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# Preparation and Molecular Structure of $\mu$-Oxo-$\mu$-Sulphido Bis[oxo-di-n-Propyldithiocarbamato Molybdenum(V)]

J. DIRAND-COLIN, L. RICARD and R. WEISS

*Institut le Bel,*[1] *Université Louis Pasteur, 67070 Strasbourg Cédex, France*

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Studies concerned with the interaction of sulphur species with oxo-molybdenum compounds have so far been limited to the reaction of $H_2S$ or organic thiocompounds with dioxo-molybdenum(VI) or $\mu$-oxo-bis(oxo-molybdenum(V)) compounds. When these are reacted with a thiol under inert atmosphere, oxo-molybdenum(IV) complexes are formed.[2] On the other hand di-$\mu$-sulphido species result from the reaction of $H_2S$ and molybdenum(V) $\mu$-oxo compounds.[3] We recently became interested in the reaction of a dioxo-molybdenum(VI) complex with $H_2S$ in an oxidizing atmosphere. Upon standing for prolonged periods, a blue material was obtained which was shown to contain a disulphur ligand: $MoO(S_2)(S_2CNR_2)_2$ (I).[4] This product is not formed when air is excluded. The mechanism of its formation is as yet unknown.

In an attempt to obtain a better preparation for this compound, we reacted the dioxo complex with $P_4S_{10}$, under similar conditions. The yields and spectrum of products obtained are essentially the same as previously reported: small amounts of (I) are formed and some di-$\mu$-sulphido molybdenum(V) complexes are obtained. However, there appear during chromatographic separation fairly large amounts of a product that is not observed in the $H_2S$ reaction. This product presents a strong I.R. absorption at 978 $cm^{-1}$ and a small shoulder at 960 $cm^{-1}$ indicating the presence of two terminal oxygen atoms. Two additional important bands are present, one at 714 $cm^{-1}$, the other at 524 $cm^{-1}$. These are in the usual range for $\mu$-oxo and $\mu$-sulphido, doubly bridged molybdenum(V) complexes and thus suggested the formulation $Mo_2O_2(\mu\text{-}O)(\mu\text{-}S)(S_2CNPr_2)_2$ (II). Such a species, although it should be formed in the reaction of $Mo_2O_3L_4$ with $H_2S$ to yield $Mo_2O_2S_2L_2$, has not been observed previously and we studied its crystal structure to confirm our hypothesis.

Crystals of the compound are triclinic, space group $P\bar{1}$, $a = 14.142(4)$ Å, $b = 10.153(3)$ Å, $c = 8.847(3)$ Å, $\alpha = 90.58(2)^\circ$, $\beta = 97.93(2)^\circ$, $\gamma = 108.95(2)^\circ$, Z = 2, M = 624. 1249 observed reflections ($\sigma(I)/I < 0.33$) were collected with a PW1100 diffractometer using MoK$\alpha$ radiation. The structure was solved by standard Patterson and Fourier methods and refined by least-squares to R = 0.054, using anisotropic temperature factors for all atoms.

The geometry of the complex is shown in the Figure and geometrical data are assembled in the Table. The environments of the metal atoms are deformed square pyramids. The essential features reported for $Mo_2O_4dtc_2$ [5] or $Mo_2S_4dtc_2$ [9] are preserved namely, the metal atoms lie some 0.7 Å above the basal planes, the angular bend of the basal planes at the bridging atoms is 148.0(5)° and the terminal oxygen atoms are coplanar and perpendicular to the basal planes. The $Mo–O_b$ and $Mo–S_b$ bond lengths are similar to previously reported values. Interestingly, the Mo–Mo distances and $O_b–Mo–S_b$ angles are very close to the average values reported for the di-$\mu$-oxo and sulphido analogues. The sum of $Mo–S_b–Mo$ and $Mo–O_b–Mo$ angles is similarly close to the sum of angles in these complexes.

Various isomers of $Mo_2O_{4-x}S_xL_2$ can be envisioned. The symmetrical complexes $Mo_2O_4L_2$, $Mo_2O_2S_2L_2$ and $Mo_2S_4L_2$ have been known for

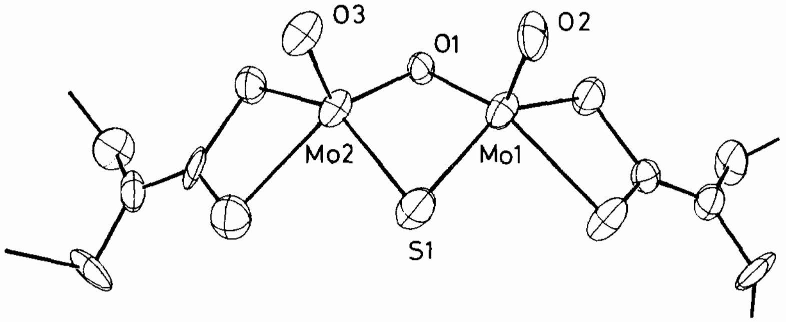

Figure. Molecular geometry of $Mo_2O_3S(Prdtc)_2$; the propyl chains have been omitted for clarity.

TABLE. Comparison of Some Di-$\mu$-bridged Complexes

Bond lengths (Å) and Bridge Angles (°)

| | $MoO_t$ | $MoO_b$ | $MoS_b$ | Mo–Mo | $MoO_bMo$ | $MoS_bMo$ | $X_b$–Mo–$X_b$ | Ref. |
|---|---|---|---|---|---|---|---|---|
| $Mo_2O_3SPrdtc_2$ | 1.665 (1) | 1.927(11) | 2.305 (5) | 2.673(3) | 87.8(4) | 70.9(2) | 97.0(1) | |
| $Mo_2O_4Etdtc_2$ | 1.678 (2) | 1.940 (2) | | 2.580(1) | 83.3(1) | | 91.9(1) | 5 |
| $Mo_2O_4L$-cyst$_2$ | 1.663(20) | 1.930(18) | | 2.562(3) | 83.0(7) | | 91.5(7) | 6 |
| $Mo_2O_2S_2L$-cyst$_2$ | 1.71 (3) | | 2.307(12) | 2.804(4) | | 74.8(4) | 101.8(5) | 7 |
| $Mo_2O_2S_2dtp_2$ | 1.657 (6) | | 2.29 (2) | 2.739(1) | | 73.3(1) | 103.8(1) | 8 |
| $Mo_2S_4Budtc_2$ | | | 2.307 (4) | 2.801(2) | | 74.7(1) | 101.8(2) | 9 |

Average Angles (°) around the Metal in Dithiocarbamato Complexes: number in parentheses are maximum deviations from the mean

| | $Mo_2O_3Sdtc_2$ | $Mo_2O_4dtc_2$ | $Mo_2S_4dtc_2$ |
|---|---|---|---|
| $O_t$–Mo–$O_b$ | 110.6(1) | 112.8(9) | |
| $O_t$–Mo–$S_b$ | 109.7(5) | | |
| $S_t$–Mo–$S_b$ | | | 108.5(8) |
| $X_t$–Mo–$S_{dtc}$ | 106.7(3.0) | 106.8(1.5) | 106.5(2.0) |
| Angle between the Basal Planes | 148.0(5) | 148.2(3) | 152.9 |

some time. The complex $Mo_2OS(\mu\text{-}O)_2Budtc_2$ has been claimed to exist.[10] We now have definite proof that dissymmetrical bridged complexes of the same type can be obtained.

## References

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