Novel Asymmetric Benzoyldiazenido-bridged Complex of Molybdenum. *X*-Ray Crystal Structure of $[Mo_2O(PhCON_2)_2(S_2CNEt_2)_2]$

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Summary The product of the reaction between $[MoO_2(S_2CNEt_2)_2]$ and benzoylhydrazine hydrochloride is shown by *X*-ray crystallography to be an asymmetric dinuclear complex $[Mo_2O(PhCON_2)_2(S_2CNEt_2)_2]$, with bridging benzoyldiazenido-ligands.

IN the presence of an excess of sodium diethyldithiocarbamate, $[MoO_2(S_2CNEt_2)_2]$ reacts with benzoylhydrazine to give the benzoyldiazenido-complex $[Mo(PhCON_2)(S_2CNEt_2)_3]$.[1] If the sodium diethyldithiocarbamate is omitted and benzoylhydrazine hydrochloride is used, a bright red air-stable complex (I) of stoicheiometry $Mo_2O(PhCON_2)_2(S_2CNEt_2)_2$ can be isolated. This complex is interesting because despite the symmetry allowed from its composition, spectroscopic evidence indicates that it has considerable asymmetry. It is a non-conductor in nitrobenzene solution, and monomeric in 1,2-dichloroethane solution. Its i.r. spectrum shows no absorptions due to ν(N–H) or ν(C=O), but has a medium intensity band at 950 cm^{-1} attributed to ν(Mo=O). The ^1H n.m.r. spectrum in CD_2Cl_2 solution showed three quartets at δ 3·48, 3·69, and 3·96 in integrated ratios 1 : 1 : 2 assigned to the CH_2 protons of the dithiocarbamate ethyl groups. Evidently the two dithiocarbamate ligands were not equivalent, and in one of them the ethyl groups were also inequivalent. The mode of bridging is not apparent from the spectroscopic measurements, and an *X*-ray crystal structure was undertaken.

Crystals of $[Mo_2O(PhCON_2)_2(S_2CNEt_2)_2]$ are triclinic with $a = 17{\cdot}53(1)$, $b = 10{\cdot}799(8)$, and $c = 9{\cdot}634(6)$ Å, $\alpha = 72{\cdot}22(1)$, $\beta = 88{\cdot}57(1)$, and $\gamma = 94{\cdot}25(2)°$, space group $P1$, $Z = 2$. The structural analysis is based on 2238 independent reflections $(I_{obs}) > 2{\cdot}5\,\sigma(I_{obs})$ (Mo–K_α, $\mu = 9{\cdot}62$ cm^{-1}) and R is currently 0·079. The essential stereochemistry is shown in the Figure and e.s.d.'s in the bond lengths average 0·004 (Mo–S), 0·006 (Mo–O and Mo–N), 0·01 (S–C), and 0·03 Å (C–C, C–N, and C–O). The Figure demonstrates the low overall symmetry of the complex, and the presence of only one terminal oxo-group in the dinuclear complex is unusual. The Mo(1) atom has approximately trigonal biprismatic co-ordination, with a twist angle of 10·8° between the S(2)–N(2)–N(4) and S(1)–O(1)–O(2) planes. The geometry about Mo(2) is essentially square pyramidal with the Mo atom displaced *ca.* 0·72 Å towards the apical oxygen atom.

The benzoyldiazenido-ligands are co-ordinated in both a chelating and a bridging mode, the terminal nitrogen atoms of each functioning as a bridging atom. The Mo_2–N_2 rhombus is non-planar, the angle between the two Mo–N(2)–N(4) planes being 140·40°. This deviation from planarity is considerably greater than that found in the oxygen-bridged complex $Na_2[Mo_2O_4(cysteine)_2]\cdot 5H_2O$[2] where the dihedral angle between the Mo(1)–O(1)–O(2) and Mo(2)–O(1)–O(2) planes is 151° and the sulphur-bridged complex $[Mo_2S_4(S_2CNBu^n{}_2)_2]$[3] (dihedral angle 152·9°). The bond lengths in the Mo(1)–N(2)–N(1)–C(1)–O(1) and Mo(1)–N(4)–N(3)–C(2)–O(2) ring systems are very similar and have values intermediate between single and double bonds. The Mo(1)–Mo(2) distance of 2·661 Å and the acute Mo(1)–N(2)–Mo(2) and Mo(1)–N(4)–Mo(2) angles (90·9 and 87·9°) suggest considerable metal–metal interaction.

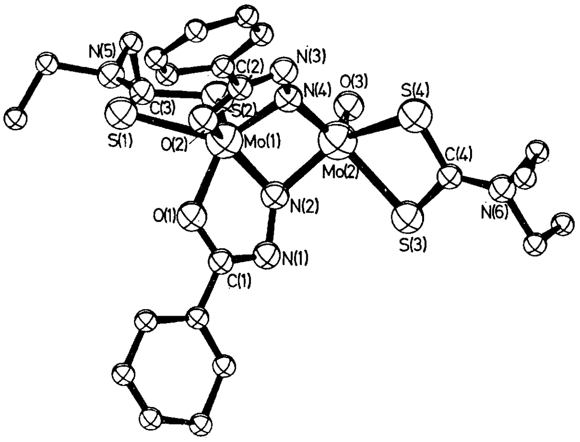

FIGURE. Stereochemistry of $[\{Mo(S_2CNEt_2)(PhCON_2)\}_2O]$ about the molybdenum atoms. Relevant bond angles: S(1)–Mo(1)–S(2), 70·1; S(3)–Mo(2)–S(4), 72·2; Mo(1)–Mo(2)–O(3), 108·2; N(2)–Mo(1)–N(4), 90·9; N(2)–Mo(2)–N(4), 87·9; O(1)–Mo(1)–N(2), 73·8; O(2)–Mo(1)–N(4), 73·0; and O(1)–Mo(1)–O(2), 81·5. Relevant bond distances: Mo(1)–Mo(2), 2·662; Mo(2)–O(3), 1·66; Mo(1)–O(1), 2·06; Mo(1)–O(2), 2·04; Mo(1)–N(2), 1·90; Mo(2)–N(2), 1·96; Mo(1)–N(4), 1·92; Mo(2)–N(4), 1·97; and Mo–S, 2·450 (av.).

The sole product isolable from the reaction of the thiohydrazide $PhCSNHNH_2$ with $[MoO_2(S_2CNEt_2)_2]$ is the complex $[Mo_2O(PhCSN_2)_2(S_2CNEt_2)_2]$ (II) and an *X*-ray crystal structure is currently in progress. The electrochemistry of complexes (I) and (II) has been investigated in methylene chloride, 0·1M in $[Bu_4N][ClO_4]$, with platinum or mercury electrodes. Each compound shows two reduction peaks by normal pulse, a.c., and cyclic voltammetry. The first of these at $E_{\frac{1}{2}} = -1{\cdot}31$ and $-1{\cdot}07$ V, respectively, against the saturated calomel reference electrode, is electrochemically reversible, *e.g.* $|E_p{}^{RED} - E_p{}^{OX}| =$ *ca.* 60 mV. The second reduction peaks at $-1{\cdot}97$ and $-1{\cdot}62$ V, respectively, are irreversible 1-electron processes. It is interesting to note that the dinuclear species shows only one reversible reduction step in accord with its assymetry. Also, the replacement of oxygen by sulphur in the diazenido-ligands lowers the energy of the lowest unoccupied molecular orbital by *ca.* 23 kJ mol^{-1}, neglecting solvation energy changes.

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