Synthesis of Soluble Complexes from a Tetradentate Dithioglyoxime Ligand

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14,15-Bis(hydroxyimino)-13,16-dithiaoctacosane (H_2L) has been prepared from the sodium salt of dodecanethiol and (*E,E*)-dichloroglyoxime. Only mononuclear complexes with a metal–ligand ratio of 1 : 2 are obtained for Ni^{II} or Co^{II} with H_2L. Both a mononuclear complex or a polymer can be obtained with Pd^{II} depending upon the stoichiometry of the reactants. With Pt^{II} only a polymeric product is isolated. For Cu^{II}, a trinuclear complex is formed in which the metal ions are co-ordinated to both thia and oxime donors. A heteropentanuclear complex and a heteronuclear polymer have been obtained by the reaction of $[Ni(HL)_2]$ with silver(I) and palladium(II) salts, respectively. All these complexes are very soluble in common organic solvents; ^1H and ^{13}C NMR, IR and UV/VIS data are presented.

The co-ordination chemistry of *vic*-dioximates is an intensive area of study and numerous transition-metal complexes of this group of ligands have been investigated.[1,2] The exceptional stability and unique electronic properties of these complexes can be attributed to their planar structure which is stabilized by hydrogen bonding. We have long had an interest in the chemical behaviour of complexes containing a planar MN_4 core structure and additional donor sites.[3,4] While phthalocyanines or *vic*-dioximes have formed the central co-ordination site, crown ethers,[5,6] monoaza crown ethers,[7,8] cyclopentadienyl groups,[9] tetrathiamacrocycles[10] or tetraazamacrocycles[11,12] have been used to bind alkali- or transition-metal ions.

In previous papers we have shown that a quite useful approach to obtain heteropolynuclear compounds is to carry out the complexation reaction in a stepwise fashion which requires ligands containing at least two different donor sites of comparable co-ordination capability.[9,11,12] According to this strategy, species of high nuclearity can be obtained from building blocks constituted of mononuclear complexes that contain unsaturated co-ordination sites.

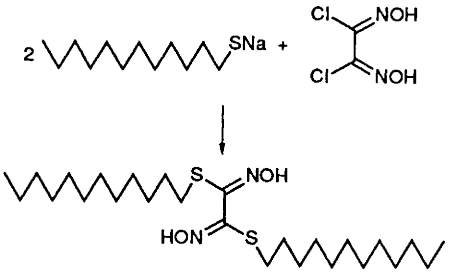
Herein we report the synthesis of a new dithioglyoxime ligand containing long alkyl chains. Mono-, tri- and penta-nuclear complexes as well as polymers have been synthesised by reaction of the dithioglyoxime with a variety of transition-metal ions.

The most exciting feature of these complexes is their solubility in common organic solvents even in the case of co-ordination polymers.

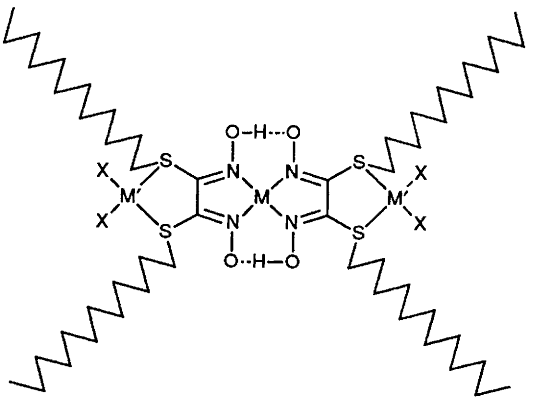
Results and Discussion

The dithioglyoxime ligand, 14,15-bis(hydroxyimino)-13,16-dithiaoctacosane (H_2L), has been prepared by a one-step reaction of *anti*-dichloroglyoxime with the sodium salt of dodecane-1-thiol (Scheme 1). This tetradentate ligand is soluble in common organic solvents, such as ethanol, chloroform, dichloromethane, *n*-hexane or diethyl ether. On the basis of the ^{13}C and ^1H NMR spectra, the ligand has a symmetric structure. The deuterium-exchangeable oxime protons appear at low field as a broad singlet (δ 8.6) which indicates an *anti* structure for the *vic*-dioxime moiety.[3,13] The presence of a singlet for the oxime group at relatively low field is in accordance with previously reported values for an *anti* oxime structure.[3,5,8]

The tetradentate dithioglyoxime derivative forms monomeric



Scheme 1



M	Ni^{II}	Co^{II}	$Co^{III}(py)Cl$	Pd^{II}	Cu^{II}	Ni^{II}
M′	—	—	—	—	Cu^{II}	$2Ag^I$
X	—	—	—	—	Cl^-	NO_3^-

Fig. 1 Mono-, tri- and penta-nuclear complexes of H_2L

co-ordination compounds with Ni^{II}, Co^{II} and Pd^{II} with a metal–ligand ratio of 1:2, a trinuclear complex with Cu^{II} and polymeric chains both homo- and hetero-nuclear polymers (metal–ligand ratio of 1:1) with Ni^{II}, Pd^{II}, Pt^{II} and Ag^I (Figs. 1 and 2). The most fascinating feature of all these complexes is their solubility in various organic solvents (*e.g.* the solubility of $[Ni(HL)_2]$ determined spectrophotometrically is 0.08 mol dm^{-3} in chloroform and 1.3×10^{-3} mol dm^{-3} in *n*-hexane) since insolubility is a well known property of dioximate complexes examplified extensively in the case of $[Ni(Hdmg)_2]$ (Hdmg =

Table 1 Analytical and physical data for H_2L and its complexes

				Analysis[a] (%)				
Compound	Colour	Yield (%)	M.p. (θ/°C)	C	H	N	M	M′
H_2L	White	65	87	(63.40)	(10.70)	(5.70)	—	—
				63.60	10.75	5.95		
$[Ni(HL)_2]$	Orange	62	97	(60.40)	(9.95)	(5.40)	(5.65)	—
				60.20	10.05	6.10	5.15	
$[Pd(HL)_2]$	Yellow	65	80	(57.70)	(9.50)	(5.20)	(9.80)	—
				57.80	9.50	5.60	10.00	
$[Co(HL)_2]$	Dark brown	30	—	(60.40)	(9.95)	(5.40)	(5.65)	—
				59.55	9.50	5.65	5.25	
$[Co(HL)_2(C_5H_5N)Cl]$	Brown	35	40	(59.60)	(9.40)	(6.10)	(5.70)	—
				60.35	9.85	5.90	5.20	
$[Cu_3(HL)_2Cl_4]$	Brown	31	135	(47.75)	(7.85)	(4.30)	(14.60)	—
				47.80	7.80	4.35	14.30	
$[Ag_4Ni(HL)_2][NO_3]_4$	Light brown	49	170	(36.45)	(6.00)	(6.55)	(3.40)	(25.20)
				36.50	6.20	6.10	3.60	25.30
$[\{NiPd(HL)_2Cl_2\}_n]$	Dark orange	48	75	(51.55)	(8.50)	(4.60)	(4.85)	(8.80)
				51.30	8.30	4.40	4.50	8.60
$[\{Pt_2(HL)_2Cl_2\}_n]$	Red	13	105[b]	(43.50)	(7.15)	(3.90)	(27.15)	—
				43.50	7.30	3.65	27.00	
$[\{Pd_2(HL)_2Cl_2\}_n]$	Red	49	95	(49.60)	(8.15)	(4.45)	(16.90)	—
				49.80	8.10	4.25	16.75	

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

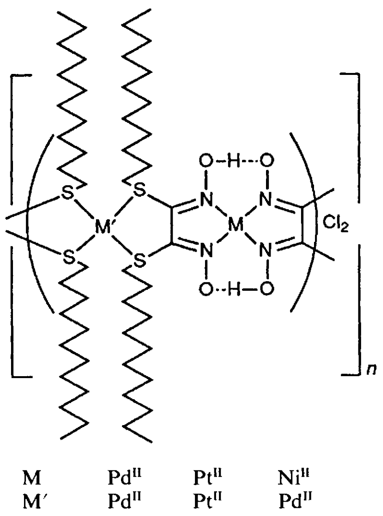


Fig. 2 Homo- and hetero-nuclear polymers

dimethylglyoximate). The bulky dodecyl chains of this new ligand as well as hindering interaction of the metal ions increases the lipophilicity of the products so enhancing their solubility in organic solvents such as chloroform, dichloromethane and hexane.

The formation of mono- or tri-nuclear complexes or polymer chains with the dithioglyoxime ligand (H_2L) depends upon the tendency of the metal ion to co-ordinate to 'hard' or 'soft' donor sites of the ligand. In the case of divalent d^8 metal ions (Ni^{II}, Pd^{II}, Pt^{II}) and with Co^{II} and Cu^{II} the first reaction is always with oxime groups, however the subsequent reaction then differs with various metal ions. With Ni^{II} and Co^{II}, only the mononuclear compound is obtained even in the presence of excess metal ions. The second-row d^8 metal ion palladium(II) forms a mononuclear complex when the metal–ligand ratio is 1:2, but a higher metal ratio leads to polymer chains. Platinum(II) and Cu^{II} simultaneously co-ordinate through both donor sites, Cu^{II} giving a trinuclear complex while Pt^{II} forms a polymer chain. Consequently mononuclear cobalt(II) and nickel(II) compounds are the only two products with potential use as intermediates in the formation of heteronuclear complexes since there is no need to protect unsaturated donor groups. Thus $[Ni(HL)_2]$ has been treated with silver(I) or palladium(II) salts to give a heteropentanuclear product with the former, and a polymer chain with the latter.

The $[Co(HL)_2]$ monomer is oxidized to a diamagnetic octahedral cobalt(III) derivative by bubbling air through a solution of the complex in the presence of a pyridine.[5,14] However, attempts to reduce the cobalt(III) complex to Co^I, a procedure used extensively to prepare alkyl cobaloxime derivatives of dmg and some other *vic*-dioximes, was not successful.[5,14,15]

The reddish colour of the mononuclear complexes is in accord with that of previously reported *vic*-dioximato complexes[16] (Table 1). In the IR spectra, the O–H ··· O bridge is characterized by a broad absorption for the bending vibrations around 1720–1760 cm^{-1} (Table 2). Proton NMR spectral data confirm the hydrogen-bridged structure with a chemical shift at lower field (δ 15–17.6) for the deuterium-exchangeable O–H protons.[3,5,8] Comparison of the ^{13}C NMR data for H_2L and its nickel(II) complex reveal a small chemical shift for the carbon atom of the oxime moiety upon complexation.

The reaction of H_2L with excess amounts of Pd^{II}, Pt^{II} or Cu^{II} results in polymeric products for Pd^{II} and Pt^{II} and a trinuclear complex with Cu^{II}. The monomeric impurity obtained during formation of the palladium(II) polymer can be separated by column chromatography. The diamagnetic nature of the palladium- and platinum-(II) polymers is confirmed by their ^1H NMR spectra which show comparable shifts with those of $[Ni(HL)_2]$. Consequently we might conclude that both of these d^8 metal ions are co-ordinated with dioximate and dithio donor sites in square-planar geometry. The rather broad nature of the observed resonances is a consequence of the polymeric structure of the complexes. In the ^{13}C NMR spectra, all peaks are identical for the complexes of Pd^{II} and Pt^{II} except for the carbon atoms of the oxime moiety, which appear at δ 150.15 for the palladium(II) derivative and at δ 146.01 for the platinum(II) polymer. The IR data of the homonuclear polymers are also consistent with the proposed structures. The bending vibrations of the O–H ··· O bridges are not identifiable for either the platinum(II) or nickel(II)palladium(II) polymer.

In order to isolate heteronuclear products, the complex

Table 2 Characteristic IR bands (cm^{-1}) of H_2L and its complexes (KBr pellets)

Compound	ν(C=N)	δ(O–H–O)	ν(N–O)	ν(CH)	Others
H_2L	1600	—	880	2920–2980	3200–3250 [ν(OH)]
$[Ni(HL)_2]$	1620	1740–1760	880	2920–2980	
$[Pd(HL)_2]$	1640	1740–1760	880	2940–3000	
$[Co(HL)_2]$	1620	1720	885	2920–2980	
$[Co(HL)_2(C_5H_5N)Cl]$	1620–1640	1730	880	2920–2980	1605 (C_5H_5N)
$[Cu_3(HL)_2Cl_4]$	1630	1730	885	2920–2980	
$[Ag_4Ni(HL)_2][NO_3]_4$	1630	1730	885	2930–2980	1380 (NO_3^-)
$[\{NiPd(HL)_2Cl_2\}_n]$	1620	*	885	2930–2980	
$[\{Pt_2(HL)_2Cl_2\}_n]$	1630	*	880	2930–2980	
$[\{Pd_2(HL)_2Cl_2\}_n]$	1630	1740	875	2930–2980	

* Unobserved.

Table 3 Proton NMR spectral data for H_2L and its complexes in $CDCl_3$

Compound	O···H–O	S–CH$_2$	SCH$_2$C*H*$_2$	–CH$_2$–	CH$_3$	Others
H_2L	—	2.89 (t, 4 H)	1.64 (q, 4 H)	1.25 (m, 36 H)	0.88 (t, 6 H)	8.6 (s, 2 H) (N–OH)
$[Ni(HL)_2]$	17.60 (s, 2 H)	3.23 (t, 8 H)	1.58 (q, 8 H)	1.26 (m, 72 H)	0.88 (t, 12 H)	
$[Pd(HL)_2]$	15.02 (s, 2 H)	3.25 (t, 8 H)	1.63 (q, 8 H)	1.26 (m, 72 H)	0.88 (t, 12 H)	
$[Co(HL)_2(C_5H_5N)Cl]$	18.38 (s, 2 H)	3.28 (m, 8 H)	1.48 (q, 8 H)	1.25 (m, 72 H)	0.88 (t, 12 H)	8.25 (d, 2 H), 7.71 (t, 2 H), 7.27 (t, 1 H) (C_5H_5N)
$[Ag_4Ni(HL)_2][NO_3]_4$*	17.58 (s, 2 H)	3.22 (t, 8 H)	1.56 (8 H)	1.26 (72 H)	0.85 (12 H)	
$[\{NiPd(HL)_2Cl_2\}_n]$*	15.41 (s, 2 H)	3.25 (8 H)	1.58 (8 H)	1.26 (72 H)	0.88 (12 H)	
$[\{Pt_2(HL)_2Cl_2\}_n]$*	18.60 (s, 2 H)	3.31 (t, 8 H)	1.59 (8 H)	1.25 (72 H)	0.87 (12 H)	
$[\{Pd_2(HL)_2Cl_2\}_n]$*	15.41 (s, 2 H)	3.36 (t, 8 H)	1.58 (8 H)	1.25 (72 H)	0.88 (t, 12 H)	

* Broad peaks.

Table 4 Carbon-13 NMR spectral data (δ) for H_2L and its complexes in $CDCl_3$

Compound	C=NOH	CH$_2$	CH$_2$–S	CH$_3$
H_2L	149.73	28.67, 29.15 29.39, 29.51 29.63, 30.86 31.95	22.71	14.14
$[Ni(HL)_2]$	146.04	28.50, 29.10 29.38, 29.54 29.67, 30.32 31.95, 32.87	22.71	14.13
$[Co(HL)_2(C_5H_5N)Cl]$*	146.48	28.49, 29.07 29.33, 29.49 29.61, 30.89 33.24	22.66	14.08
$[Pd(HL)_2]$	147.32	28.49, 29.06 29.34, 29.61 30.27, 31.90 32.98	22.67	14.09
$[Ag_4Ni(HL)_2][NO_3]_4$	146.13	28.49, 29.08 29.36, 29.64 30.30, 31.93 32.90	22.70	14.12
$[\{NiPd(HL)_2Cl_2\}_n]$	146.71	29.62, 31.91	22.70	14.13
$[\{Pt_2(HL)_2Cl_2\}_n]$	146.01	28.52, 29.66 30.30, 31.94	22.70	14.12
$[\{Pd_2(HL)_2Cl_2\}_n]$	150.19	29.64, 31.92	22.69	14.11

* Signals from pyridine moiety at δ 127.16, 139.06 and 152.58.

Table 5 Electronic spectra of H_2L and its complexes in chloroform

Compound	λ_{max}/nm ($10^{-4}\varepsilon$/dm^3 mol^{-1} cm^{-1})
H_2L	230 (0.675)
$[Ni(HL)_2]$	234 (2.325), 256 (2.480), 375 (1.040), 402 (1.095)
$[Pd(HL)_2]$	231 (2.735), 282 (sh) (1.185), 340 (1.425)
$[Co(HL)_2]$	248 (3.440)
$[Co(HL)_2(C_5H_5N)Cl]$	230 (1.350), 320 (0.600)
$[Cu_3(HL)_2Cl_4]$	260 (0.510)
$[Ag_4Ni(HL)_2][NO_3]_4$	230 (3.560), 313 (2.040)
$[\{NiPd(HL)_2Cl_2\}_n]$	235 (3.550), 319 (1.970), 408 (sh) (1.050)
$[\{Pt_2(HL)_2Cl_2\}_n]$	232 (3.505), 364 (1.625)
$[\{Pd_2(HL)_2Cl_2\}_n]$	230 (2.540), 310 (sh) (1.855), 425 (1.680)

$[Ni(HL)_2]$ was utilized owing to its unique structure and high yield. This complex reacts with monovalent Ag^I to give a pentanuclear compound or divalent Pd^{II} to give a heteronuclear polymer. The products are a deeper red colour than the nickel(II) monomer. In addition to elemental analytical data, IR spectroscopy indicates the presence of nitrate counter ions at 1380 cm^{-1} for the silver complex. The ^{1}H and ^{13}C NMR spectra of the heteronuclear polymers are almost identical to those of the homonuclear products. The comparable chemical shifts for the bridging hydrogens of homo- and hetero-nuclear polymers to those of the monomers indicate retention of a hydrogen-bridged chelate of the *vic*-dioxime moiety upon polymerization. The planarity of the molecules is retained after complexation of the thia donor groups with Pd^{II} and the molecules are diamagnetic confirming this geometry.

As can be suggested from their reddish colours, all the complexes show intense charge-transfer absorptions at *ca.* 400 nm. No weak d–d transitions can be observed. The general character of these spectra is very similar to that of corresponding complexes of symmetrically disubstituted dioximate ligands. The similarity is probably a consequence of the fact that for charge-transfer transitions the donor electrons remain at closely similar energies and the ligand acceptor orbitals are not greatly altered by chelation of different transition-metal ions.

In conclusion we can propose the use of this novel dithioglyoxime ligand to prepare monomeric and heteronuclear polymeric complexes with high solubilities in common organic solvents.

Experimental

Dichloroglyoxime was prepared by a reported procedure.[17] Dodecane-1-thiol was purchased from Merck. Proton and ^{13}C NMR spectra were recorded on a Bruker 200 MHz spectrometer. Routine IR spectra were recorded on a Perkin-Elmer 983 spectrophotometer as KBr pellets. 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 subsequent digestion in concentrated HCl. For the pentanuclear silver complex decomposition was achieved in concentrated HNO_3.

Synthesis of 14,15-*Bis* (*hydroxyimino*)-13,16-*dithiaoctacosane* H_2L.—Dodecane-1-thiol (1.003 g, 4.95 mmol) was dissolved in absolute ethanol (40 cm^3) under argon and metallic sodium (0.118 g, 5.13 mmol) was added while cooling in an ice-bath. To this solution (*E,E*)-dichloroglyoxime (0.389 g, 2.47 mmol) in absolute ethanol (20 cm^3) was added dropwise during 1 h and stirred at room temperature overnight. The mixture was filtered off, the volume of ethanol reduced to 30 cm^3 and crystallization completed at low temperature (−40 °C). The white crystals were filtered off, washed with water and dried, m.p. 87 °C. The ligand was soluble in *n*-hexane, ethanol and diethyl ether.

Mononuclear Complexes $[M(HL)_2]$ M = Ni^{II}, Co^{II}, Pd^{II} *and* Co^{III}.—To an ethanol solution (20 cm^3) of H_2L (147 mg, 0.3 mmol) was added an ethanol solution of the appropriate metal salt $\{NiCl_2 \cdot 6H_2O$ (36 mg, 0.15 mmol), $Na_2[PdCl_4]$ (7.2 cm^3, 2.08×10^{-2} mol dm^{-3}) or $CoCl_2 \cdot 6H_2O$ (36 mg, 0.15 mmol)$\}$ with stirring at 60 °C. A distinct change in colour and a decrease in the pH of the solution was observed. Potassium hydroxide (17 mg, 0.3 mmol) in ethanol (6 cm^3) was then added (pH ≈ 3.5) and precipitation occurred leading to orange (Ni^{II}) or yellow (Pd^{II}) precipitates or a brown viscous oil (Co^{II}). The products were filtered off, washed with water and ethanol and then dried. These compounds were soluble in *n*-hexane, diethyl ether, chloroform and dichloromethane. In the case of $[Co(HL)_2(py)Cl]$ (py = pyridine), H_2L (147 mg, 0.3 mmol) was dissolved in ethanol (20 cm^3) and a solution of $CoCl_2 \cdot 6H_2O$ (36 mg, 0.15 mmol) in ethanol (5 cm^3) was added. A solution of pyridine (2.5 cm^3, 0.496 mol dm^{-3}) in ethanol was then added and air was bubbled through the mixture for 1 h. The pale brown precipitate was filtered off, washed with water and ethanol, and dried.

$[Cu_3(HL)_2Cl_4]$.—A solution of $CuCl_2 \cdot 2H_2O$ (76.7 mg, 0.45 mmol) in ethanol (10 cm^3) was added to a solution of H_2L (147 mg, 0.3 mmol) in ethanol (20 cm^3). The mixture was stirred at 30 °C and a solution of KOH (17 mg, 0.3 mmol) in ethanol (6 cm^3) added. The resulting precipitate was filtered off, washed with water and ethanol, and dried.

$[Ag_4Ni(HL)_2][NO_3]_4$.—A solution of the mononuclear complex $[Ni(HL)_2]$ (40 mg, 0.04 mmol) in acetone (30 cm^3) was treated with a refluxing acetone solution of $AgNO_3$ (45 mg, 0.26 mmol, 10 cm^3) and the mixture was refluxed for 3 h with continuous stirring. The precipitate was filtered off, washed with water and ethanol, and dried.

Homonuclear Polymers $[\{M_2(HL)_2Cl_2\}_n]$ (M = Pd^{II} *or* Pt^{II}).—A solution of Pd^{II} or Pt^{II} [prepared by dissolving K_2PtCl_4 (124.53 mg, 0.3 mmol) in ethanol–water (2:5, 7 cm^3) or by refluxing $PdCl_2$ (53.2 mg, 0.3 mmol) and NaCl (35.1 mg, 0.6 mmol) in ethanol (10 cm^3)] was added to a solution of H_2L (147 mg, 0.3 mmol) in ethanol (20 cm^3). The mixture was stirred for 2 h under an argon atmosphere. The resulting precipitate was filtered off, washed with water and ethanol, and dried. Both the palladium and platinum complexes were dark red.

$[\{NiPd(HL)_2Cl_2\}_n]$.—A solution of Pd^{II} prepared by refluxing $PdCl_2$ (14.30 mg, 0.08 mmol) and NaCl (9.36 mg, 0.16 mmol) in ethanol (5 cm^3) was added to a solution of the mononuclear complex $[Ni(HL)_2]$ (40 mg, 0.04 mmol) in acetone (30 cm^3). The mixture was refluxed for 4 h with continuous stirring and the resulting precipitate filtered off, washed with water and ethanol, and dried.

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Received 13*th January* 1992; *Paper* 2/00141A