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The Reaction of *cis*-Dioxo-bis(N-methylhydroxylamido(1–)-(O,N))molybdenum(VI) with Alkyl-isocyanates.

Crystal Structure of *cis*-Dioxo-bis(N-tert.butyl-N′-methyl-N′-oxo-ureato(1–)-(O,O′))molybdenum(VI)

M. HAHN, K. WIEGHARDT*

Lehrstuhl Anorganische Chemie I der Ruhr-Universität, D-4630 Bochum, F.R.G.

W. SWIRIDOFF and J. WEISS

Anorganisch-Chemisches Institut der Universität, D-6900 Heidelberg, F.R.G.

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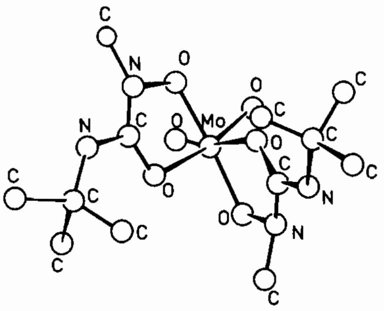
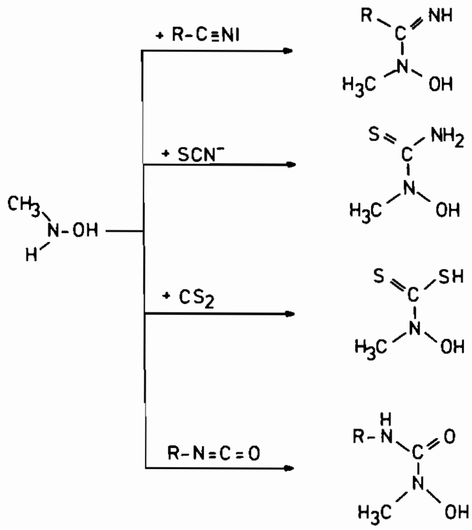


Fig. 1. View of the molecule $[O_2Mo(ON(CH_3)C(NH\text{-}Bu^t)O)_2]$.



The reaction of N-methyl-hydroxylamine and MoO_4^{2-} in aqueous solution has been shown to yield the colorless compound $[MoO_2(CH_3NHO)_2]$ containing two O,N-coordinated N-methylhydroxylamido(1–) ligands [1]. Subsequently we have reported that this complex reacts readily with alkylnitriles, thiocyanate and CS_2 to produce molybdenum(VI) complexes with new ligands [2–4]. These ligands are thought to be generated by nucleophilic attack of an uncoordinated electron pair of the N-atom of N-methyl-hydroxylamide at the electrophilic centers of the added heterocumulenes. It is not clear whether this reaction occurs at coordinated or uncomplexed derivatives of hydroxylamine. We have now studied the reaction of N-methylhydroxylamine and alkylcyanates in the presence of molybdenum(VI).

Reactions of $[MoO_2((CH_3)HNO)_2]$ in toluene or $CHCl_3$ with ethylisocyanate, phenylisocyanate and tert. butylisocyanate afford yellow complexes of molybdenum(VI). The infrared spectra clearly indicate the presence of *cis*-dioxomolybdenum(VI) moieties in each case (ν(Mo=O): 885, 920 cm^{-1}). In addition two N-alkyl (phenyl)-N′-methyl-N′-oxo-urea monoanions are O,O′-coordinated to Mo(VI) centers.

Yellow crystals of $[MoO_2(ON(CH_3)C(NHBu^t)O)_2]$ were suitable for X-ray determinations. X-ray data were collected on a Syntex R 3 diffractometer with monochromated MoKα radiation. Data for this complex: $C_{12}H_{26}N_4O_6Mo$, monoclinic, $a = 13.155(6)$, $b = 20.159(8)$, $c = 14.875(7)$ Å, $\beta = 107.99(4)°$ (at 22 °C), space group, $P2_1/n$ and $Z = 8$ (two independent molecules per unit cell). 1613 independent reflections with $I \geqslant 2.5\sigma(I)$ were used (θ–2θ scan, $3 > 2\theta > 55°$) in the refinement. The structure was solved by Patterson and Fourier methods, and least-squares refinement has reduced R to 0.049 and 0.039. An empirical correction of intensity data for absorption has been carried out. The program system SHELXTL [5] was used throughout the calculations.

The structure of one of the two very similar neutral molecules of the unit cell is shown in Fig. 1. The molybdenum center is in a pseudo-octahedral environment of two terminal oxo-groups (av. Mo=O distance: 1.726 Å) and four oxygen atoms of two O,O′-coordinated N-tert.butyl-N′-methyl-N′-oxo-ureato(1–) ligands. The ligands form planar five membered rings. Averaged bond distances and angles of such a five membered ring are given in Fig. 2.

Both N-atoms of these rings are sp^2-hybridized. The bonding within the rings is adequately described by three mesomeric formulae in Fig. 2.

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*Author to whom correspondence should be addressed.

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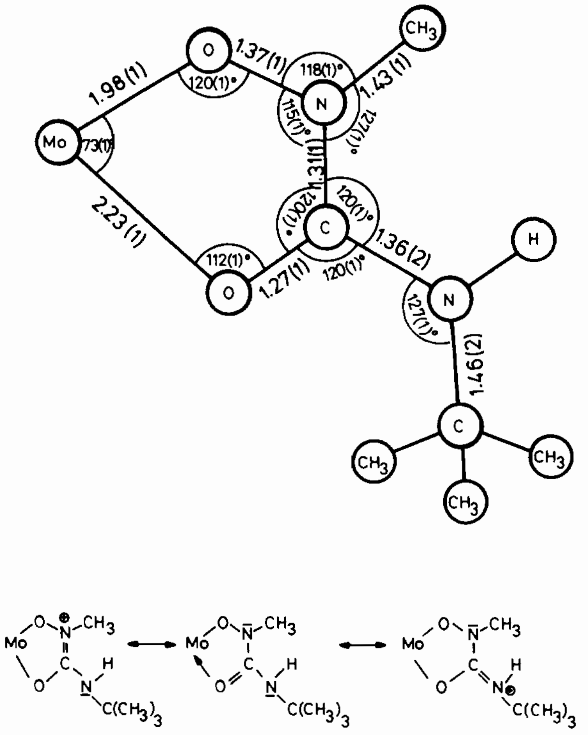

Fig. 2. Selected bond lengths [Å] and -angles of the five-membered rings in $[O_2Mo(ON(CH_3)C(NH\text{-}Bu^t)O)_2]$.

Experimental

$[MoO_2(CH_3HNO)_2]$ (1 g) was suspended in 50 ml of toluene and ethylisocyanate (1.5 g), phenylisocyanate (1.5 g) tert.butylisocyanate (4 g) was added. The suspension was stirred for 24 h. at room temperature. The color of the suspension changed gradually from colorless to yellow. The precipitate was filtered off, washed with ethanol and ether, and air-dried. *Anal.* Calculated for 1) $[MoO_2(ON(CH_3)C(NHC_2H_5)O)_2]\cdot 2H_2O$ (found values in parentheses): C 24.13(23.8); H 4.56(4.5), N 14.07(14.1), Mo 24.09(24.3). 2) $[MoO_2(ON(CH_3)C(NHC_6H_5)O)_2]\cdot 3H_2O$: C 37.51(37.1), H 4.72(4.5), N 10.94(10.3), Mo 18.73(20.1). 3) $[MoO_2(ON(CH_3)C(NHC_4H_9)O)_2]$: C 34.45(34.6), H 6.27(6.3), N 13.39(13.7), Mo 22.94(23.2).

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References

1 K. Wieghardt, W. Holzbach, J. Weiss, B. Nuber and B. Prikner, *Angew. Chem. Int. Ed. Engl., 18,* 548 (1979).
2 K. Wieghardt, W. Holzbach, E. Hofer and J. Weiss, *Chem. Ber., 114,* 2700 (1981).
3 K. Wieghardt, E. Hofer, W. Holzbach, B. Nuber and J. Weiss, *Inorg. Chem., 19,* 2927 (1980).
4 W. Holzbach, K. Wieghardt and J. Weiss, *Z. Naturforsch., 36b,* 289 (1981).
5 Computations were performed on a NOVA 3 (General Data) computer using the SHELXTL crystallographic calculation Program (G. M. Sheldrick, Universität Göttingen; Revision 3.0 (1981)).