Syntheses of Diethyldithiocarbamate Chelates of Chromium(III) and Molybdenum(V) by Oxidative Decarbonylation

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Chromium hexacarbonyl reacts with $[Hg(S_2CNEt_2)_2]$ under nitrogen in refluxing toluene to give $[Cr(S_2CNEt_2)_2]$ with deposition of mercury. This easily oxidised compound was not isolated but work up of the reaction products in air gave $[Cr(S_2CNEt_2)_3]$. Reaction of $[Mo(CO)_6]$ with $[Hg(S_2CNEt_2)_2]$ under the same conditions goes through a series of reactions leading to the isolation of $Mo^VO(S_2CNEt_2)_3$.

THE diethyldithiocarbamates (S_2CNEt_2) $[Mo(S_2CNEt_2)_4]$,[1] $[Mo(S_2CNEt_2)_4]X$ (X = Cl, Br, I, or I_3),[2] and $[NBu_4][M(S_2CNEt_2)(mnt)_2]$ (M = Mo or W; mnt = maleonitriledithiolate)[3] have previously been prepared by oxidative decarbonylation of $[Mo(CO)_6]$[1] or $[Mo(CO)_5X]^-$ (X = halide). The present investigation describes the reactions of $[Cr(CO)_6]$ and $[Mo(CO)_6]$ with $[Hg(S_2CNEt_2)_2]$.

RESULTS AND DISCUSSION

Reaction of Chromium Hexacarbonyl with Bis(diethyldithiocarbamato)mercury(II).—A dark blue crystalline material was obtained as the final product from a reaction mixture containing $[Cr(CO)_6]$ and $[Hg(S_2CNEt_2)_2]$ in the molar ratio of 2 : 3. The product showed the bands in the i.r. spectrum at 1 496, 1 296, 1 211, 1 148, 1 075, 913, and 846 cm^{-1},[4] and is formulated as $[Cr(S_2CNEt_2)_3]$. Melting points of an authentic sample and the product were identical, 250 °C.

E.s.r. investigations of chromium(III) systems show that the stereochemistry about the metal ion is close to regular octahedral, the value of the parameter D, related to the axial component of the low-symmetry ligand field, being quite small ($|D| < 0.1$ cm^{-1}).[5] The e.s.r. spectrum due to a quickly frozen toluene–chloroform (1 : 1) solution of $[Cr(S_2CNEt_2)_3]$ is shown in Figure 1. By computer simulation of the e.s.r. spectrum, $|D|$ has been calculated as ≈ 0.01 cm^{-1}.[6] The observed spectrum is very similar to that reported by Pederson and Toftlund[5] for *trans*-$[Cr(py)_4(OH)_2]^+$ (py = pyridine) where $|D|$ was estimated at 0.01 cm^{-1}. A small distortion along the z axis is therefore indicated, although it is noted that this value of $|D|$ is one of the smallest recorded for chromium(III) systems. On the basis of the irregular lineshape of the low-field line, a small $|E|$ term was also proposed ($|E| \leqslant 0.003$ cm^{-1}).[6] The polarised single-crystal spectra of the chromium(III) chelate doped into a sample of the indium(III) complex has also been reported and it was proposed that trigonal distortions were present.[7]

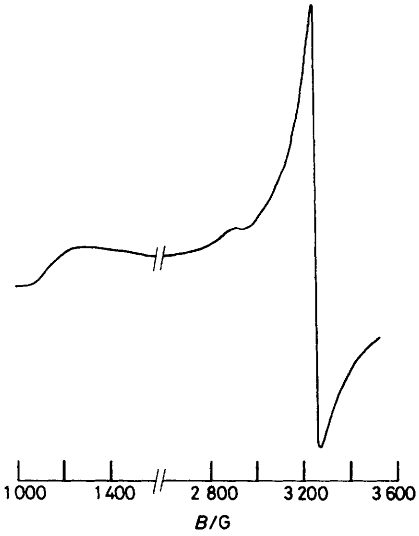

FIGURE 1 E.s.r. spectrum of a quickly frozen toluene–chloroform solution of $[Cr(S_2CNEt_2)_3]$ (−140 °C)

The reaction of $[Cr(CO)_6]$ and $[Hg(S_2CNEt)_2]$ in toluene under a nitrogen atmosphere with rigorous exclusion of oxygen produces, after heating for *ca*. 10 min, a green solution which persists for 1 h on further heating. Indeed, the green toluene solution possessed the same electronic spectrum as $[Cr(S_2CNEt_2)_2]$ prepared by Fackler and Holah.[8] The green toluene solution of $[Cr(S_2CNEt_2)_2]$ is extremely air sensitive producing $[Cr(S_2CNEt_2)_3]$ immediately on exposure to molecular oxygen. These observations provide evidence for the reaction pathway proceeding through the formation of $[Cr(S_2CNEt_2)_2]$ with deposition of mercury and formation of $[Cr(S_2CNEt_2)_3]$ in the isolation procedure involving exposure to air.

Reaction of Molybdenum Hexacarbonyl with Bis(diethyldithiocarbamato)mercury(II).—During the course of the reaction of $[Mo(CO)_6]$ with $[Hg(S_2CNEt_2)_2]$ in refluxing toluene under nitrogen the reaction mixture changes from pink to red-pink to light brown to dark brown. The final product is a brown microcrystalline powder whose analytical data are consistent with the empirical formulation $MoO(S_2CNEt_2)_3$. An i.r. spectrum showed bands at 1 495, 1 456, 1 296, 1 205, 1 142, 1 070, 995, 905, and 835 cm^{-1} which are consistent with other diethyldithiocarbamate complexes. The band at 995 cm^{-1} is tentatively assigned as a molybdenum–oxygen terminal stretching frequency. An e.s.r. spectrum of a frozen toluene solution showed a strong, well resolved signal centred on $g \approx 2$ (Figure 2). The room-temperature magnetic moment of the solid compound confirmed that the complex was paramagnetic, $\mu_{eff.} = 0.65$ B.M.,* showing a marked decrease from the spin-only value of 1.73 B.M. anticipated for molybdenum(V); it is possible that the molybdenum(V) compound is monomeric in toluene solution but dimeric in the solid state.

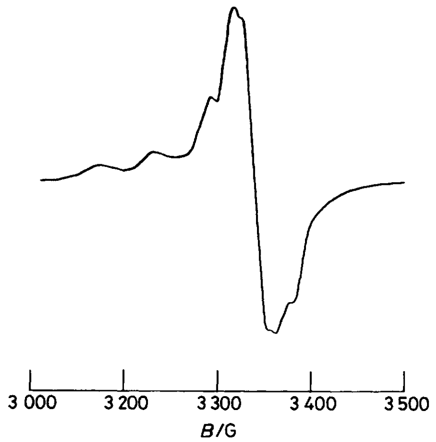

FIGURE 2 E.s.r. spectrum of $MoO(S_2CNEt_2)_3$ in frozen toluene solution (−140 °C)

EXPERIMENTAL

E.s.r. spectra, recorded as the first derivative of the absorption signal, were measured on a Varian E-12 spectrometer and carried out at sample temperatures between 20 and −140 °C. Low-temperature measurements were made in a solution cell consisting of narrow-bore silica tubing. A Varian E246 flat quartz cell, designed to minimise dielectric loss, was employed for X-band measurements on solutions. Microanalyses were carried out by the Australian Microanalytical Service. The magnetic susceptibilities were determined by means of a Gouy balance. Infrared spectra were recorded as Nujol mulls on a Perkin-Elmer 257 (4 000—625 cm^{-1}) spectrophotometer and calibrated with polystyrene film. All compounds were examined under a microscope to test for homogeneity and crystal habit.

The source of mercury(II) was analytical grade mercury(II) acetate obtained from Koch-Light. Sodium diethyldithiocarbamate was obtained from May and Baker and the transition-metal carbonyl compounds from Alfa Inorganics. Bis(diethyldithiocarbamato)chromium(II) was prepared as outlined by Fackler and Holah.[8]

Preparation of Bis(NN-*diethyldithiocarbamato*)*mercury*(II).—Mercury(II) acetate (6.37 g) was dissolved in refluxing absolute ethanol, containing a small quantity of glacial acetic acid (5%), to produce a clear, colourless solution. The hot, filtered solution was added to a refluxing ethanolic solution of $Na(S_2CNEt_2)$ (6.85 g), which produced a colour change to dark yellow and when left to reflux for longer than 10 min a darkening to black occurred. This latter change was associated with the production of small amounts of the β form of mercury(II) sulphide. The hot solution was filtered and from the yellow filtrate, crystals separated on cooling. The product was recrystallised from toluene (yield 70%) (Found: C, 24.2; H, 4.0; S, 25.9. $C_{10}H_{20}HgN_2S_4$ requires C, 24.15; H, 4.05; S, 25.8%).

Reaction of Bis(NN-*diethyldithiocarbamato*)*mercury*(II) *with Chromium Hexacarbonyl.*—To a solution of $[Cr(CO)_6]$ (0.88 g) in sodium-dried toluene (20 cm^3) was added a solution (20 cm^3) of $[Hg(S_2CNEt_2)_2]$ (3.0 g). The reaction mixture was refluxed for 6 h under a nitrogen atmosphere. Subsequent transfer operations were carried out in air. The final product was isolated after filtration of the hot solution. On reduction of the volume of the filtrate, dark blue crystals were formed (yield 1.35 g). By comparison of the melting point (250 °C uncorrected) and i.r. spectrum (Nujol mull, 4 000—625 cm^{-1}) with an authentic sample, the product was identified as $[Cr(S_2CNEt_2)_3]$.

E.s.r. spectra were collected of a powdered sample, a toluene solution (0 °C), a frozen toluene solution (−140 °C), and also of a mixed toluene–dichloromethane (1 : 1) frozen solution (−140 °C). The presence of the dichloromethane (20%) was found to enhance glass formation.

Reaction of Bis(NN-*diethyldithiocarbamato*)*mercury*(II) *with Molybdenum Hexacarbonyl.*—A quantity of $[Hg(S_2CNEt_2)_2]$ (2.98 g) was dissolved in sodium-dried toluene (30 cm^3) and refluxed under a nitrogen atmosphere. Molybdenum hexacarbonyl (1.06 g) in toluene (70 cm^3) was added and the reaction continued for another 4 h. The isolation procedure was carried out in air. After decanting the solution from the metallic mercury and filtering, the product was isolated as a precipitate by addition of hexane (40 cm^3) (Found: C, 30.2; H, 5.75; N, 7.10; S, 32.4. $C_{15}H_{30}MoN_3OS_6$ requires C, 30.4; H, 5.80; N, 7.10; S, 32.45%). An i.r. spectrum (Nujol mull, 4 000—625 cm^{-1}) was recorded as well as a room-temperature magnetic moment ($\mu_{eff.} = 0.65$ B.M.). An e.s.r. spectrum of a frozen toluene solution (−140 °C) confirmed that the complex was paramagnetic. Comparison with an e.s.r. spectrum of a equimolar sample of copper(II) diethyldithiocarbamate in a frozen chloroform–toluene (1 : 1) mixture showed that the signals from the two compounds possessed similar intensities.

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* Throughout this Note: 1 B.M. = 9.274 08 × 10^{-24} J T^{-1}; 1 G = 10^{-4} T.