New Organocobaloximes Derived from *N,N*-disubstituted Monothiocarbamic Acid *S*-vinyl Esters

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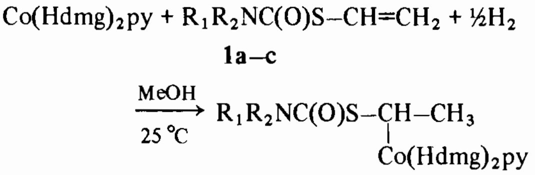
N,N-disubstituted monothiocarbamate ions ($R_1R_2NCOS^-$) form mostly *S*- and/or *O*-bonded complexes with transition metal ions. The synthesis, properties and structure of these compounds have been the subject of a recent review [1]. *N,N*-disubstituted monothiocarbamic acid *O*-esters have also been reported to function as ligands in a few cases, forming metal-to-*S* bonds with Pd [2–5], Pt [2, 6–8], Hg [9], Cr [10], Bi [11], and a metal-to-N bond with Sn [12].

Monothiocarbamic *S*-esters have apparently not been described as ligands and, to our knowledge, there are only two reports on compounds in which such ligands are bonded to a metal through a carbon atom: one is a Ni carbene species [13] and the other has a lithium-to-carbon bond [14].

We now report the synthesis of some organocobaloxime derivatives in which *N,N*-disubstituted monothiocarbamic esters are attached to the cobalt atom via a Co–C σ-bond. The complexes were prepared by reacting pyridinebis(dimethylglyoximato)cobalt(II), $Co(Hdmg)_2py$, with the corresponding monothiocarbamic vinyl esters (**1a–c**) in the presence of molecular hydrogen:



$$\mathrm{Co(Hdmg)_2py + \underset{\textbf{1a–c}}{R_1R_2NC(O)S{-}CH{=}CH_2} + \tfrac{1}{2}H_2} \xrightarrow[25\,^{\circ}\mathrm{C}]{\mathrm{MeOH}} \mathrm{R_1R_2NC(O)S{-}\underset{\substack{|\\ Co(Hdmg)_2py}}{CH}{-}CH_3} \qquad (1)$$

2a–c

a: $R_1 = R_2$ = n-Pr
b: R_1 = Et; R_2 = n-Bu
c: R_1 = Et; R_2 = cyclohexyl

where $Hdmg^-$ is the monoanion of dimethylglyoxime and py is pyridine. This synthetic route is based on the reactivity of the unstable hydridocobaloxime toward olefinic compounds [15], utilized recently for preparing the cobaloxime derivative of enolpyruvic acid [16].

The products of the above reaction were identified by elemental analysis, IR and ^1H NMR spectroscopy (*cf.* 'Experimental'). In all of the new organocobaloximes (**2a–c**) the cobalt is bonded to the α-carbon, implying Markovnikov addition of $HCo(Hdmg)_2py$ across the double bond. Compounds **2a–c** are stable for about 2 days in neutral solution, but decompose at 25 °C in 0.2 M HCl (*ca.* 12 h) and 0.1 M NaOH (*ca.* 24 h).

Attempts were made at the catalytic hydrogenation of **1a** in the presence of 10% pyridinecobaloxime at 40 °C; however, H_2 uptake practically ceased after the amount corresponding to eqn. 1 had been adsorbed. Thus compounds **2a–c** are not reactive intermediates in the vinyl group hydrogenation of **1a–c.**

A structural feature deserves consideration. The methyl groups of coordinated $Hdmg^-$ are nonequivalent, showing a doublet at 2.12 and 2.16 ppm (6H each). Similar behaviour has been observed first by Gaudemer [17] then by others [18] and attributed to the presence of asymmetric centers or to restricted rotation. In the present case it seems that the *N,N*-substituents are preferentially directed toward one pair of methyl groups when bending back to the equatorial plane. This may be due to hydrophobic interaction between the methyl and the *N*-alkyl groups, which hinders free rotation about the Co–C bond and makes the two CH_3 pairs magnetically nonequivalent.

Experimental

Vinyl monothiocarbamates **1a–c** were prepared by a known procedure [19]. Satisfactory microanalyses, IR and ^1H NMR spectra were obtained for all 3 compounds.

General Procedure for the Synthesis of Organocobaloximes 2a–c

To a stirred mixture of 5.8 g (0.05 mol) dimethylglyoxime, 2.0 g (0.05 mol) finely powdered NaOH and 2.5 ml (0.03 mol) pyridine in 100 ml MeOH was added, under H_2 atmosphere, 9.15 g (0.025 mol) $Co(ClO_4)_2 \cdot 6H_2O$ dissolved in 20 ml MeOH. After about 2 min stirring, 0.03 mol of the *S*-vinyl monothiocarbamate **1a** or **1b** or **1c** was added, and the solution was stirred until the H_2-uptake ceased (*ca.* 230 ml hydrogen was consumed). The mixture was then cooled in ice, diluted with 200 ml water, stirred for 30 min, filtered off and washed with water. Recrystallization occurred from methanol/water containing 1 ml pyridine.

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Yields: **2a**, 7.4 g (53%); **2b**, 6.5 g (47%); **2c**, 5.8 g (40%). *Anal.* **2a**: Found: C, 47.53; H, 6.77; N, 15.09; S, 5.77. Calc. for $\mathrm{C_{22}H_{37}N_6O_5SCo}$ (556.58): C, 47.48; H, 6.70; N, 15.10; S, 5.76%. **2b**: Found: C, 47.20; H, 6.76; N, 15.02; S, 5.62. Calc. for $\mathrm{C_{22}H_{37}N_6O_5SCo}$ (556.58): same as for **2a**. **2c**: Found: C, 48.23; H, 6.42; N, 14.07; S, 5.32. Calc. for $\mathrm{C_{24}H_{39}N_6O_5SCo}$ (582.62): C, 49.48; H, 6.75; N, 14.42; S, 5.50%.

^{1}H NMR spectra (ppm): **2a**: 0.86 (d, 3H, $\underline{\mathrm{CH}}_3\mathrm{CH}$); 0.90 (t, 6H, $\underline{\mathrm{CH}}_3\mathrm{CH_2}$); 1.61 (sextet, 4H, $\mathrm{CH_3}\underline{\mathrm{CH}}_2\mathrm{CH}$); 2.12 (s, 6H, $\underline{\mathrm{CH}}_3\mathrm{C{=}NOH}$); 2.16 (s, 6H, $\underline{\mathrm{CH}}_3\mathrm{C{=}NOH}$); 3.25 (t, 4H, $\mathrm{CH_3CH_2}\underline{\mathrm{CH}}_2$); 3.86 (q, 1H, $\mathrm{S}\underline{\mathrm{CH}}\mathrm{CH_3}$); 7.17–8.65 (m, 5H, pyridine); 18 (broad s, 2H, O–H••O). **2b**: 0.86 (d, 3H, $\underline{\mathrm{CH}}_3\mathrm{CH}$); 0.91 (t, 3H, $\underline{\mathrm{CH}}_3\mathrm{CH_2CH_2CH_2}$); 1.14 (t, 3H, $\underline{\mathrm{CH}}_3\mathrm{CH_2}$); 1.23–1.7 (m, 4H, $\mathrm{CH_3}\underline{\mathrm{CH}}_2\underline{\mathrm{CH}}_2\mathrm{CH_2}$); 2.12 (s, 6H, $\underline{\mathrm{CH}}_3\mathrm{C{=}NOH}$); 2.16 (s, 6H, $\mathrm{C}\underline{\mathrm{H}}_3\mathrm{C{=}NOH}$); 3.28 (t, 2H, $\mathrm{CH_3CH_2CH_2}\underline{\mathrm{CH}}_2$); 3.30 (q, 2H, $\mathrm{CH_3}\underline{\mathrm{CH}}_2$); 3.85 (q, 1H, $\mathrm{S}\underline{\mathrm{CH}}\mathrm{CH_3}$); 7.18–8.65 (m, 5H, pyridine); 18 (broad s, 2H, O–H••O). **2c**: 0.86 (d, 3H, $\underline{\mathrm{CH}}_3\mathrm{CH}$); 1.17 (t, 3H, $\underline{\mathrm{CH}}_3\mathrm{CH_2}$); 1.18–1.96 (m, 10H, $\mathrm{CH_2}$ cyclohexyl); 2.12 (s, 6H, $\underline{\mathrm{CH}}_3\mathrm{C{=}NOH}$); 2.16 (s, 6H, $\underline{\mathrm{CH}}_3\mathrm{C{=}NOH}$); 3.27 (q, 2H, $\mathrm{CH_3}\underline{\mathrm{CH}}_2$); 3.93 (q, 2H, $\mathrm{S}\underline{\mathrm{CH}}\mathrm{CH_3}$ + CH cyclohexyl); 7.15–8.65 (m, 5H, pyridine); 17.9 (broad s, 2H, O–H••O).

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