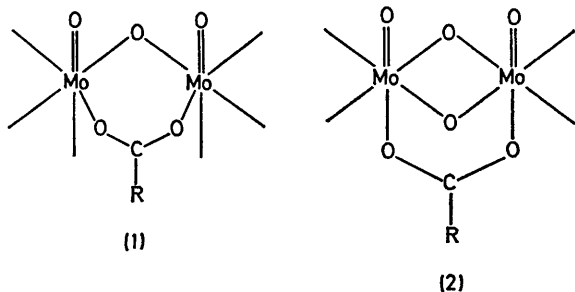


X-Ray Structure of an Oxomolybdenum(v) Dimer Containing a Novel Bridging System: Pyridinium Di- μ -oxo- μ -acetato-bis[oxodi(isothiocyanato)molybdate(v)]

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Summary X-Ray diffraction has established the structure of $[\text{Mo}_2\text{O}_4(\text{MeCO}_2)(\text{NCS})_4]^{3-}$ ions as containing molybdenum atoms linked by a double oxygen bridge and an acetate anion.

RECENT studies¹ have shown that the reactions of $[\text{Mo}_2\text{O}_4(\text{NCS})_6]^{4-}$ complexes with sulphuric and perchloric acids give dimeric oxomolybdates containing bridging μ -sulphato and μ -perchlorato ligands. Oxalic acid behaves similarly leading to an analogous product containing oxalato ligands. We now report the synthesis of similar complexes with bridging anions of several monocarboxylic acids.



There are two possible modes of bridging the molybdenum atoms by carboxylic acid anions as shown in (1) and (2). Structure (1) was proposed, from i.r. spectral studies for pyridinium μ -oxo- μ -oxalato-bis[oxotris(isothiocyanato)molybdate(v)].¹ During the reaction of $[\text{Mo}_2\text{O}_4(\text{NCS})_6]^{4-}$ with acetic acid a dimer of type (2) $[\text{Mo}_2\text{O}_4(\text{MeCO}_2)(\text{NCS})_4]^{3-}$ was obtained and fully characterized by X-ray studies. Its i.r. spectrum differs significantly from that of the μ -oxo- μ -oxalato oxomolybdenum(v) dimer. $\{[\text{Mo}_2\text{O}_4(\text{MeCO}_2)(\text{NCS})_4]^{3-}$ 953, s, $\nu(\text{Mo}-\text{O}_t)$, 721, s, $\nu(\text{Mo}-\text{O}_b)$, 492, m, $\nu(\text{Mo}-\text{O}_b)$, 1540, s, $\nu_{\text{asym}}(\text{COO})$, 1400, m, $\nu_{\text{sym}}(\text{COO})$, 2060 vs, $\nu(\text{C}\equiv\text{N})$, 471, m, $\delta(\text{NCS})$, 292, m, $\nu(\text{Mo}-\text{N})$, 390 cm^{-1} , m, $\nu[\text{Mo}-\text{O}(\text{COO})]$. The $\text{Mo}-\text{O}_t$ and $\text{Mo}-\text{O}_b$ stretches and the vibrations due to the NCS^- ligands are very close to those observed for the initial $[\text{Mo}_2\text{O}_4(\text{NCS})_6]^{4-}$ complex indicating the presence of a four-membered Mo_2O_2 ring.

Crystal data: $\text{C}_{21}\text{H}_{21}\text{N}_7\text{O}_6\text{S}_4\text{Mo}_2$, $M = 787.6$, monoclinic, space group $P2_1/c$, $a = 8.515(1)$, $b = 20.975(3)$, $c = 18.620(3)$ Å, $\beta = 116.19(1)^\circ$, $Z = 4$. Intensities were collected on a Syntex $P2_1$ four-circle diffractometer using graphite

monochromated $\text{Cu}-K_\alpha$ radiation. The structure was solved by heavy-atom methods. Full-matrix least-squares refinement based on 2587 reflections with $F > 3.92\sigma(F)$ yielded a final $R = 0.034$.

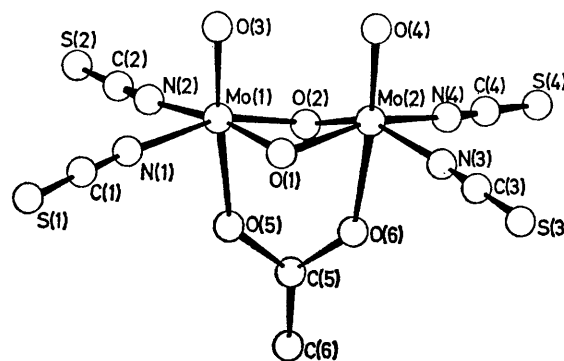


FIGURE. Structure of $[\text{Mo}_2\text{O}_4(\text{MeCO}_2)(\text{NCS})_4]^{3-}$ ion; $[\text{Mo}(1)-\text{Mo}(2)$, 2.560(1); $\text{Mo}(1)-\text{O}(1)$, 1.954(6); $\text{Mo}(1)-\text{O}(2)$, 1.933(5); $\text{Mo}(1)-\text{O}(3)$, 1.690(6); $\text{Mo}(1)-\text{O}(5)$, 2.277(7); $\text{Mo}(2)-\text{O}(1)$, 1.961(5); $\text{Mo}(2)-\text{O}(2)$, 1.931(6); $\text{Mo}(2)-\text{O}(4)$, 1.675(6); $\text{Mo}(2)-\text{O}(6)$, 2.335(6) Å; $\text{Mo}(1)-\text{O}(1)-\text{Mo}(2)$, 81.7(2); $\text{Mo}(1)-\text{O}(2)-\text{Mo}(2)$, 83.0(2)°.

A perspective drawing of the complex anion is shown in the Figure. Molybdenum atoms are linked by a double oxygen bridge and by an acetate anion. The dimensions of the double oxygen bridge are close to those found in other systems.² The $\text{Mo}-\text{O}(\text{acetate})$ distances are considerably increased (ca. 0.2 Å) compared with those determined for $\text{Mo}_2(\text{MeCO}_2)_4^{3-}$ and for μ -acetato-di- μ -hydroxo- μ -(NN')ethylenediaminetetraacetato-bis[molybdenum(III)].⁴ The NCS ligands are N -bonded with the mean $\text{Mo}-\text{N}$ distance of 2.136(9) Å. The average bond distances in co-ordinated isothiocyanato groups are $\text{N}-\text{C}$, 1.15(1); $\text{C}-\text{S}$, 1.61(1) Å. These distances as well as the $\text{Mo}-\text{N}-\text{C}$ and $\text{N}-\text{C}-\text{S}$ angles do not show significant deviations from those reported for $\text{K}_3\text{Mo}(\text{NCS})_6 \cdot \text{H}_2\text{O} \cdot \text{MeCO}_2\text{H}$.⁵

X-ray investigations of other carboxylato-bridged oxomolybdates (V) also suggest that the structures of di- μ -oxo- μ -carboxylato cores do not show essential differences from those described here.

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¹ B. Jeżowska-Trzebiatowska, M. F. Rudolf, L. Natkaniec, and H. Sabat, *Inorg. Chem.*, 1974, **13**, 617.

² L. T. J. Delbaere and C. K. Prout, *Chem. Comm.*, 1971, 162 and references therein.

³ D. Lawton and R. Mason, *J. Amer. Chem. Soc.*, 1965, **87**, 922.

⁴ G. G. Kneale and A. J. Geddes, *Acta Cryst.*, 1975, **B31**, 1233.

⁵ J. R. Knox and K. Eriks, *Inorg. Chem.*, 1968, **7**, 84.