SHORT PAPER

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Synthesis and characterization of 1,2-bis(1-mercapto-4,7,10-trioxaundecyl)-glyoxime and Ni^{II} and Pd^{II} complexes[†]

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Oligoethyleneoxythia functional *vic*-dioxime and complexes with Ni(II) and Pd(II) are prepared starting from 1-mercapto-4,7,10-trioxaundecane by the reaction of (*E*,*E*)-dichloroglyoxime.

Oximes constitute an important class of compound having versatile reactivities[1]. Since the pioneering work of Schrauzer[2], cobaloximes have been widely studied as the model for coenzyme B_{12}. These are bis complexes of dimethylglyoximate. The exceptional stability and unique electonic properties of these complexes can be attributed to their planar structure which is stabilized by hydrogen bridges. The reaction of amines or thiols with (*E*,*E*)-dichloroglyoxime or cyanogen-di-N-oxide yielded various symmetrically substituted diaminoglyoxime or dithioglyoxime derivatives[3–9]. In previous papers we have synthesized *vic*-dioximes and their transition metal complexes containing crown ethers[9,10], monoaza crown ethers[11,12], ferrocene groups[13], tetrathiamacrocycles[14] or N_2O_2 macrocycles[15]. The liquid crystalline[16,17] and gas sensor[18] properties of these compounds and their complexes were also investigated.

In the present work, we have prepared a new dithioglyoxime ligand containing oligoethyleneoxythia chains. The metal complexes have been synthesized by the (*E*,*E*)-dithioglyoxime with nickel and palladium salts.

The dithioglyoxime derivative, 1,2-bis(1-mercapto-4,7,10-trioxaundecyl)glyoxime (H_2L), was prepared by a one step reaction of (*E*,*E*)-dichloroglyoxime with 1-mercapto-4,7,10-trioxaundecane (Scheme 1). This tetradentate ligand is soluble in common organic solvents, such as diethyl ether, ethanol, chloroform, acetonitrile, *etc*.

The IR spectrum of H_2L exhibited OH and C=N streching bands at 3240 and 1580 cm^{-1} respectively. These values are confirmed with spectral data reported for similar compounds[10,15]. In the ^1H NMR spectrum of H_2L in $(CD_3)_2SO$, the OH proton resonance appear as singlet at δ=11.95 ppm. This singlet disappears by deuterium exchange. A single chemical shift for the OH proton indicates that the oxime groups are in the *(E,E)* form.[9–11,19] The carbon resonance of the oxime moiety was found at δ=145.43 ppm.[20] The protons of the CH_2 group attached to the S atoms showed chemical shift at higher field (2.50 ppm) than those of the other CH_2 (3.60–3.41 ppm) groups. The molecular ion peak at m/z 445 in the EI mass spectrum of H_2L also confirms the proposed structure.

The tetradentate dithioglyoxime derivative forms mononuclear coordination compounds with Ni(II) **4** and Pd(II) **5** with metal-ligand ratio of 1:2. The most fascinating feature of all these complexes is their solubility in various organic solvents (*e.g.* diethylether, chloroform, ethanol). $Ni(HL)_2$ is soluble even in water.

The orange colour of the complexes are in accord with that previously reported *vic*-dioximato complexes.[21] In the IR spectra, the O–H--O bridge is characterized by a broad absorption for the bending vibrations around 1720–1760 cm^{-1}. ^1H NMR spectral data in $CDCl_3$ confirm the hydrogen-bridged structure with a chemical shift at lower field (δ=17.6 ppm for $Ni(HL)_2$, not observed for $Pd(HL)_2$) for the deuterium exchangeable OH protons.[10,11] The ^1H and ^{13}C NMR spectra were also measured in $(CD_3)_2SO$. In this case, $Ni(HL)_2$ decomposed partially to the ligand H_2L, and the ligand peaks are observed in addition to the complex peaks. The structures of $Ni(HL)_2$ and $Pd(HL)_2$ are also confirmed by mass spectroscopy, which gives a $[M+1]^+$ peak at *m/z* 946 and $[M+1]^+$ peak at *m/z* 994 respectively.

Experimental

^1H and ^{13}C NMR spectra were measured on a Bruker 200 MHz spectrometer. Infrared spectra (sodium chloride cell or KBr pellets) were obtained on a Perkin-Elmer 983 spectrophotometer. Elemental analysis were obtained using a Carlo-Erba Instrument. Mass spectra were recorded on a VG ZAB-SPEC spectrometer with electron impact or fast atom bombardment methods (35 KV, MNBA was used as matrix). 1-mercapto-4,7,10-trioxaundecane[22] **1** and (*E*,*E*)-diclorogly-oxime[23] **2** were prepared by reported procedures.

*1,2-Bis(1-mercapto-4,7,10-trioxaundecyl)glyoxime (H_2L) **3***: **1** (28 mmol, 5 g) was dissolved in absolute ethanol (100 ml) under argon. After cooling, metallic sodium (28 mmol, 0.64 g) was added in an ice-bath. To this reaction mixture, (*E*,*E*)-dichloroglyoxime **2** (14 mmol, 2.18 g) in absolute ethanol (50 ml) was added dropwise during 1h and stirred at room temperature overnight. After the solvent was evaporated, 100 ml water was added to the reaction mixture and the aqueous phase was extracted with diethylether. The combined extracts were dried over sodium sulfate, the solvent was evaporated to dryness and the oily product was precipitated with petroleum ether (40:60). Yield: 2.7 g (43 %), oil (Found; C, 42.77; H, 7.23; N, 5.87; $C_{16}H_{32}N_2O_8S_2$ requires C, 43.23; H, 7.26; N, 6.30 %). ν_{max}/cm^{-1} 3240 (NH), 2980–2880, 1580 (C=N), 1450, 1400, 1350, 1290, 1250, 1200, 1140–1100 (C–O–C), 1050, 980 (NO), 870. δ_H $[(CD_3)_2SO]$ 11.95 (s, 2 H, NOH, disappeared upon D_2O exchange), 3.60–3.41 (m, 20 H, OCH_2), 3.25 (s, 6 H, OCH_3), 2.50 (t, 4 H, SCH_2); δ_C $[(CD_3)_2SO]$, APT 145.43 (C=NOH), 71.15, 69.50, 69.19 (OCH_2), 57.91 (CH_3), 29.28 (SCH2); *m/z* (EI) (%) 445 $[M]^+$ (18), 427 $[M–H_2O]^+$ (10), 298 $[M–((CH_2CH_2O)_3CH_3)]^+$ (10), 265 $[M–S(CH_2CH_2O)_3CH_3]^+$ (36).

*N,N-coordinated complexes [M=Ni(II) **4** and Pd(II) **5**]*: To a solution of 200 mg (0.45 mmol) of H_2L in 20 ml of ethanol, the appropriate metal salt {$NiCl_2.6H_2O$ (0.225 mmol, 53 mg) and $Na_2[PdCl_4]$ (10.8 ml of 2.08×10^{-2} mol/l solution in ethanol)}was added. A distinct change in colour and a decrease in the pH of the solution was observed. The mixture was stirred and heated to 60oC for 2 h while an equivalent amount of KOH was added dropwise to maintain a pH value of 7. The solvent was removed and the residue was dissolved in dichloromethane. The insoluble salt was filtered and the solvent was evaporated. The orange products were obtained as oil. The complexes (**4** and **5**) were purified by preparative thin-layer chromatograhpy (Silicagel, eluent: dichloromethane:methanol, 20:1). Pd(II) complex was lighter orange than Ni(II).

$Ni(HL)_2$: Yield: 70 mg (33 %), oil (Found; C, 39.72; H, 6.97; N, 5.91 $C_{32}H_{62}N_4NiO_{16}S_4$ requires C, 40.64; H, 6.61; N, 5.92 %); ν_{max}/cm^{-1} 2980–2880 (CH_2, CH_3), 1760 (O–H--O), 1640 (C=N), 1470, 1350,

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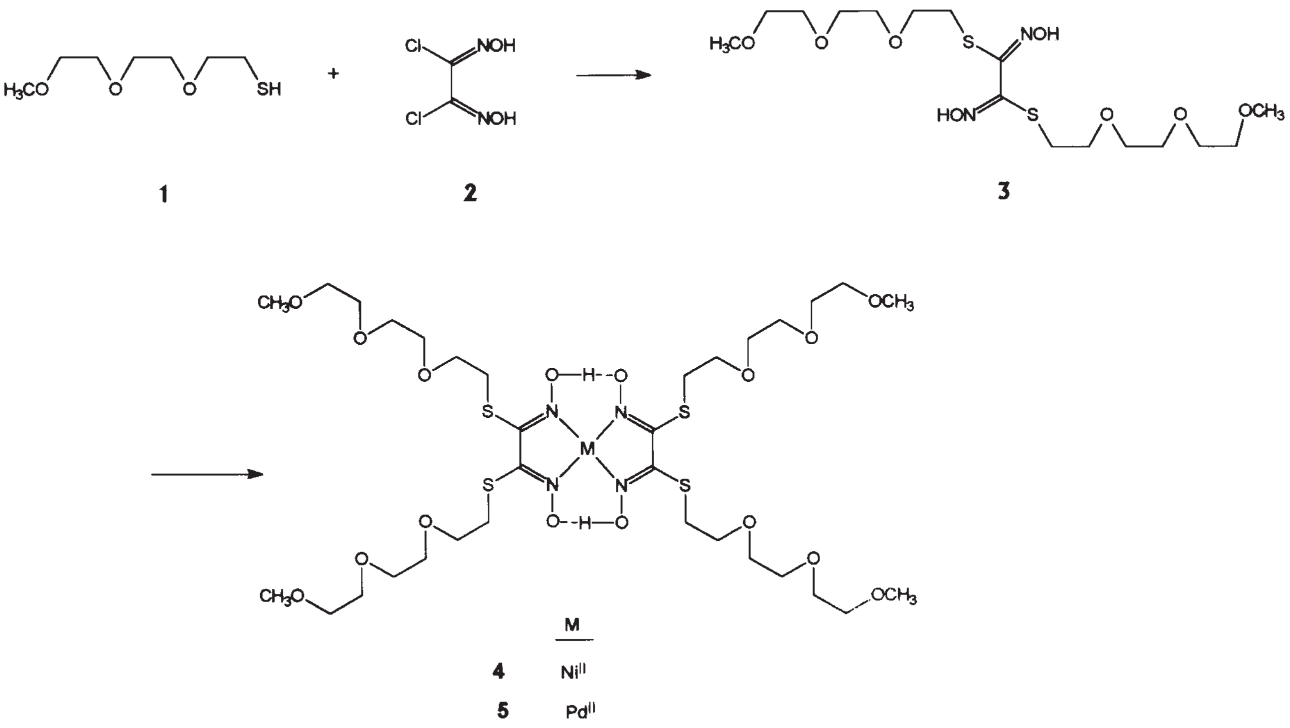
[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*



Scheme

1290, 1240, 1200, 1190 (C–O–C), 930 (NO), 890; δ_H (CDC_{13}) 17.59 (s, 2 H, O–H–O, disappeared by D_2O exchange), 3.69–3.53 (m, 40 H, OCH_2), 3.41 (t, 8 H, SCH_2), 3.38 (s, 12 H, OCH_3); δ_C $[(CD_3)_2SO]$ 144.98, 142.84, 70.73, 69.08, 68.75, 57.49 (OCH_3), 30.74, 28.74 (SCH_2); *m/z* (FAB) (%) 946 $[M+1]^+$ (6), 237 (100), 177 (10).

Pd(HL)$_2$: Yield: 45 g (20 %), oil (Found; C, 38.39; H, 6.20; N, 5.09 $C_{32}H_{62}N_4O_{16}S_4Pd$ requires C, 38.69; H, 6.29; N, 5.64 %); ν_{max}/cm^{-1} 2940–2880, 1720 (O–H···O), 1640 (C=N), 1460, 1420, 1350, 1290, 1250, 1200 (C–O–C), 1110, 1130, 890, 850; δ_H $(CDCl_3)$ 3.38 (s, 12 H, OCH_3), 3.54–3.63 (m, 48 H, CH_2); *m/z* (FAB) (%) 1017 $[(M+1)+23]^+$ (84), 994 $[M+1]^+$ (90), 815 $[(M+1)–S(CH_2CH_2O)_3CH_3]^+$ (5), 553 $[(M+1)–3x(CH_2CH_2O)_3CH_3]+$ (23), 373 $[(M+1)- (S(CH_2CH_2O)_3$ $CH_3+3x(CH_2CH_2O)_3CH_3)]^+$ (9).

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