

## Unexpected Formation of a Novel Mixed Hydroxamato/Hydroximato Complex

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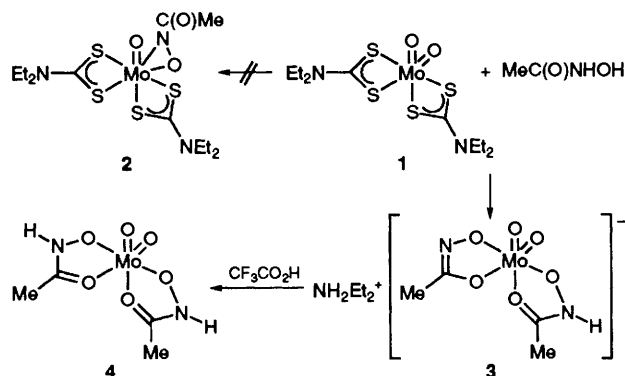
The reaction of  $[\text{MoO}_2(\text{dedtc})_2]$  ( $\text{dedtc} = N,N$ -diethyl dithiocarbamate) with  $\text{MeCONHOH}$  produces the salt  $\text{cis}[\text{NH}_2\text{Et}_2][\text{Mo}^{\text{VI}}\text{O}_2(\text{MeCONHO}-O,O)(\text{MeCONO}-O,O)]$  **3** whose novel H-bonded polymeric structure is established by X-ray diffraction; **3** undergoes  $N$ -protonation to form  $[\text{MoO}_2(\text{MeCONHO}-O,O)_2]$ .

As part of a study of the chemistry of metallocloxaziridine  $\{\text{ML}_n(\eta^2\text{-RNO})\}$  complexes and their involvement as intermediates in molybdenum-catalysed allylic aminations by hydroxylamines,<sup>1</sup> we examined the reaction of  $[\text{MoO}_2(\text{dedtc})_2]$  **1** with acetohydroxamic acid expecting to produce the corresponding molybdooxaziridine species **2** (Scheme 1).<sup>2</sup> We report herein that rather than **2** the product of this reaction is a novel complex hydroxamate salt **3**, apparently derived from ligand substitution and subsequent deprotonation.

Treatment of **1** with 2.0 equiv. of  $\text{MeCONHOH}$  in acetone (20 °C, 24 hours) produced a yellow precipitate (ca. 50%) of **3** whose IR spectrum (KBr) exhibited bands attributed to a  $\text{MoO}_2$  unit and whose NMR spectrum ( $\text{CD}_3\text{OD}$ ) indicated the presence of both  $\text{MeC(=O)-}$  and  $\text{EtN-}$  fragments (1:1).<sup>†</sup> However, the colour of **3**, its water solubility, and NMR integration, were inconsistent with those expected for the neutral molybdooxaziridine complex **2** so we undertook an X-ray diffraction analysis of crystals of **3** grown from acetone-methanol.<sup>‡</sup> The resulting molecular structure of **3** is shown in Fig. 1.

Compound **3** is thus a salt,  $\text{cis}[\text{NH}_2\text{Et}_2][\text{Mo}^{\text{VI}}\text{O}_2(\text{MeCONHO}-O,O)(\text{MeCONO}-O,O)]$ , consisting of isolated diethylammonium cations and pseudooctahedral complex anions. The latter features a  $\text{cis-MoO}_2$  unit coordinated by  $O,O$ -hydroxamato(1-) and hydroximato(2-) ligands. The complex anions of **3** form an infinite chain linked by linear  $\text{N}\cdots\text{H}\cdots\text{N}$  hydrogen bonds (Fig. 2). This feature has not been found in the other examples of anionic hydroxamato complexes, probably being prevented by the presence of bulky  $N$ -aryl groups. Moreover, compound **3** provides a rare example of a complex possessing both hydroxamate and hydroximato ligands,<sup>3</sup> allowing direct comparison of the bond lengths within the respective chelate rings. This comparison reveals distinctly shorter  $\text{Mo-O}$  bonds within the  $N$ -deprotonated chelate ring, consistent with stronger bonding of  $\text{Mo}$  to the (2-) ligand. The longer  $\text{N-O}$  bond and marginally greater bond alternation in the deprotonated ring suggests a slightly larger contribution of resonance form **d**.

Compound **3** is presumed to arise *via* proteolytic displacement of  $\text{Hdedtc}$  from **1**, which decomposes to  $\text{CS}_2$  and  $\text{NH}_2\text{Et}_2$ , followed by deprotonation of the resulting complex **4** by the released amine. Such a process, which implies considerably acidity for **4** ( $\text{p}K_a$  ca. 5), has rarely been observed directly.<sup>4</sup>



Scheme 1

Consistent with this picture, **3** was found to undergo protonation by  $\text{CF}_3\text{CO}_2\text{H}$ , quantitatively giving the neutral bis-(hydroxamate) complex  $[\text{MoO}_2(\text{MeCONHO}-O,O)_2]$  **4** as a white solid<sup>§</sup> along with diethylammonium trifluoroacetate (Scheme 1).

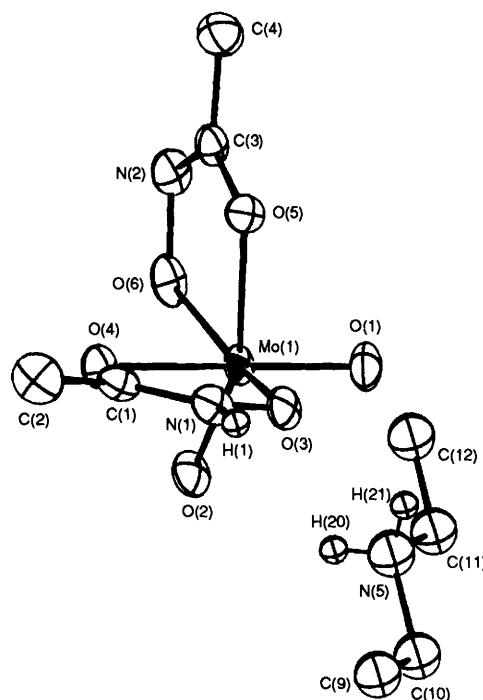


Fig. 1 ORTEP drawing and atomic labels for one of the two independent molecules of **3** in the crystallographic asymmetric unit. Selected bond lengths (Å) and angles (°):  $\text{Mo}(1)-\text{O}(1)$  1.714(3),  $\text{Mo}(1)-\text{O}(2)$  1.719(3),  $\text{Mo}(1)-\text{O}(3)$  2.008(3),  $\text{Mo}(1)-\text{O}(6)$  1.954(3),  $\text{Mo}(1)-\text{O}(4)$  2.228(3),  $\text{Mo}(1)-\text{O}(5)$  2.109(3),  $\text{O}(4)-\text{C}(1)$  1.265(5),  $\text{O}(5)-\text{C}(3)$  1.292(5),  $\text{C}(1)-\text{N}(1)$  1.301(6),  $\text{C}(3)-\text{N}(2)$  1.289(6),  $\text{N}(1)-\text{O}(3)$  1.365(5),  $\text{N}(2)-\text{O}(6)$  1.415(5),  $\text{O}(1)-\text{Mo}(1)-\text{O}(2)$  103.4(1),  $\text{O}(3)-\text{Mo}(1)-\text{O}(4)$  73.1(1),  $\text{O}(5)-\text{Mo}(1)-\text{O}(6)$  73.8(1),  $\text{N}(3)-\text{N}(4)$  2.817(6),  $\text{N}(1)-\text{N}(2)$  2.817(6),  $\text{N}(3)-\text{H}(8)$  0.81(6),  $\text{N}(1)-\text{H}(1)$  0.91(5),  $\text{N}(3)-\text{H}(8)-\text{N}(4)$  179(1),  $\text{N}(1)-\text{H}(1)-\text{N}(2)$  178(1).

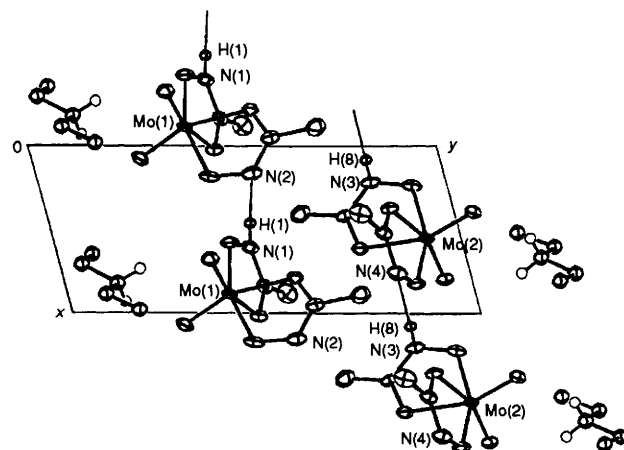
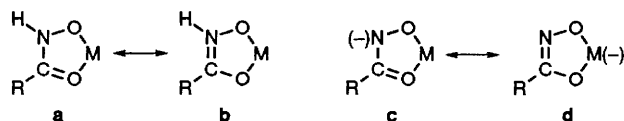


Fig. 2 Crystal packing diagram for **3** showing H-bonding interactions



The above findings indicate that in the present system ligand substitution (dithiocarbamate by hydroxamate) competes favourably with oxidative complexation of the acetohydroxamic acid to form an  $\eta^2$ -MeCONO-*N,O* complex.

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### Footnotes

† *Spectroscopic data* for **3**  $C_8H_{19}MoN_3O_6$ : IR (KBr,  $\tilde{\nu}/cm^{-1}$ ) 912, 878;  $^1H$  NMR ( $CD_3OD$ ,  $\delta$ ) 2.98 (q,  $J = 8$ , 4H), 1.87 (2, 6H), 1.25 (t,  $J = 8$ , 6H); MS (FAB, noba matrix,  $m/z$ , %) 352 (30,  $M^+$  for **3** with  $^{98}Mo$ ), 227 (100%); satisfactory elemental analysis.

‡ *Crystal data* for **3**:  $M$  349.20, triclinic, space group  $P\bar{1}$  (no. 2),  $a = 7.740(3)$ ,  $b = 12.553(4)$ ,  $c = 15.706(4)$  Å,  $\alpha = 71.13(3)$ ,  $\beta = 83.95(3)$ ,  $\gamma = 79.54(3)^\circ$ ,  $V = 1418.2$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.635$  g cm<sup>-3</sup>,  $\mu(Mo-K\alpha) = 9.2$  cm<sup>-1</sup>,  $F(000)$  712. Data were collected at 295 K using Mo-K $\alpha$  radiation ( $\lambda = 0.71069$  Å), data collection range,  $2\theta$  2–50°, and were

corrected for Lorentz and polarization effects. The structure was solved by heavy atom methods and refined by the full-matrix least-squares method (SHELX76). 4973 reflections measured, 3690 reflections used [ $I > 2\sigma(I)$ ],  $R(\Sigma||F_o| - |F_c|/|\Sigma|F_o|) = 0.0333$ ,  $R_w[\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{1/2} = 0.039$ , GOF 1.4. There are two independent molecules in the asymmetric unit. All non-hydrogen atoms were refined anisotropically, and all the hydrogen atoms were located and refined isotropically. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

§ *Spectroscopic data* for **4**:  $C_4H_8MoN_2O_6$ :  $^1H$  NMR [ $(CD_3)_2CO$ ,  $\delta$ ] 2.88 (s, 2H), 2.12 (s, 6H); MS (FAB, noba matrix,  $m/z$ , %) 278 (3,  $M^+$  for **4** with  $^{98}Mo$ ), 180 (100%); satisfactory elemental analysis.

### References

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