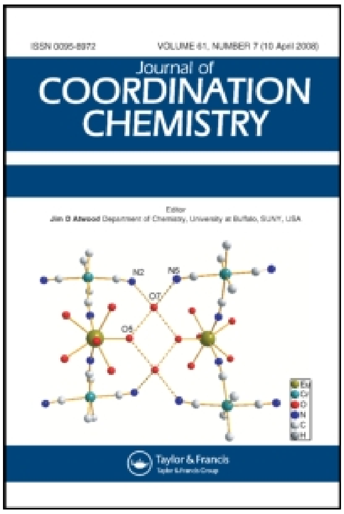

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SYNTHESIS AND COMPLEX FORMATION OF NOVEL 12-MEMBERED MACROCYCLIC (E,E)-DIOXIMES

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SYNTHESIS AND COMPLEX FORMATION OF NOVEL 12-MEMBERED MACROCYCLIC (E,E)-DIOXIMES

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Dibenzo[e,k]-2,3-bis(hydroxyimino)1.4.7.10-tetrathia-2,3,8,9-tetrahydrocyclododecine (S_4H_2) and dibenzo-[e,k]-2,3-bis(hydroxyimino)-1,4-dithia-7,10-dioxa-2,3,8,9-tetrahydrocyclododecine ($O_2S_2H_2$) have been prepared from (E,E)-dichloroglyoxime, 2,3,8,9-dibenzo-1,4,7,10-tetrathiadecane (DTT) and 2,3,8,9-Dibenzo-4,7-dioxa-1,10-dithiadecane (DDD) which was synthesized by treating 1,2-bis(o-aminophenoxy)ethane with HNO_2 and potassium ethylxsanthate. The structures of these *vic*-dioximes have been determined as the (E,E)-forms according to ^{1}H-NMR and IR data. Only mononuclear complexes with a metal-ligand ratio of 1:2 have been isolated with Co(II), such as $[(S_4H)_2Co(III)L'Cl]$ and $[(O_2S_2H)_2Co(III)L'Cl]$; Cu(II) forms only trinuclear complexes. Reaction of the mononuclear complexes with Pd(II) gives heterotrinuclear complexes.

KEY WORDS: Dioximes, macrocycles, polynuclear complexes, synthesis.

INTRODUCTION

During the past thirty years, macrocyclic ligands have attracted widespread attention due to two unique properties: their ability to discriminate among closely related metal ions based on the relative fit of the ligand cavity size to the metal ion radius and the significant enhancement in complex stability constants which is generally exhibited by optimally fitting macrocyclic ligands relarive to their open-chain analoqies.[1–2]

Thioether ligands have been identified as possible selective metal extraction agents for "soft" metal ions such as lead and mercury[3] and, as such, may have important utility in terms of sequestering agents for treatment of heavy-metal poisoning.[4]

The coordination chemistry of quatridentate tetrathia[5] abd dithiadioxa macrocycles[6] and bidentate *vic*-dioximes has been the subject of great interest.[7] Metal complexes with macrocyclic quadridentate ligands in the equatorial plane of metal ions have been described,[8] the majority of which have four nitrogens as donors. Macrcycles containing one or more sulfide linkages include thia crown ethers and crypates, sulfur-containing cyclophanes, other ligands of defined shape and bonding properties for complexing metal ions,[9] or compounds useful for examination of, for examples, sulfur-sulfur bonding or electron transfer between sulfur atoms.[10] The sulfide linkage occurs also in some macrocyclic natural products.[11]

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Thioethers coordinated to copper ions have been investigated to elucidate the structure of the blue copper proteins plastocyanin and azurin,[6] as have dithiodioxoethers coordinated to thallium(I) and mercury(II).[12] As might be anticipated, the macrocyclic polyoxapolythiaether ligands exhibit a range of properties intermediate between those of the macrocyclic polythiaethers and the macrocyclic polyethers.

vic-Dioximes have received considerable attention as model compounds of vitamin B_{12}.[12] Their metal chelates are biologically active and semiconducting.[13] The relevance of bimetallic compounds to bioinorganic system is the reason for the increase research on polynuclear compounds.[14] In this context, a number of new *vic*-dioximes[15] and dithioglyoxime derivatives and their transition metal complexes have been prepared.

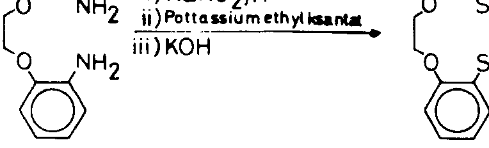
In the present work, we have prepared two new 12-membered macrocyclic (E,E)-dioximes, one of which contains four sulfur and the other two sulfur and two oxygen binding sites. Homo- and heterotrinuclear complexes of these ligands with various transition metals have been investigated.

RESULTS AND DISCUSSION

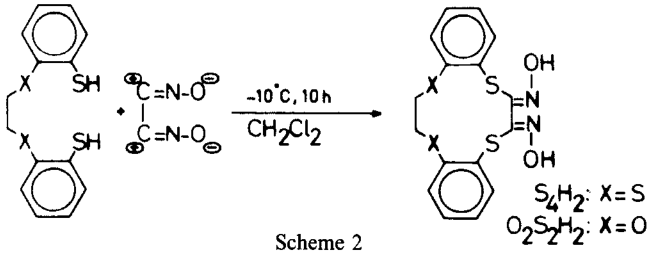
Dibenzo[e,k]-2,3-bis(hydroxyimino)-1,4,7,10-tetrathia-2,3,8,9-tetrahydro-cyclododecin (S_4H_2) and dibenzo[e,k]-2,3-bis(hydroxyimino)-1,4-dithia-7,10-dioxa-2,3,8,9-tetrahydro-cyclododecin [$O_2S_2H_2$] were synthesized by the reaction of 2,3,8,9-dibenzo-1,4,7,10-tetrathiadecane[5] and 2,3,8,9-dibenzo-4,7-dioxa-1,10-dithiadecane and cyanogen-*N*,*N'*-dioxide, which was prepared from (E,E)-dichloroglyoxime and 0.5M Na_2CO_3 in dichloromethane. The structures of S_4H_4 and $O_2S_2H_2$ were determined by a combination of elemental analysis, ^1H NMR, IR and electronic spectroscopy.

In the ^1H NMR spectrum of 1,2-bis(*o*-aminophenoxy)ethane, there is one singlet at δ 4.55 ppm for primary aromatic amine protons.[16] This singlet disppears after the diazonation reaction (Scheme 1) and the SH protons of 2,3,8,9-dibenzo-4,7-dioxa-1,10-dithiadecane appear at δ 3.85 ppm. The SH protons are also identified easily by deuterium exchange. A singlet at δ 2.62 ppm and a multiplet at δ 6.80 ppm corresponding to (CH_2-CH_2) and aromatic protons, respectively, shift little as compared to the starting material.[16] The IR spectrum of the new compound has ν(S-H) as a broad band at 2505 cm^{-1}. The aromatic and aliphatic stretching vibrations are very close to those of starting compound.

In the ^1H NMR spectrum of the *vic*-dioximes, signals for N-OH groups occur at δ 11.30 (S_4H_2) and δ 10.11 ($O_2S_2H_2$) ppm, and disappear on deuterium exchange. The presence of singletd for OH protons are consistent with the assumption of the



Scheme 1



Scheme 2

(E,E)-cofiguration for S_4H_2 and $O_2S_2H_2$.[17] Singlets at δ 3.85 and δ 4.15 ppm for SH protons belong to DDD and DTT, respectively. After the formation reaction of *vic*-dioximes these singlets disappear. The chemical shifts of the aromatic (7.29-6.72 and 7.35-6.85) and methylene (2.89 and 2.72) protons of the *vic*-dioximes are in accord with those of the macrocyclic compounds in the literature.[7,18]

In the IR spectrum of the *vic*-dioximes, (O-H) and (C = N) stretching vibrations are observed at 3205, 3180, 1660 and 1645 cm^{-1} as sharp bands. (N-O) and (C-H) stretching vibrations are at 960-945 cm^{-1} and 2920-2910 cm^{-1}, respectively. In the IR spectra of DDD and DTT, the vibrations at 2510-2505 cm^{-1} of the mercapto groups disappear upon macrocycle formation. Aromatic (C-H) bands are very close for DDD, DTT and S_4H_2 and $O_2S_2H_2$.

Reactions of S_4H_2 and $O_2S_2H_2$ with salts of Co(II) and Cu(II) give products with metal-ligand ratios of 1:2 or 3:2. In the case of Co(II), only mononuclear octahedral Co(II) complexes were obtained, as with a previously reported complex of pyrazine.[15b] Pyridine ligands coordinate axially to the metal in these octahedral complexes[19] (Fig. 1). The deuterium exchangrable, intramolecular bridging O-H..O protons appear as singlets at δ 17.65 and δ 17.42 ppm for the pyridine derivative. In these complexes, weak bands assigned to O-H..O bending vibrations were observed at 1715 cm^{-1} $[(O_2S_2H)_2CoL'Cl]$ and 1718 cm^{-1} $[(S_4H)_2CoL'Cl]$. These spectra are important because the usual hydrogen bridges of square-planar (E,E)-dioxime complexes are characterized by weak deformation bands. C = N bands of oximes groups were observed as combined bands at 1645 and 1630 cm^{-1}. These values are lower than those of the free ligands.[20] Electronic absorption spectra of $[Co(S_4H)_2(L')Cl]$ and $[Co(S_2O_2H)_2(L')Cl]$ in *N*-*N*′-dimethylformamide show a broad absorption at 428 nm (log $\epsilon = 4.41$) and 436 nm (log $\epsilon 4.56$), respectively;* these bands are most likely due to charge transfer. S_4H_2 gives a homotrinuclear complex of Cu(II) with a metal-ligand

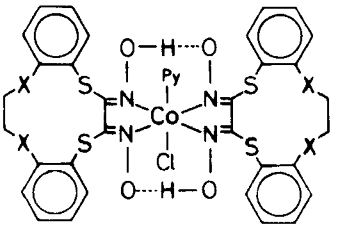


Figure 1

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* For ϵ units of $M^{-1} cm^{-1}$.

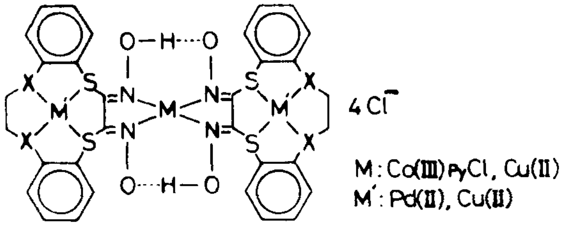

Figure 2

ratio of 3:2 (Fig. 2). In this complex, one metal ion is trapped in each macrocycle and another is coordinated through the *N* atoms of the oxime groups of the ligand molecule. In the IR spectra of $[Cu_3(S_4H)_2]Cl_4$, weak (O-H..O) deformation and (C = N) stretching vibrations are observed around 1700–1710 cm^{-1} [17,20] and 1635 cm^{-1}, respectively. The usual intramolecular hydrogen bridges of the square-planar *vic*-dioxime complexes are characterized by the above mentioned (O-H..O) deformation band.[7,15] N-O stretching vibrations of oxime groups are shifted to 940 cm^{-1} and re broadened upon coordination. Some values are slightly lower as compared to those of free ligands observed in most *N*,*N'*-chelated (E,E)-dioxime complexes.

In order to synthesize heterotrinuclear complexes of the type $[MM'_2(X_2S_2H)_2]Cl_4$, heterogeneous reactions of $[Co(S_4H)_2(L')Cl]$ or $[Co(S_2O_2H)_2(L')Cl]$ with a solution of Pd(II) were carried out. In these compounds, while Co(III) is still coordinated to the *vic*-dioxime groups, two other metal ions are co-ordinated to two macrocyclic tetrathia and dioxadithia groups. A common feature of these heterotrinuclear complexes of S_4H_2 and $S_2O_2H_2$ is their insolubility which hindered ^1H NMR investigations. A close examination of IR spectra (KBr pellets), shows a high degree of similarity which suggests that they all have the same geometrical configuration.[18b,21] In the IR spectra of these complexes, intramolecular hydrogen bridge vibrations are observed at 1712-1709 cm^{-1} and are slightly shifted, compared with the mononuclear Co(III) complexes (Fig. 2). The aromatic, aliphatic, (N-O) and (C = N) bands are very close in $[(S_4H)_2CoL'Cl]$ and $[(O_2S_2H)_2CoL'Cl]$, as well as in the heterotrinuclear complexes.

EXPERIMENTAL

IR and electronic spectra were recorded on a Perkin Elmer 1600 FT-IR in KBr pellets and cells and a GBC 911 spectrophotometer (1 cm quartz cells), respectively. ^1H NMR spectra were recorded on Bruker AC-200 FT-NMR and Varian T-60 spectrometers. Elemental analyses and metal contents were determined by Hewlett Packard 85 CHN analyzer and a Hilgen-Watts A.A.H.1550 instruments. 1,2-Bis(*o*-aminophenoxy)ethane,[16] 2,3,8,9-dibenzo-1,4,7,10-tetrathiadecane[5] and dichloroglyoxime[22] were prepared according to literature methods. The synthesis of 2,3,8,9-dibenzo-4,7-dioxa-1,10-dithiadecane was carried out under nitrogen.

2,3,8,9-dibenzo-4,7-dioxa-1,10-dithiadecane

$NaNO_2$ (6.4 g, 9.2 mmol) was dissolved in conc. H_2SO_4 (32 cm^3) at −5°C, and 1,2-bis(*o*-aminophenoxy)ethane (9.76 g, 40 mmol) in acetic acid (45 cm^3) was added dropwise with stirring at the above temperature. To this solution was added diethyl ether (100 cm^3) and the yellow diazonium salt was precipitated. This precipitate was added with stirring in small portions to solutions of potassium ethyl xanthate (52 g, 0.36 mol) in water (45 cm^3). The product was extracted with diethylether (3 × 50 cm^3) and then dried with anhydrous $MgSO_4$. The solution was evaporated to dryness, added to a solution of KOH (24 g, 0.42 mol) in ethanol (75 cm^3) and then refluxed for 1 h. After decanting this cooled mixture, water (50 cm^3) was added and then mixture acidified with conc. HCl to pH 2.5. The product formed was extracted with diethylether (3 × 50 cm^3), washed with water (2 × 50 cm^3) then dried with $MgSO_4$. Yield 2.58 g (23.2%). ^1H NMR ($CDCl_3$, TMS, δ, ppm): 2.62 (s, CH_2-H_2, 4H), 3.85 (s, -SH, 2H), 6.80 (m, arom-H, 8H). IR ($CHCl_3$, cells, cm^{-1}): 2505 (S-H), 3025 $(C\text{-}H)_{arom}$, 2095 $(C\text{-}H)_{aliph}$.

Dibenzo[e,k]-2,3-bis(hydroxyimino-1,4-dithia-7,10-dioxa-2,3,8,9-tetrahydro-cyclododecine ($O_2S_2H_2$) and *Dibenzo[e,k]-2,3-bis(hydroxyimino)-1,4,7,10-tetrathia-2,3,8,9-tetrahydrocyclododecine* (S_4H_2).

A solution of 5 mmol of 2,3,8,9-dibenzo-1,4,7,10-tetrathiadecame (DTT) or 2,3,8,9-dibenzo-4,7-dioxa-1,10-dithiadecane (DDD) [DTT (1.56 g) or DDD (1.39 g)] in dichloromethame (25 cm^3) was cooled to −10°C. A solution of cyanogen-*N,N'*-dioxane[23] in dichloromethane (30 cm^3) which was prepared from (E,E)-dichloroglyoxime (0.785 g, 5 mmol) and aqueous Na_2CO_3 (25 cm^3, 0.5 M) solution was added. Reaction was continued for 10 h at the above temperature and the dark yellow compound separated by filtration, washed with cold dichloromethane and dried *in vacuo*. The filtrate was reduced (20 cm^3) under vacuum and further product precipitated by addition of diethylether.

$O_2S_2H_2$ was recrystallized from acetonitrile/petroleum ether (1:4) as pale yellow crystals. Yield: 1.42 g (78.45%), m.p. 162°C. ^1H NMR (DMSO-d_6): δ 10.11 (s, OH, 2H), 7.29-6.72 (m, C_6H_4, 8H), 2.89 (s, CH_2, 4H). IR (KBr, cm^{-1}): 3205 (O-H), 3035 $(C\text{-}H)_{arom}$, 2920 $(C\text{-}H)_{aliph}$, 1660 (C=N), 960 (N-O)- Electronic spectra (DMF, log ε): λ_{max} 426 (4.13), 307 (3.73), 278 (4.22), 250 (4.91). Analysis: found: C, 52.84; H, 3.363; N, 7.59%. Calculated for $C_{16}H_{14}N_2O_4S_2$: C, 53.03; H, 3.86; N, 7.73%.

S_4H_2 was recrystallized from acetonitrile/diethylether (1:3) as pale-yellow crystals. Yield: 1.64 g (84.2%), m.p. 187°C. ^1H NMR (DMSO-d_6): δ 11.30 (s, OH, 2H), 7.35-6.85 (m, C_6H_4, 8H), 2.72 (s, CH_2, 4H). IR (KBr, cm^{-1}): 3180 (O-H), 3042 $(C\text{-}H)_{arom}$, 2910 $(C\text{-}H)_{aliph}$, 1645 (C=N), 945 (N-O). Electronic spectra (DMF, log ε): λ_{max} 423 (4.17), 318 (4.21), 256 (4.16). Analysis: found: C, 48.52; H, 3.37; N, 6.95%. Calculated for $C_{16}H_{14}N_2O_2S_4$: C, 48.73; H, 3.55; N, 7.11%.

$[(O_2S_2H)_2Co(L')Cl]$ *and* $[(S_4H)_2Co(L')Cl]$

A solution of $CoCl_2.6H_2O$ (0.237 g, 1 mmol) in ethanol (20 cm^3) was added to a solution of ligand [$O_2S_2H_2$ (0.724 g, 2 mmol) or S_4H_2 (0.788 g, 2 mmol)] in ethanol (80 cm^3). Pyridine (0.355 g, 4.5 mmol) in ethanol (5 cm^3) was added to the mixture and O_2 was bubbled through the solution for 2 h while heating at 70°C. The brown precipitate was filtered off, washed with cold water, cold ethanol and diethylether and dried *in vacuo* over P_4O_{10}.

Brown $[(O_2S_2H)_2Co(py)Cl]$: Yield: 0.863 g (96.38%), m.p. 240°C (decomp.). ^1H NMR (DMSO-d_6): δ 17.42 (s, O-H..O, 2H), 7.26-6.72 (m, C^6H_4, 16H), 7.82-7.38 (br m, Py, 5H), 3.24 (s, CH_2, 8H). IR (KBr, cm^{-1}): 3030 $(C\text{-}H)_{arom}$, 2910 $(C\text{-}H)_{aliph}$, 1715 (O-H..O), 1645 (C=N), 935 (N-O). Electronic spectra (DMF, log ε): λ_{max} 476 (3.97), 428 (4.41), 316 (4.12), 275 (4.33), 255 (4.37). Analysis: found: C, 49.37; H, 3.25; N, 7.59; Co, 6.31%. Calculated for $C_{37}H_{31}N_5O_8S_4ClCo$: C, 49.58; H, 3.46; N, 7.82; Co, 6.57%.

Dark-brown $[(S_4H)_2Co(py)Cl]$: Yield: 0.918 g (95.68%), m.p. 228°C (decomp.). ^1H NMR (DMSO-d_6): δ 17.65 (s, O-H..O, 2H), 7.38–6.82 (m, C_6H_4, 16H), 7.95-7.47 (br m, py, 5H), 3.19 (s, CH_2, 8H). IR (KBr, cm^{-1}): 3032 $(C\text{-}H)_{arom}$, 2905 $(C\text{-}H)_{aliph}$, 1718 (O-H..O), 1630 (C=N), 940 (N-O). Electronic spectra (DMF, log ϵ): λ_{max} 496 (4.28), 436 (4.56), 316 (4.19), 261 (4.23). Analysis: found: C, 46.05; H, 3.11; N, 7.13; Co, 5.87%. Calculated for $C_{37}H_{31}N_5O_4S_8ClCo$: C, 46.27; H, 3.23; N, 7.29; Co, 6.13%.

$[(S_4H)_2Cu_3]Cl_4$

A solution of $CuCl_2.2H_2O$ (0.255 g, 1.5 mmol) in ethanol (20 cm^3) was added to a solution of S_4H_2 (0.394 g, 1 mmol) in dioxane/ethanol (2:1) (60 cm^3) with stirring. After heating on a water bath for ten mins the pH was 1.75, 0.1 M KOH in ethanol was used to adjust the pH to about 4.5, when precipitation of the complex started. The mixture was heated on a water bath for another 3 h; during this time precipitation was completed. The dark-brown complex was filtered off, washed with ethanol, then ether and dried *in vacuo* over P_4O_{10}.

Yield: 0.345 g (61.69%), m.p. 236°C (decomp.). IR (KBr, cm^{-1}): 3405 $(C\text{-}H)_{arom}$, 2900 $(C\text{-}H)_{aliph}$, 1710 (O-H..O), 1635 (C=N), 940 (N-O). Electronic spectra (DMF, log ϵ): λ_{max} 483 (3.54), 427 (4.19), 355 (4.28), 300 (3.84), 282 (4.03). Analysis: found: C, 34.14; H, 2.17; N, 4.78; Cu, 16.81%. Calculated for $C_{32}H_{26}N_4O_4S_8Cu_3Cl_4$: C, 34.33; H, 2.32; N, 5.00; Cu, 17.03%.

$[(O_2S_2H)_2MM'_2(py)Cl]Cl_4$ and $[(S_4H)_2MM'_2(py)Cl]Cl_4$ (M = Co(III); M' = Pd(II))

A suspension of the mononuclear complex {(0.4797 g, 0.5 mmol) $[(S_4H)_2Co(III)(py)Cl]$; or (0.447 g, 0.5 mmol) $[(O_2S_2H)_2Co(III)(py)Cl]$} in dioxane/ethanol (1:3) (100 cm^3) was treated with an excess of the second metal salt prepared by refluxing $PdCl_2$ (0.238 g, 1 mmol) and NaCl (0.117 g, 2 mmol) in ethanol (90 cm^3), and the mixture was refluexed for 20 h with continuous stirring. The precipitate was filtered off, washed with water, ethanol and diethylether, and then dried *in vacuo* over P_4O_{10}.

Dark-brown $[(O_2S_2H)_2Co(III)Pd_2(py)Cl]Cl_4$: Yield: 0.508 g (63.36%), m.p. 281°C (decomp.). IR (KBr, cm^{-1}): 3022 $(C\text{-}H)_{arom}$, 2940 $(C\text{-}H)_{aliph}$, 1709 (O-H..O), 1642 (C=N), 942 (N-O). Electronic spectra (DMF, log ϵ): λ_{max} 480 (3.94), 436 (4.11), 325 (3.56), 314 (4.12), 278 (4.23). Analysis: found: C, 35.29; H, 2.32;, N, 5.41; Co, 4.49; Pd, 16.78%. Calculated for $C_{37}H_{31}N_5O_8S_4CoPd_2Cl_5$: C, 35.53; H, 2.48; N, 5.60; Co, 4.71; Pd, 17.02%.

Dark-brown $[(S_4H)_2Co(III)Pd_2(py)Cl]Cl_4$: Yield: 0.573 g (68.72%), m.p. 248°C (decomp.). IR (KBr, cm^{-1}): 3030 $(C\text{-}H)_{arom}$, 2900 $(C\text{-}H)_{aliph}$, 1712 (O-H..O), 1625 (C=N), 938 (N-O). Electronic spectra (DMF, log ϵ): λ_{max} 482 (3.94), 424 (4.29), 326 (3.78), 313 (4.14), 253 (4.36). Analysis: found: C, 33.54; H, 2.19; N, 5.11; Co, 4.28; Pd, 15.93%. Calculated for $C_{37}H_{31}N_5O_4S_8CoPd_2Cl_5$: C, 33.78; H, 2.35; N, 5.32; Co, 4.48; Pd, 16.19%.

Acknowledgements

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