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Facile Cleavage of Mo=O in Molybdenum Oxytrichloride by Diethylthiocarbamate (Et$_2$dtc) to Yield the Eight-coordinate Monomeric [Mo(Et$_2$dtc)$_4$]Cl

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Although reactions of $MoOCl_3$ with neutral ligands to give $MoOCl_3 \cdot L$ and $MoOCl_3 \cdot L_2$ are well known[1], reactions of $MoOCl_3$ with anionic ligands to give monomeric molybdenum(V) species in which one or more of the chlorine atoms have been replaced are rare; under normal conditions dimerization occurs via oxygen or dioxygen bridges. Here we report the synthesis of the monomeric [Mo(Et$_2$dtc)$_4$]Cl and [Mo(Et$_2$dtc)$_4$]BPh$_4$ (Et$_2$dtc = diethylthiocarbamate), complex cations formed by the facile cleavage of Mo=O in $MoOCl_3$ by Et$_2$dtc.

Experimental

Molybdenum oxytrichloride was obtained from Climax Molybdenum Company and used without further purification. Diethylammonium diethyldithiocarbamate, [Et$_2$NH$_2$][S$_2$CNEt$_2$], was obtained from British Drug Houses Ltd. Acetonitrile was purified by distillation under nitrogen from P_4O_{10}. All operations were performed under a dry nitrogen atmosphere in specially constructed Schlenk apparatus and glove box.

[Mo(S$_2$CNEt$_2$)$_4$]Cl

Molybdenum oxytrichloride (1.82 g, 0.008 mol) and diethylammonium diethyldithiocarbamate (7.32 g, 0.032 mol) were mixed in a dry flask and dry, degassed acetonitrile (150 ml) was distilled into it to form a dark brown solution which was stirred at room temperature for 12 hours. The resulting mixture was filtered yielding a yellow–brown solid and a dark brown filtrate. The latter was reduced in volume to 20 ml and allowed to stand. After 12 hours dark red–brown crystals appeared which were filtered, washed with benzene and ether and dried *in vacuo. Anal.* Calc. for $MoC_{20}H_{40}N_4S_8Cl$: C, 33.1; H, 5.7; N, 7.5; Cl, 4.9. Found: C, 32.6; H, 6.5; N, 7.8; Cl, 4.9%. Yield 0.62 g (15%).

[Mo(S$_2$CNEt$_2$)$_4$]BPh$_4$

Tetrakis(diethyldithiocarbamato)molybdenum(V) chloride (0.36 g, 0.0005 mol) was dissolved in acetonitrile (10 ml) and a solution of sodium tetraphenylborate (0.17 g, 0.0005 mol) in acetonitrile (5 ml) was added. After mixing for a few minutes the dark red solution deposited dark red crystals. These were filtered, washed with benzene and ether and dried *in vacuo. Anal.* Calc. for $MoC_{44}H_{60}N_4S_8B$: C, 52.1; H, 5.9; N, 5.5; S, 25.3. Found: C, 51.8; H, 5.8; N, 5.3; S, 25.3%. Yield was quantitative.

Physical Measurements

These were obtained as previously described[2].

Results and Discussion

Molybdenum oxytrichloride reacts with ammonium diethylthiocarbamate, NH$_4$Et$_2$dtc, in methyl cyanide at room temperature and under anaerobic conditions, yielding tetrakisdiethyldithiocarbamatomolybdenum(V) chloride, [Mo(Et$_2$dtc)$_4$]Cl. Addition of NaBPh$_4$ to an acetonitrile solution of [Mo(Et$_2$dtc)$_4$]Cl precipitates [Mo(Et$_2$dtc)$_4$]BPh$_4$ in quantitative yield. In this reaction it is evident that all of the Mo–Cl bonds as well as the terminal Mo=O bond have been cleaved. Although all four Mo=O bonds in MoO_4^{2-} have been replaced by dithiolene ligands[3] the only analogous reaction in molybdenum(V) chemistry has been the replacement of oxygen by sulphur in some dimeric complexes to yield, for example, MoS(SR)(S$_2$COEt)[4].

The complexes isolated here contain the eight-coordinate [Mo(Et$_2$dtc)$_4$]$^+$ cation, a species previously detected in solution during the electrolytic oxidation of Mo(Et$_2$dtc)$_4$ [5] and reported to be isolated from the reaction of tetraethylthiuramdisulphide with a hot solution of tetrabutylammonium pentacarbonylchloromolybdate(0) [6]. The analogous eight-coordinate [Mo(Me$_2$dtc)$_4$]X (X = Br, Br$_3$, I, I$_3$) have been prepared by oxidation of Mo(Me$_2$dtc)$_4$ with the appropriate halogen[7]. Our own route can thus be seen as a facile method of obtaining this new class of compound.

Although the reaction itself is very air and moisture sensitive the products are air-stable dark red crystalline solids. The IR spectra of the complexes exhibit absorptions typical of bidentate dithiocarbamate coordination, and there are no bands in the 1460 - 1470 cm^{-1} region characteristic of monodentate dithiocarbamate ligands,[8] there is a single strong absorption at 350 cm^{-1} assigned to ν(Mo–S),[9] and there are no absorptions due to ν(Mo=O) in the 900 - 970 cm^{-1} region and no absorptions which could be assigned to Mo–Cl vibrations. EPR spectra in dichloromethane at room temperature consist of a single strong line due to Mo atoms without nuclear spin (75%) and hyperfine splitting consisting of six lines due to interaction of the unpaired electron with Mo nuclei having nuclear spin 5/2 (25%). The isotropic g values were found to be 1.980 and a values 35G.

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