

## The X-Ray Crystal and Molecular Structure of a Molybdenum(v)-L-Histidine Complex $\text{Mo}_2\text{O}_4(\text{L-histidine})_2, 3\text{H}_2\text{O}$

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**Summary** The crystal structure of  $\text{Mo}_2\text{O}_4(\text{L-histidine})_2 \cdot 3\text{H}_2\text{O}$  has been determined by X-ray methods.

THE presence of Mo in certain enzymes<sup>1</sup> has led to studies of the interaction of Mo with  $\alpha$ -amino-acids.<sup>2</sup> The structure of the  $\text{Mo}^{\text{V}}$ -L-cysteine complex, prepared by Kay and Mitchell,<sup>3</sup> has been determined by X-ray crystallography.<sup>4</sup> Now we report the structure of the  $\text{Mo}^{\text{V}}$ -L-histidine complex which was prepared by Melby.<sup>5</sup>

**Crystal data:**  $\text{C}_{12}\text{H}_{16}\text{Mo}_2\text{N}_6\text{O}_8, 3\text{H}_2\text{O}$ ,  $M = 618$ , monoclinic,  $a = 9.80(1)$ ,  $b = 10.94(1)$ ,  $c = 9.92(1)$  Å,  $\gamma = 107.9(1)^\circ$ ,  $F(000) = 616$ ,  $D_m = 2.04$  g cm<sup>-3</sup> (floatation),  $D_c = 2.03$  g cm<sup>-3</sup>,  $Z = 2$ , space group  $P2_1$  (No. 4) Mo- $K_\alpha$  radiation,  $\mu = 13$  cm<sup>-1</sup>.

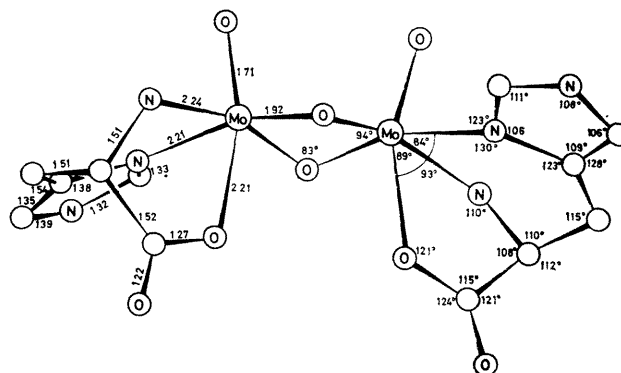
The intensities of 2793 reflections with counts  $>3 \times$  the background were collected on a Hilger and Watts four-circle diffractometer. Lorentz and polarization corrections were applied but no absorption corrections were made.

The structure was solved by the heavy-atom method and refined by least-squares techniques with anisotropic temperature factors for all the non-hydrogen atoms. The final residual  $R$  is 0.070. Although all of the atoms are in general positions there is an approximate non-crystallographic two-fold axis (bisecting the molybdenum-dioxo-bridge) in the molecule as in the cysteine complex.<sup>4</sup>

The two histidine residues are not significantly different from each other except in their pattern of hydrogen-bond formation. There is extensive hydrogen bonding involving both the histidine complex and the water molecules. The final average bond distances and angles are shown in the Figure.

The two halves of the  $\text{Mo}_2\text{O}_2$  bridge are tilted at an angle of  $153^\circ$  to each other and an Mo-Mo bond (2.552 Å) is

formed as in  $\text{BaMo}_2\text{O}_4(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2$ <sup>6</sup> and also in  $\text{Na}_2\text{Mo}_2\text{O}_4 \cdot [\text{SCH}_2\text{CH}(\text{NH}_2)_2\text{CO}_2]_2 \cdot 5\text{H}_2\text{O}$ .<sup>4</sup> The Mo atoms are similarly displaced (by 0.34 Å) out of the N-N-O-O plane towards the terminal oxygen atoms.



FIGURE

The Mo-O(carboxyl) distance of 2.21 Å is 0.09 Å shorter than that in the cysteine compound, indicating that the tridentate histidine ligand is sterically more capable of forming this bond than is the tridentate cysteine ligand.

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<sup>6</sup> F. A. Cotton and S. M. Morehouse, *Inorg. Chem.*, 1965, **4**, 1377.