Synthesis of a 13-Membered Macrocyclic Tetrathiadioxime and its Mono- and Tri-nuclear Complexes with Tetrahedrally Co-ordinated Palladium(II)†

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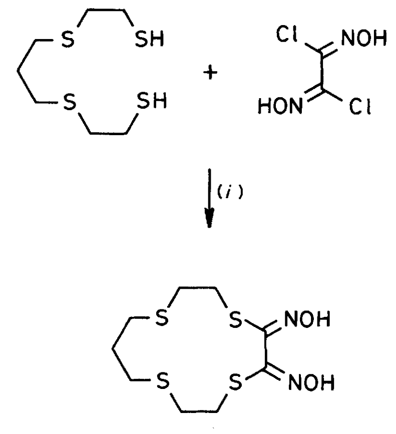
2,3-Bis(hydroxyimino)-1,4,7,11-tetrathiacyclotridecane (H_2L) has been prepared from 1,9-dimercapto-3,7-dithianonane and *anti*-dichloroglyoxime. Only mononuclear complexes with a metal–ligand ratio of 1:2 have been isolated with Ni^{II} and Co^{II}; Cu^{II} and Pd^{II} form only trinuclear complexes. The reaction of the mononuclear complexes with Cu^{II} and Pd^{II} gives heterotrinuclear complexes. Tetrahedral distortion of the 13-membered macrocycle is observed in the paramagnetic $[Pd_3(HL)_2]Cl_4$ and $[Pd_2Ni(HL)_2]Cl_4$ compounds. All these complexes are insoluble in common solvents; structures are proposed according to elemental analysis, i.r., and magnetic susceptibility measurements.

The co-ordination chemistry of quadridentate tetrathiamacrocycles[1,2] and bidentate *vic*-dioximes[3,4] has been the subject of intensive research. While thioethers co-ordinated to copper ions have been investigated to elucidate the structure of the blue copper proteins plastocyanine and azurin,[2,5] cobalt(II) *vic*-dioxime complexes have been taken as model compounds for B_{12} vitamins.[6,7] The relevance of bimetallic compounds to bioinorganic systems has been one of the reasons for the increase in the amount of research on polynuclear compounds.[8]

We have previously reported on the synthetic chemistry of MN_4 core-containing compounds, namely phthalocyanines[9] and *vic*-dioximes.[3,4,10] Among these, there have also been thioglyoximes, which co-ordinate essentially through the *vic*-dioxime moieties.[11–13] Macrocyclic *vic*-dioximes with four aza groups are capable of forming trinuclear complexes,[14] but with two aza and two to four oxa groups co-ordination was realized only through the *vic*-dioxime donors.[15] For the present work, we synthesized a new 13-membered tetrathiamacrocycle with a *vic*-dioxime unit incorporated to obtain trinuclear complexes.

Results and Discussion

The ligand used for this study, namely 2,3-bis(hydroxyimino)-1,4,7,11-tetrathiacyclotridecane (H_2L), contains four thioether sulphur donors and a *vic*-dioxime group. Its synthesis was accomplished in 45% yield by the reaction of dichloroglyoxime and 1,9-dimercapto-3,7-dithianonane[16] as shown in the Scheme.



Scheme. (*i*) NaOEt, −NaCl

The structure of H_2L was demonstrated by a combination of elemental analysis, ^1H and ^{13}C n.m.r., mass, and i.r. spectral data. The disappearance of the S–H stretching band along with the appearance of new absorptions at 3 230 [ν(OH)], 1 605 [ν(C=N)], and 990 cm^{-1} [ν(N–O)] are in agreement with the structure in the Scheme. The deuterium-exchangeable protons of the N–OH groups show chemical shifts at 12.1 while the aliphatic ether protons appear between 3.12 and 1.77. More detailed information about the structure of H_2L is provided by ^{13}C n.m.r. spectroscopy. The carbon resonance of the oxime groups is found to be at lower fields (145.52 p.p.m.) as given in the literature.[3,17] The proton-decoupled ^{13}C spectrum contains four shifts for the aliphatic carbon atoms between 30.66 and 28.09 p.p.m. The mass spectrum of H_2L, which shows a molecular ion at *m/z* 312, confirms the proposed structure and rules out an undesired polymeric form.

The reaction of H_2L with salts of Ni^{II}, Co^{II}, Pd^{II}, and Cu^{II} gives products with metal–ligand ratios of 1:2 or 3:2. In the case of Ni^{II} and Co^{II}, only mononuclear complexes were obtained even when the metal ions were used in excess (Table 1). Since a distinct lowering in the pH of the solution was observed during the complex formation, deprotonation of the ligand with subsequent N,N′-chelation with the *vic*-dioxime groups probably occurs. The usual hydrogen bridges of the square-planar *vic*-dioxime complexes were characterized by the weak deformation bands around 1 710 cm^{-1} in the case of $[Ni(HL)_2]$ and $[Co(HL)_2]$. Even though stable complexes of tetrathia-donor groups with Ni^{II} and Co^{II} have been isolated and characterized under anhydrous conditions, these compounds were reported to react instantaneously with solvents of good 'class a' donor ability, such as water, ethanol, and dimethyl sulphoxide, to liberate the free ligand and the metal salt.[16] Consequently, one should not expect the tetrathia group of H_2L to form complexes with Co^{II} or Ni^{II} simultaneously when the *vic*-dioxime group is chelating in a solvent such as ethanol. The six-co-ordinated cobalt(III) complex $[Co(HL)_2(py)Cl]$ was obtained when air was bubbled through a suspension of $[Co(HL)_2]$ in ethanol in the presence of pyridine (py).

In contrast to Ni^{II} and Co^{II}, Pd^{II} and Cu^{II} give trinuclear complexes with H_2L with a metal–ligand ratio of 3:2. Even

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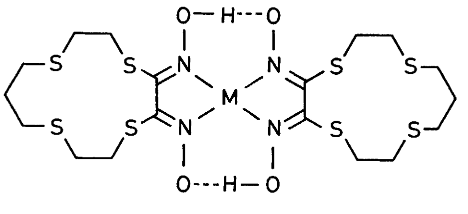
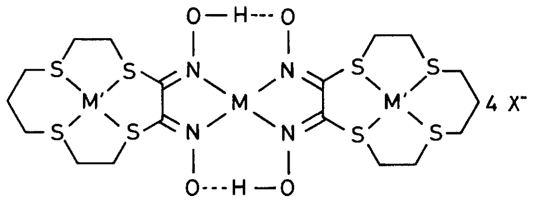
† *Non-S.I. unit employed:* B.M. ≈ 9.27 × 10^{-24} J T^{-1}.



M = Ni^{II}, Co^{II}, or $Co^{III}(py)Cl$



M = Ni^{II}, Pd^{II}, Cu^{II}, Co^{II}, or $Co^{III}(py)Cl$
M′ = Pd^{II} or Cu^{II}
X = Cl or NO_3

when the ratio of the reactants was 1:2, the same product $[M_3(HL)_2]X_4$, where M = Pd^{II} or Cu^{II} and X = univalent anion, was formed. The stability of the thioether complexes of these two metal ions in solvents such as water and ethanol is the most important reason for the formation of these trinuclear complexes.

In order to synthesize heterotrinuclear complexes of the type $[MM'_2(HL)_2]X_4$, heterogeneous reactions of mononuclear $[Ni(HL)_2]$, $[Co(HL)_2]$, or $[Co(HL)_2(py)Cl]$ with a solution of Cu^{II} or Pd^{II} was carried out. In these products, while Ni^{II}, Co^{II}, or Co^{III} are still co-ordinated to the *vic*-dioxime groups, two other metal ions are co-ordinated to two macrocyclic tetrathia groups.

The common feature of the complexes of H_2L is their insolubility which also hindered spectral investigations on their solutions. A close look at the i.r. spectra of these trinuclear complexes, taken as KBr pellets, shows a high degree of similarity which suggests that they all have the same geometrical configuration. I.r. data were especially useful for the identification of the i.r.-active anions (*e.g.* nitrate) participating in the complex formation. Magnetic susceptibility measurements provide sufficient data to characterize the structures (Table 2). The mononuclear complex $[Ni(HL)_2]$ is diamagnetic as expected for a d^8 metal ion in a square-planar field.[3,10,12,13] While the magnetic moment of $[Co(HL)_2]$ at 20 °C is 2.05 B.M. confirming the same structure, octahedral $[Co(HL)_2(py)Cl]$ is diamagnetic.

The trinuclear complexes of H_2L are all paramagnetic. The magnetic susceptibility results closely follow the spin-only formula calculated for a square-planar central metal ion and two tetrahedrally co-ordinated ones. While Ni^{II}, Pd^{II}, and Co^{III} form diagmagnetic structures with *vic*-dioxime moieties, the 13-membered tetrathiamacrocycle is distorted to form tetrahedral complexes; similar distortions were reported for palladium(II) complexes of tetra-aza macrocyclic ligands.[18] When the magnetic moments of the trinuclear complexes $[Pd_3(HL)_2]Cl_4$ and $[Pd_2Ni(HL)_2]Cl_4$ are calculated as per Pd the result is about 2.6 B.M., comparable with values reported for slightly distorted tetrahedral nickel(II) complexes.[19] Another important conclusion derived from the data in Table 2 is that there is no substantial interaction at room temperature among the three metal ions in the trinuclear complexes.

Experimental

1,9-Dimercapto-3,7-dithianonane[16] and *anti*-dichloroglyoxime[20] were prepared by reported procedure. Proton and ^{13}C n.m.r. spectra were recorded on a Bruker 200-MHz spectro-

Table 1. Analytical[a] and physical data for the complexes

Complex	Colour	Yield (%)	M.p.[b] (θ/°C)	Analysis (%) C	H	N	M	M′
$[Ni(HL)_2]$	Orange	64	(230)	(31.70)	(4.45)	(8.20)	(8.60)	—
				31.30	4.25	8.05	8.50	
$[Co(HL)_2]$	Pale brown	73	(205)	(31.70)	(4.45)	(8.20)	(8.65)	—
				31.25	4.20	8.10	8.75	
$[Co(HL)_2(py)Cl]$	Pale yellow	88	(205)	(34.70)	(4.45)	(8.80)	(7.4)	—
				34.25	4.40	8.60	7.5	
$[Cu_3(HL)_2]Cl_4$	Dark brown	40	(188)	(22.65)	(3.15)	(5.85)	(19.95)	—
				21.85	3.25	5.15	20.45	
$[Pd_3(HL)_2]Cl_4$	Dark red	71	(280)	(19.95)	(2.80)	(5.15)	(29.45)	—
				19.95	2.55	5.40	30.15	
$[Cu_2Ni(HL)_2]Cl_4$	Dark green	49	(205)	(22.75)	(3.20)	(5.40)	(6.15)	(13.35)
				22.30	3.00	6.05	5.85	13.85
$[Cu_2Ni(HL)_2][NO_3]_4$	Dark green	68	(240)	(20.45)	(2.85)	(10.60)	(5.55)	(12.05)
				19.85	2.65	10.05	5.10	12.55
$[Pd_2Ni(HL)_2]Cl_4$	Dark green	72	(230)	(20.85)	(2.90)	(5.40)	(5.65)	(20.55)
				20.45	2.60	5.20	5.25	21.05
$[Cu_2Co(HL)_2]Cl_4$	Brown	46	(195)	(22.75)	(3.20)	(5.90)	(6.20)	(13.35)
				23.10	3.00	5.75	6.15	13.95
$[Pd_2Co(HL)_2]Cl_4$	Dark brown	63	(250)	(20.85)	(2.90)	(5.40)	(5.70)	(20.55)
				20.05	2.80	5.35	5.30	21.00
$[Cu_2Co(HL)_2(py)Cl]Cl_4$	Yellow-green	57	(198)	(25.95)	(3.30)	(6.55)	(5.55)	(11.95)
				26.75	3.60	6.75	5.40	12.20

[a] Required values are given in parentheses. [b] With decomposition.

Table 2. Magnetic moments and characteristic i.r. bands (cm^{-1}) of the complexes (KBr pellets)

Compound	Magnetic moment (B.M.)	ν(CH)	δ(O–H–O)	ν(C=N)	ν(N–O)	Others
$[Ni(HL)_2]$	Diamagnetic	2 920—2 950	1 710	1 630	880	
$[Co(HL)_2]$	2.05	2 920	1 720	1 625	880	
$[Co(HL)_2(py)Cl]$	Diamagnetic	2 925	1 730	1 625	880	3 050—1 605 (py)
$[Cu_3(HL)_2]Cl_4$	4.72	2 920	1 720	1 625	885	
$[Pd_3(HL)_2]Cl_4$	5.10	2 960—2 980	1 710	1 620	875	
$[Cu_2Ni(HL)_2]Cl_4$	3.37	2 960	1 710	1 625	875	
$[Cu_2Ni(HL)_2][NO_3]_4$	3.85	2 920—2 950	1 760	1 630	885	1 380 (NO_3^-)
$[Pd_2Ni(HL)_2]Cl_4$	5.18	2 960—2 980	1 705	1 620	885	
$[Cu_2Co(HL)_2]Cl_4$	5.53	2 960	1 710	1 625	875	
$[Pd_2Co(HL)_2]Cl_4$	7.37	2 960—2 980	1 705	1 615	875	
$[Cu_2Co(HL)_2(py)Cl]Cl_4$	3.54	2 920—2 960	1 705	1 630	875	3 050—1 605 (py)

meter. Routine i.r. spectra were recorded on a Perkin-Elmer 983 spectrophotometer, as KBr pellets. The magnetic moments of the complexes were measured according to the Gouy method with a Newport Instruments type D-104 magnet power supply. Mass spectra were measured on a Varian Mat 711 spectrometer. The metal contents of the complexes were determined by a Hitachi 180-80 atomic absorption spectrophotometer in solutions prepared by decomposing the compounds in *aqua regia* and then subsequently digesting in concentrated HCl.

Syntheses.—2,3-*Bis*(*hydroxyimino*)-1,4,7,11-*tetrathiacyclotridecane* (H_2L). A solution of the sodium salt of 1,9-dimercapto-3,7-dithianonane was prepared by portionwise addition of the latter (2.28 g, 10 mmol) to NaOEt solution obtained by dissolving sodium metal (0.46 g, 20 mmol) in absolute ethanol (70 cm^3). This solution, together with a solution of *anti*-dichloroglyoxime (1.57 g, 10 mmol) in ethanol (70 cm^3), was simultaneously added dropwise over 4 h to absolute ethanol (130 cm^3) stirred at room temperature under an argon atmosphere; stirring was continued overnight. Then the pale yellow precipitate was filtered off and the filtrate was concentrated by evaporation (100 cm^3) to precipitate the rest of the product. The combined precipitates were treated with water (40 cm^3) at 35 °C to dissolve completely the NaCl formed and the *vic*-dioxime was filtered off, washed with acetone and diethyl ether, and dried. Recrystallization in ethanol gave 1.4 g (45%) of white product, m.p. 180 °C. It is soluble in dimethyl sulphoxide and ethanol (Found: C, 34.85; H, 5.40; N, 9.00. $C_9H_{16}N_2O_2S_4$ requires C, 34.60; H, 5.15; N, 8.95%). N.m.r. $[(CD_3)_2SO]$, ^1H, δ 12.1 (s, 2 H, disappears upon deuterium exchange), 3.12 (t, 4 H), 2.83 (t, 4 H), 2.72 (t, 4 H), and 1.77 (m, 2 H); ^{13}C (^1H decoupled), δ 145.52 (C=NOH), 30.66, 30.26, 28.94, and 28.09 p.p.m.; m/z 312 (M^+); $\nu_{max.}$ 3 230 (OH), 3 015, 2 920 (CH), 1 605 (C=N), 1 425, 1 255, 1 220, 1 010, 990 (N–O), 960, 905, 875, 730, and 640 (C–S) cm^{-1}.

$[Ni(HL)_2]$ *and* $[Co(HL)_2]$. When a solution of $NiCl_2{\cdot}6H_2O$ (0.12 g) or $CoCl_2{\cdot}6H_2O$ (0.12 g, 0.5 mmol) in ethanol (30 cm^3) was added to a solution of H_2L (0.312 g, 1 mmol) in ethanol (100 cm^3) at room temperature, a distinct change in colour to dark red and a decrease in the 'pH' of the solution was observed. Then, KOH (0.056 g, 1 mmol) in ethanol (10 cm^3) was added (pH ≈ 4) and an orange (Ni^{II}) or pale brown (Co^{II}) precipitate formed. After refluxing the mixture overnight, the precipitate was filtered off, washed with water, ethanol, and then diethyl ether, and dried.

$[Co(HL)_2(py)Cl]$. A solution of $CoCl_2{\cdot}6H_2O$ (0.12 g, 0.5 mmol) in absolute ethanol (30 cm^3) was added to a solution of H_2L (0.312 g, 1 mmol) in absolute ethanol (100 cm^3). Pyridine (0.24 g, 3 mmol) in ethanol (10 cm^3) was added and air was bubbled through the solution for 2 h while heating at 60 °C. The pale yellow precipitate was filtered off, washed with water, ethanol, and then with diethyl ether, and dried.

$[Cu_3(HL)_2]Cl_4$ *and* $[Pd_3(HL)_2]Cl_4$. A solution of metal salt (3 mmol) prepared by dissolving $CuCl_2{\cdot}2H_2O$ (0.51 g) in ethanol (30 cm^3) or by refluxing $PdCl_2$ (0.532 g, 3 mmol) and NaCl (0.351 g, 6 mmol) in ethanol (100 cm^3) was added to a solution of H_2L (0.614 g, 2 mmol) in ethanol (200 cm^3). The mixture was stirred on a water-bath at 60 °C and a solution of KOH (2 mmol, 0.112 g) in ethanol (10 cm^3) was added. The precipitate was filtered off, washed with water, then with ethanol and diethyl ether, and dried. The palladium(II) complex was dark red and the copper(II) complex was dark brown.

Heterotrinuclear complexes $[MM'_2(HL)_2]X_4$ (M = Ni^{II}, Co^{II}, *or* Co^{III}; M′ = Pd^{II} *or* Cu^{II}; X = Cl *or* NO_3). A suspension of mononuclear complex {0.44 mmol; 0.30 g $[Ni(HL)_2]$, 0.30 g $[Co(HL)_2]$, or 0.35 g $[Co(HL)_2(py)Cl]$} in ethanol (150 cm^3) was treated with an excess of the second metal salt prepared by dissolving $CuCl_2{\cdot}2H_2O$ (1.14 mmol, 0.195 g) or $Cu(NO_3)_2{\cdot}3H_2O$ (1.14 mmol, 0.275 g) in ethanol (40 cm^3) or by refluxing $PdCl_2$ (1.14 mmol, 0.202 g) and NaCl (2.28 mmol, 0.133 g) in ethanol (50 cm^3), and the mixture was refluxed for 14 h with continuous stirring. The precipitate was filtered off, washed with water, then with ethanol and diethyl ether, and dried.

The colours, yields, melting points, elemental analyses, characteristic i.r. absorptions, and magnetic moments of the complexes are given in Tables 1 and 2.

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