Carbon–Sulphur Bond Cleavage. Structure of $[Mo(SCNPr_2)(S_2CNPr_2)]_2S_2$

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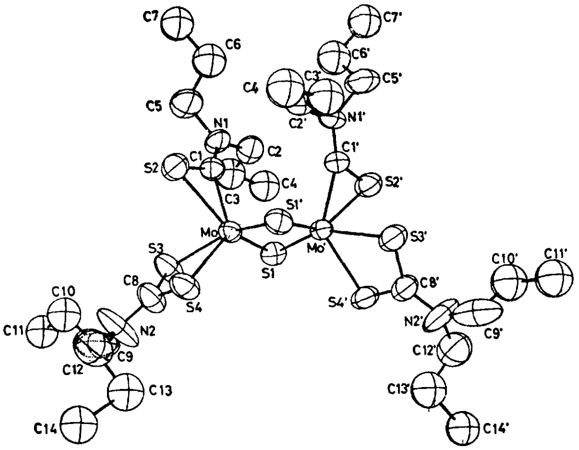
Summary The molecular structure of a molybdenum dithiocarbamate showed that its formation proceeds *via* an oxidative carbon–sulphur bond cleavage followed by formation of a molybdenum–carbene bond.

Molybdenum(II) acetate reacts with an ethanolic solution of ammonium *NN*-di-n-propyldithiocarbamate to give a product of composition $Mo(S_2CNPr_2)_2$.[1] *X*-Ray diffraction methods revealed that this compound should be formulated as $[Mo^{IV}(SCNPr_2)(S_2CNPr_2)]_2S_2$ (I).

The crystals are monoclinic with $a = 11{\cdot}920(3)$, $b = 14{\cdot}486(3)$, $c = 24{\cdot}713(6)$ Å; $\beta = 101{\cdot}82(2)°$, $D_{obs} = 1{\cdot}42 \pm 0{\cdot}01$ g cm^{-3} (flotation), $D_c = 1{\cdot}426$ g cm^{-3} with $Z = 4$.

Three-dimensional intensity data were collected with Mo-K_α radiation on a Picker four-circle automatic diffractometer using four crystals of approximate dimensions $0{\cdot}2 \times 0{\cdot}2 \times 0{\cdot}2$ mm^3. A total of 2182 independent non-zero ($\sigma(I)/I < 0{\cdot}33$) reflections were obtained, $R = 0{\cdot}060$.

The molecular structure of (I) is reproduced in the Figure.[2]



As evidenced by the $C_1 \cdots S_1$ and $C_1 \cdots S'_1$ distances of $3{\cdot}285(10)$ and $3{\cdot}591(10)$ Å respectively, a dithiocarbamate carbon–sulphur bond has been cleaved. This led to a compound containing a double sulphur–molybdenum bridge and to the formation of a carbene-type carbon–molybdenum bond. Consequently, molybdenum has a formal oxidation state of four. Surprisingly, the bridging sulphur S_1 remains coplanar with atoms Mo, C_1, S_2, and N_1, as is the case in a normal dithiocarbamate. This fact and the shorter $C_1 \cdots S_1$ distance could indicate that this bond has been cleaved.

The thiocarbamoyl group formed is linked to molybdenum in a way that is reminiscent of the CS_2 bonding in $Pt(PPh_3)_2CS_2$.[3] However, the Mo–C bond of $2{\cdot}066(8)$ Å is considerably shorter than that found in most alkyl-molybdenum derivatives.[4] It has approximately the same value as the Mo–C distance of $2{\cdot}092(12)$ Å reported in the nitrogeno-molybdenum carbene chelate $(\pi\text{-}C_5H_5)(CO)_2MoNHNC(CO_2Et)COH$.[5] The Mo–C bond must then be considered as a carbene bond with an approximate bond order of $1{\cdot}5$.[6] The Mo–S distance of $2{\cdot}517(2)$ Å is consistent with a single Mo^{IV}–S bond, whereas the C_1–S_2 and C_1–N_1 bonds are comparable to similar bonds in dithiocarbamate complexes.

The Mo-bridging sulphur S_1 and S_1' bonds have values of $2{\cdot}243(2)$ and $2{\cdot}342(2)$ Å respectively. The Mo–Mo distances of $2{\cdot}707(2)$ Å and the Mo–S–Mo' angle of $72{\cdot}33°$ (8) indicate a direct metal–metal interaction. The bonds and angles within the dithiocarbamate anion have the excepted values.

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