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A Molybdenum Complex with a Chelating Diazenido and a Tridentate Hydrazido(2−) Ligand

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Alkyl dithiocarbazates are very versatile ligands: complexes are known of the neutral or singly deprotonated ligands, reactions with dioxomolybdenum(VI) species lead to mono- or dinuclear diazenido–hydrazido complexes with 'end on', 'side on' or 'bridging' N–N-moieties [1].*

$NH_2NH–CS–SCH_3$ S-methyl-dithiocarbazate

Continuing systematic investigations of the ligating behaviour of alkyl dithiocarbazates, we reacted S-methyl dithiocarbazate (in fivefold excess) with dioxo-bis(2,4-pentanedionato)-molybdenum(VI) in dichlor–methane. A dark brown precipitate was formed, which changed within several days to dark red needle-like crystals (yield 75%). The nature of the crystals was investigated by X-ray diffraction at 140 K.

Crystal data: space group $Pna2_1$, $a = 1723.0(8)$, $b = 1367.0(5)$, $c = 923.4(3)$ pm; $Z = 4$; structure solution and refinement (234 parameters) were based on 2006 reflections to give the final discrepancy factors $R = 0.043$ and $R_w = 0.038$.

The new compound turned out to be a neutral, seven-coordinated complex with the formula $Mo(Me_2CNNC(S)SMe)(N_2C(S)SMe)(MeSC(S)NNC(S)SMe)$ (**I**). An ORTEP view of the molecule is presented in Fig. 1, including selected bond lengths and angles. **I** contains a unique combination of three different chelating ligands. Remarkable features are: the presence of the highly bent chelating diazenido ligand $N_2C(S)SMe$ and of the S,N,S-donor ligand $[MeSC(S)NNC(S)SMe]^{2-}$. Its parent compound $MeSC(S)N(H)–N(H)C(S)SMe$ has not yet been prepared in the uncomplexed state [3].

Very few complexes with chelating diazenido ligands are known so far: two examples are $Mo(NHNC(S)Ph)(N_2C(S)Ph)(PhC(S)N(Me)O)$ [2] and $Mo(NHNC(S)R)(N_2C(S)R)(RC(S)NNCMe_2)$ with $R = p\text{-}ClC_6H_5$ [4]. Usually, the diazenido ligand adopts a linear structure and then acts as a three electron donor. In the present case, the molybdenum atom, which is already six-coordinated, can reach a 16-electron configuration only, if it is coordinated by the linear diazenido ligand. Therefore, coordination of the thiocarbonyl sulfur atom occurs as well. By this the two missing electrons are delivered, which implies bending of the diazenido ligand to a MoNN angle of 142.1(5)° by steric reasons.

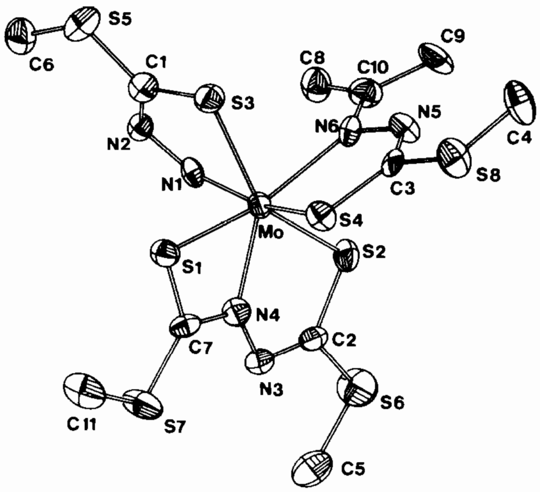

Fig. 1. Molecular structure of I. Selected bond lengths (pm) Mo–S1 252.7(2), Mo–S2 245.6(2), Mo–S3 251.6(2), Mo–S4 244.0(2), Mo–N1 179.1(6), Mo–N4 213.2(6), Mo–N6 223.9(6), N1–N2 132.3(8), C1–N2 134.5(10), C7–N4 129.5(10), C2–N3 130.6(11), N3–N4 136.1(9), N5–N6 141.6(9), C10–N6 131.7(11), C3–N5 128.7(10), C3–S4 173.2(2); selected bond angles (deg): Mo–N1–N2 142.1(5), S4–Mo–N1 154.4(2), Mo–S3–C1 95.3(3).

The diazenido ligand parameters in **I** are similar to those in the compounds mentioned above [2, 4]. Herein the Mo–S bond distances are slightly shorter than in **I**, where the central atom is seven-coordinated.

The novel tridentate ligand in **I** can be described most reasonably as the enol form of a hydrazido(2−) ligand $MeSC(S^-)=N–N=C(S^-)SMe$. Coordination occurs through the two negatively charged sulfur atoms and one of the nitrogen atoms, forming four- and five-membered chelate rings. The N–N distance of 136.1(9) pm is slightly shorter than in the related gauche-configurated hydrazine derivatives $MeSC(O)N_2H_2C(O)SMe$ and $MeOC(S)N_2H_2C(S)OMe$ [5]. The C–N distances of 129.5(10) and 130.6(11) pm are in the double bond region. The whole ligand is strictly planar. So far experiments to prepare the free ligand $MeSC(S)N(H)–N(H)C(S)SMe$ by methylation of the potassium salt $K_2[S_2CN_2H_4CS_2]$ have been unsuccessful. H_2S was split off and the cyclic 2,5-di-(methylthio)-1,3,4-thiodiazole [3] was formed. The hydrazine(2−) ligand can be alternatively formulated as a neutral diazene derivative. Starting from acyldiazenes $RC(O)NNC(O)R$ with $R = Me$ and Ph, a number of transition metal complexes have been prepared [6, 7]. According to structural work,

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*For details of nomenclature see ref. 2.

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dibenzonyldiazene is unsymmetrically coordinated through a carbonyl oxygen atom and one of the nitrogen atoms, forming a five-membered chelate ring. With the exception of the N–N bond distance, which is approximately 5 pm longer, the Mo–N and C–N distances in $OMo(S_2CNMe_2)_2(PhC(O)NNC(O)Ph)$ are similar to **I** [6].

The remaining ligand $Me_2C{=}NNC(S)SMe^-$ is a Schiff base chelate, which is formed by condensation of acetone (liberated from 2,3-pentanedione) and S-methyldithiocarbazate. Several complexes of this ligand have been structurally characterized in the past [8, 9]. The double bonds are localized and the geometry varies very little from compound to compound.

The reaction mechanism leading to the formation of **I** is unknown: probably acetone is liberated from the starting material dioxo(2,4 pentanedionato)-molybdenum, and redox reactions take place. In their course N2 may finally be released from S-methyldithiocarbazate. Then the C(S)SMe-moiety is transferred to a second S-methyldithiocarbazate molecule, thus forming the tridentate S,N,S-donor ligand.

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