+$ which supports the formulation. Since the IR spectrum is quite similar that of the free ligand, discussion is confined to the most important vibrations. Monomeric **[Cu(HL)₂]** has appreciable IR absorption at 1715 cm^{-1} due to bending vibrations of the hydrogen-bonded O–H O groups. The C=N stretch decreases from 1645 cm^{-1} in the free ligand to 1620 cm^{-1} in **4**, whereas the N–O stretch increases from 1015 cm^{-1} in H_2L to 1031 cm^{-1} in **4**. These shifts are in accord with deprotonation of the oxime groups.[9] As shown in **4**, copper(II) assumes square-planar coordination geometry, in which the plane is composed of N donors of the oxime ligands.



4

A solution of 1,10-phenanthroline or 2,2′-bipyridyl and $Cu(NO_3)_2 \cdot 3H_2O$ in THF was added to **$[Cu(HL)_2]$** in THF at reflux to obtain trinuclear copper(II) complex using phen or dipy as end-cap ligands. Formation of these trinuclear complexes is verified by the molecular ion peaks at $m/z =$ 1290 $[M+1]^+$ and 1242 $[M+1]^+$, respectively, from fast atom bombardment mass spectra. These complexes consist of a dinuclear cation **$[Cu(L)_2(CuL')_2]^{2+}$** ($L' =$ phen or dipy) and uncoordinated nitrate anions **5**. **$Cu(HL)_2$** coordinates to two copper(II) ions through deprotonated oximate oxygens to afford a trinuclear skeleton doubly bridged by oximate moieties. The stretching vibrations of C=N groups for the trinuclear complexes are situated at significantly higher frequency than for the complex containing only one copper(II) ion. Contrary to this fact, it is noteworthy that the N–O stretch is shifted towards lower frequency. The nitrate ions N–O stretching vibrations around 1391–1377 cm^{-1}, typical of ionic nitrate groups.[12]



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EXPERIMENTAL

^1H NMR spectra were recorded on a Varian XL-300 spectrometer in DMSO-d_6, and chemical shifts are reported (δ) relative to Me_4Si as internal standard. IR spectra were recorded on a Mattson 1000 FT-IR spectrometer with samples in compressed KBr discs. Electron impact and fast atom ombardment mass spectra were measured on a VG AutoSpec from VG Analytical Instruments. 1,11-Dithio-3,6,9-trioxaundecane[13] and (*E*, *E*)-dichloroglyoxime[14] were prepared according to reported procedures.

Commercially available, pure grade solvents, dried and purified by conventional procedures,[15] were used throughout.

1,15-*Bis*(hydroxyimino)-2,14-dithia-5,8,11-trioxacyclopentadecane, (H_2L)

Sodium (0.81 g, 35.4 mmol) dissolved in dry ethanol (30 cm^3) was added drop wise to a solution of 1,11-dithio-3,6,9-trioxaundecane (4.0 g, 17.7 mmol) in dry ethanol (20 cm^3) under argon and (*E*, *E*)-dichloroglyoxime (2.8 g, 17.7 mmol) in dry ethanol (50 cm^3) were added simultaneously *via* a syringe pump to 1000 cm^3 of dry ethanol in a three-necked flask at room temperature. Addition was adjusted to a rate of 2 $cm^3 h^{-1}$. The mixture was stirred continuously for an additional 24 h under argon and then filtered to remove a white precipitate. The filtrate was concentrated under reduced pressure to a volume of 30 cm^3 and allowed to stand in a refrigerator at −18°C overnight. The pale yellow, solid product was filtered off, washed with water and dried *in vacuo*. The crude product was recrystallized from ethanol to give pale yellow crystals which were collected and dried *in vacuo* to yield 2.8 g (51.1%) of the 15-membered macrocyclic dioxime (**H_2L**), m.p. 220–222°C (dec.). ^1H NMR (DMSO-d_6): δ 7.85 (s, 2H, OH), 3.60–3.87 (m, 12H, OCH_2), 2.80–3.04 (m, 4H, SCH_2). IR (KBr pellet, cm^{-1}): 3260 (O–H), 2960–2855 (C–H), 1645 (C=N), 1015 (N–O). *Anal.* Calcd. for $C_{10}H_{18}N_2O_5S_2$ (%): C, 38.70; H, 5.80; N, 9.03: Found: C, 38.57; H, 5.61; N, 8.86. Electron impact (EI) mass spectrum: $m/z = 310$.

[Cu(HL)$_2$], 4

A solution of $CuCl_2 \cdot 2H_2O$ (0.49 g, 2.9 mmol) in hot ethanol (30 cm^3) was added to a hot solution of **H_2L** (1.8 g, 5.8 mmol) in ethanol (50 cm^3) with continuous stirring at 60°C. A change in colour and a significant decrease in the pH of the reaction mixture (pH = 0.95) was observed, and 0.1 M KOH in ethanol was added to adjust the pH to about 4.0 when precipitation of the complex started. After heating for 4 h at the same temperature, precipitation was complete. After cooling to room temperature, the reaction mixture was filtered off, washed with water, ethanol and diethylether and the black solid was dried *in vacuo* to afford 1.2 g (30.4%) of the mononuclear copper(II) complex, m.p. 234–236°C (dec.). IR (KBr pellets, cm^{-1}): 2948–2861 (C–H), 1705 (O–HO), 1620 (C=N), 1031 (N–O). *Anal.* Calcd. for $C_{20}H_{34}N_4O_{10}S_4Cu$ (%): C, 35.21; H, 4.99; N, 8.22; Cu, 9.32. Found: C, 35.14; H, 4.81; N, 8.07; Cu, 9.13. Fast atom bombardment (FAB positive) mass spectrum: $m/z = 681\ [M+1]^+$.

$[Cu(L)_2(CuL')_2](NO_3)_2$, ($L'$ = phen or bipy), 5

The mononuclear complex of **3** (0.49 g, 0.72 mmol) was suspended in THF ($40\,cm^3$). A solution of 1.7 mmol of phen (0.33 g) or bipy (0.27 g) in THF ($10\,cm^3$) and a solution of $Cu(NO_3)_2 \cdot 3H_2O$ (0.40 g, 1.7 mmol) in THF ($10\,cm^3$) was added to the suspension at reflux temperature. After refluxing for 5 h, the reaction mixture was filtered hot and concentrated to $10\,cm^3$ under reduced pressure. Diethylether was slowly added with continuous stirring to precipitate the complex. The product was filtered off, washed with water, ethanol and diethylether and dried *in vacuo*.

For the phenanthroline complex, yield: 0.21 g (23.14%), m.p. 186–188°C. IR (KBr pellet, cm^{-1}): 2965–2870 (C–H), 1640 (C=N), 1377 (N–O), 995 (N–O). *Anal.* Calcd. for $C_{44}H_{48}N_{10}O_{16}S_4Cu_3$ (%): C, 40.91; H, 3.72; N, 10.85; Cu, 14.76. Found: C, 40.78; H, 3.58; N, 10.70; Cu, 14.59. Fast atom bombardment (FAB positive) mass spectrum: $m/z = 1290\,[M{+}1]^+$.

For the bipyridyl complex, yield: 0.28 g (31.5%), m.p. 198–200°C. IR (KBr pellet, cm^{-1}): 2971–2873 (C–H), 1645 (C=N), 1391 (N–O), 1000 (N–O). *Anal.* Calcd. for $C_{40}H_{48}N_{10}O_{16}S_4Cu_3$ (%): C, 38.63; H, 3.86; N, 11.26; Cu, 15.33. Found: C, 38.50; H, 3.67; N, 11.05; Cu, 15.44. Fast atom bombardment (FAB positive) mass spectrum: $m/z = 1242\,[M + 1]^+$.

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