The Structure of a Molybdenum(V)-L-Cysteine Chelate: $Na_2Mo_2O_4(cysteine)_2,5H_2O$

By J. R. KNOX* and C. K. PROUT
(*Chemical Crystallography Laboratory, South Parks Road, Oxford*)

THE e.s.r. signals of Mo^V in the reduced form of xanthine oxidase have been studied.[1] The signals indicate the presence of sulphur bonds, probably from cysteine, around octahedral molybdenum.[2] Following earlier work[3] on the solution spectra of Mo^{V-VI} cysteine systems, Kay and Mitchell[4] recently isolated a Mo^V cysteine compound, the structure of which we now report.

$Na_2Mo_2O_4[SCH_2CH(NH_2)Co_2],5H_2O$, $M = 630$, orthorhombic; $a = 14{\cdot}830 \pm 0{\cdot}003$, $b = 19{\cdot}446 \pm 0{\cdot}003$, $c = 6{\cdot}482 \pm 0{\cdot}002$ Å; $D_m = 2{\cdot}201$ g.cm.$^{-3}$; $Z = 4$, $D_c = 2{\cdot}238$ g. cm.$^{-3}$; Mo-K_α radiation, $\mu = 15$ cm.$^{-1}$; space group $P2_12_12_1$ (D_2^4 No. 19); 1417 reflections exceeding the background by 3 σ were collected with a Pailred diffractometer. No absorption correction was made.

The structure was solved by Patterson and Fourier methods and refined by full-matrix least squares with isotropic temperature factors ($R = 0{\cdot}066$).

In the binuclear complex anion each molybdenum atom is co-ordinated with bridging and terminal oxygen atoms and a tridentate cysteine ligand to form two distorted octahedra sharing a common edge. A non-crystallographic diad perpendicular to this edge very nearly relates the two halves. Each molybdenum atom is displaced 0·38 Å out of the O–O–S–N plane (±0·01 Å) toward the multiple-bonded terminal oxygen. The 150° angle between the MoO_2 bridge planes, that presumably facilitates the formation of the direct Mo–Mo bond (2·569 Å) without expanding the O–Mo–O angles, is common to $BaMo_2O_4(C_2O_4)_2(H_2O)_2$.[5]

In the cysteine and oxalato-complexes the "*trans* effect"[6] of the Mo=O π-system should cause similar lengthening of Mo–O(carboxyl) bonds in each complex. However, in the cysteine complex this bond (2·29 Å) is significantly longer than in the oxalate (2·12 Å). For the carboxy-group in the cysteine complex to come into bonding position, (1) the C_α and C_β carbon atoms must be displaced (by 0·9 and 0·3 Å) from the N–Mo–S plane in the direction of the molybdenum–carboxy bond and (2) the carboxy-group must be twisted to become coplanar with the molybdenum atom to maximise the strength of the bond. This rotation around C–C_α cannot be completed because of the close intraligand oxygen–sulphur approach (3·04 Å *cf.* 3·71 Å in free L-cysteine[7]) and the result is the abnormally long Mo–O bond.

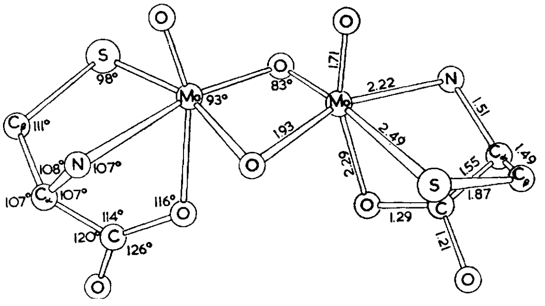

FIGURE. *The* $Mo_2O_4(cysteine)_2^{-2}$ *anion. Average distances and angles are shown.*

The dihedral angle S–C_α–C_β–N about C_α–C_β (56°, *cf.* Gordon Conference convention[8]) need not change in this process and is equal to that in the unsubstituted aminoethanethiol chelate $[(\pi\text{-}C_5H_5)_2MoS(CH_2)_2NH_2]^+I^-$,[9] but the O–C–$C_\alpha$–N dihedral angle ($\psi_2 = -23°$) is larger than in free L-cysteine (−3°) with the molybdenum still 0·5 Å from the carboxy-plane.

The carboxyl group, rather than water, bonds *trans* to the Mo=O (terminal) bond because the carboxyl-group is better able to relieve the build-up of charge density on the metal atom resulting from the $p\pi$–$d\pi$ bonding.

There are no significant differences in the bond lengths of the chelated and free amino-acid; the carbon–sulphur bond is rather long in both cases.

The angles inside the chelate rings, particularly the internal O–C–C_α angle, tend to be smaller than those in the free acid, in agreement with the requirements of this tridentate co-ordination.

We thank Professor R. Mason, Sheffield University, for use of the diffractometer and the National Institute of General Medical Sciences, U.S. Public Health Service for financial support.

(*Received, July 19th, 1968; Com.* 970.)

[1] R. C. Bray and P. F. Knowles, *Proc. Roy. Soc.*, 1968, **302**, *A*, 351; R. C. Bray, P. F. Knowles, F. M. Pick, and T. Vanngard, *Biochem. J.*, 1968, **107**, 601.
[2] L. S. Meriwether, W. F. Marzluff, and W. G. Hodgson, *Nature*, 1966, **212**, 465.
[3] J. T. Spence and H. Y. Chang, *Inorg. Chem.*, 1963, **2**, 319.
[4] A. Kay and P. C. H. Mitchell, *Nature*, 1968, **219**, 267.
[5] F. A. Cotton and S. M. Morehouse, *Inorg. Chem.*, 1965, **4**, 1377.
[6] F. A. Cotton and R. M. Wing, *Inorg. Chem.*, 1965, **4**, 314.
[7] M. M. Harding and H. A. Long, *Acta Cryst.*, 1968, **24**, 1096.
[8] J. T. Edsall, P. J. Flory, J. C. Kendrew, A. M. Liquori, G. Nemethy, G. N. Ramachandran, and H. A. Scherager, *J. Mol. Biol.*, 1966, **15**, 399.
[9] J. R. Knox and C. K. Prout, to be published.