# Ligation by a *cis*-Dithio-Molybdenum(VI) Moiety: Preparation and Crystal Structure of $[\{(\text{Piperidine-N-oxide}(1-))_2\text{Mo-}(\mu_2\text{-S})_2\text{Cu-}\mu_2\text{-Cl}\}_2]$

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The recent isolation of the terminal thio-complexes of molybdenum(VI), *cis*-[MoOS(piperidine-*N*-oxide(1−))$_2$] (= *cis*-$[\text{MoOS}(C_5H_{10}NO)_2]$) and *cis*-$[\text{MoS}_2(C_5H_{10}NO)_2]$, by Wieghardt *et al.* [1], represents a valuable contribution to molybdenum-sulphur chemistry. As an extension of this work, we have shown that $B_2S_3$ can be used to sequentially replace one or two of the terminal oxo-groups of *cis*-$[\text{MoO}_2(C_5H_{10}NO)_2]$ by terminal thio-groups; also, we have confirmed the identity of *cis*-$[\text{MoOS}(C_5H_{10}NO)_2]$ in an X-ray crystallographic study [2]. The extensive use of $[\text{MoS}_4]^{2-}$ as a ligand, in particular the observation that in a large number of complexes this moiety functions as a bidentate ligand, prompted the investigation of the ligating properties of *cis*-$[\text{MoS}_2(C_5H_{10}NO)_2]$. Herein, we report the preparation and crystallographic characterisation of the complex, $[\{(C_5H_{10}NO)_2\text{Mo-}(\mu_2\text{-S})_2\text{Cu-}\mu_2\text{-Cl}\}_2]$, which involves the *cis*-$\text{MoS}_2$ groups coordinating as a bidentate ligand to a copper atom.

## Experimental

An immediate reaction ensued between CuCl and *cis*-$[\text{MoS}_2(C_5H_{10}NO)_2]$ (1:1) in MeCN under dinitrogen at room temperature. Analytically pure crystals of the product $[\{(C_5H_{10}NO)_2\text{Mo-}(\mu_2\text{-S})_2\text{-Cu-}\mu_2\text{-Cl}\}_2]$ were obtained as dark green blocks from the reaction mixture. The unit cell dimensions: $a$ = 11.049(1), $b$ = 12.039(1), $c$ = 12.704(1) Å, $\beta$ = 94.92(1)°, $U$ = 1683.7 Å$^3$; $Z$ = 2 dimers/cell, $D_c$ = 1.812 g cm$^{-3}$, space group $P2_1/c$. Single crystal X-ray diffraction data were collected on a Stoe-Siemens AED diffractometer with graphite-monochromated Mo-$K_\alpha$ radiation for reflections with $2\theta \leqslant 53°$. 3176 absorption corrected data with $F > 4\sigma$ were used in the solution and refinement of the crystal structure. The structure was solved by Patterson and Fourier methods and refined with anisotropic thermal parameters, to $R$ = 0.050, $R_g = (\Sigma w\Delta^2/\Sigma wF_o^2)^{1/2}$ = 0.070, with $w^{-1} = \sigma 2(F) + 0.00052F^2$ and $\Delta = |F_o| - |F_c|$. Hydrogen atoms, clearly revealed in a difference synthesis after refinement of the other atoms, were subject to constraints on geometry and thermal parameters [4].

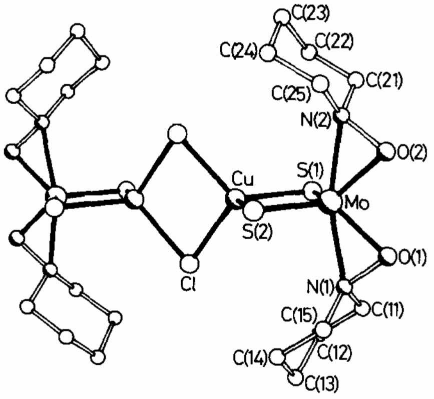

Fig. 1. Molecular structure of [{(piperidine-N-oxide(1−))$_2$-Mo−($\mu_2$-S)$_2$−Cu−$\mu_2$-Cl}$_2$]. Mo•••Cu = 2.639(1); Mo−S(1) = 2.175(1); Mo−S(2) = 2.182(1); Mo−O(1) = 1.959(4); Mo−N(1) = 2.160(4); Mo−O(2) = 1.951(4); Mo−N(2) = 2.164(4); O(1)−N(1) = 1.435(6); O(2)−N(2) = 1.430(5); Cu−S(1) = 2.267(1). Cu−S(2) = 2.266(1); Cu−Cl = 2.375(1); Cu−Cl′ = 2.341(2) Å; S(1)−Mo−S(2) = 110.3(1); S(1)−Mo−O(1) = 116.7(1); S(2)−Mo−O(1) = 115.0(1); S(1)−Mo−O(2) = 114.9; S(2)−Mo−O(2) = 116.2(1); S(1)−Mo−N(1) = 95.1(1); S(2)−Mo−N(1) = 95.6(1); S(1)−Mo−N(2) = 94.4(1); S(2)−Mo−N(2) = 95.6(1); O(1)−Mo−N(1) = 40.4(2); O(2)−Mo−N(2) = 40.2(1); O(1)−Mo−O(2) = 81.3(2); O(1)−Mo−N(2) = 121.5(1); N(1)−Mo−O(2) = 121.6(2); N(1)−Mo−N(2) = 161.9(1); S(1)−Cu−S(2) = 104.1(1); S(1)−Cu−Cl = 111.3(1); S(2)−Cu−Cl = 115.9(1); S(1)−Cu−Cl′ = 117.1(1); S(2)−Cu−Cl′ = 112.0(1); Cl−Cu−Cl′ = 97.1(1); Mo−S(1)−Cu = 72.9(1); Mo−S(2)−Cu = 72.8(1); Cu−Cl−Cu′ = 82.9(1)°.

## Results and Discussion

The molecular structure of $[\{(C_5H_{10}NO)_2\text{Mo-}(\mu_2\text{-S})_2\text{Cu-}\mu_2\text{-Cl}\}_2]$ is shown in Fig. 1, the caption to which summarises the important intramolecular dimensions. Coordination to the copper atom lengthens the Mo−S bonds, from 2.145(2) Å in *cis*-$[\text{MoS}_2(C_5H_{10}NO)_2]$ to 2.179(4) Å in the title

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complex; concomitantly, the S–Mo–S interbond angle is reduced from 115.0(1) to 110.3(1)°. Both of these variations are typical of the coordination of $[MoS_4]^{2-}$ as a bidentate ligand to copper(I) and other metals [3–5]. The other intramolecular dimensions of *cis*-$[MoS_2(C_5H_{10}NO)_2]$ remain essentially unchanged in the copper(I) chloride complex. The dimerisation via the $\mu_2$-chloride bridges, to produce a molecule, with the hitherto unreported $MoS_2CuCl_2CuS_2Mo$ arrangement, which closely approximates to $D_{2h}$ symmetry, gives each copper(I) atom an essentially tetrahedral geometry. This is in contrast to the complexes [5] $[MoS_4(CuCl)_3]^{2-}$, in which the copper(I) atom has a trigonal planar $S_2Cl$ coordination. However, the Cu····Mo separations are essentially the same (2.63 ± 0.01 Å) in each case and are sufficiently short for a direct metal–metal interaction to be considered.

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