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The Structure of a Cysteine Complex of Molybdenum(V): $Na_2Mo_2O_4[SCH_2CH(NH_2)CO_2]_2.5H_2O$

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$Na_2Mo_2O_4[SCH_2CH(NH_2)CO_2]_2.5H_2O$ crystallizes in space group $P2_12_12_1$ with $a=14{\cdot}83$, $b=19{\cdot}45$, $c=6{\cdot}48$ Å; $Z=4$. The structure was refined by the method of least squares to $R=0{\cdot}062$ for 1415 observed reflexions. The binuclear anion contains tridentate cysteine ligands with the weakest bond to carboxyl (2·30 Å). The bonds Mo–S and Mo–N are 2·49 and 2·23 Å. Two oxygen atoms bridge two molybdenum atoms which are also joined by a direct Mo–Mo (2·57 Å). A terminal oxo ligand completes the distorted octahedral coordination of each molybdenum atom. Hydrogen bonding involving cysteine is of two types: carboxyl groups with water molecules and amino groups with sulphur atoms from neighbouring anions.

Introduction

The role of molybdenum(V) in the enzymatic activity of milk xanthine oxidase is currently being studied by electron spin resonance techniques (Bray & Knowles, 1968). The observation of two types of signal shows that during the catalytic cycle the metal can exist in two different environments, each of surprisingly high symmetry. Doubling of the $\alpha\beta$ signal thought to be a result of molybdenum–proton interaction. The high g values and near-axial symmetry of both $\alpha\beta$ and $\gamma\delta$ signals indicate the presence of sulphur atoms, probably from cysteine, around an octahedrally coordinated molybdenum atom (Meriwether, Marzluff & Hodgson, 1966).

Following earlier work with Mo(V)- and Mo(VI)-cysteine solutions (Spence & Chang, 1963), a compound formulated as $Na_2Mo_2O_4(cysteine)_2(H_2O)_2.3H_2O$ has recently been isolated (Kay & Mitchell, 1968). A binuclear oxo-bridged structure was proposed in which the cysteine ligands are bidentate with uncoordinated carboxyl groups. To gauge the reasonableness of this system as a model for molybdenum in oxidation-reduction enzymes, we undertook an X-ray analysis of this compound. Preliminary results have been published (Knox & Prout, 1968*a*).

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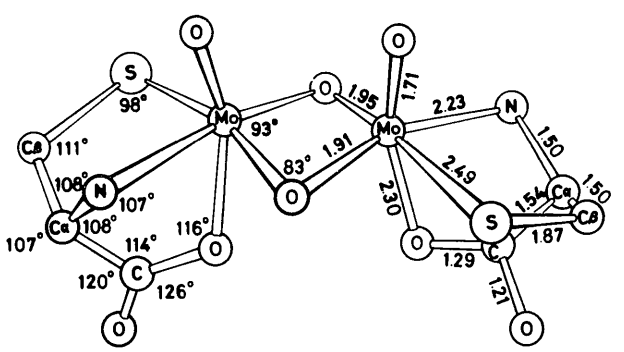


Fig. 1. The di-μ-oxobis{oxo[cysteinatomolybdenum(V)]} anion. Distances and angles are average values from both halves of the anion.

Experimental

Orange air-stable crystals were prepared and supplied by P. C. H. Mitchell of Reading University. The crystal data are: $Na_2Mo_2O_4[SCH_2CH(NH_2)CO_2]_2.5H_2O$; $M=630$, $F(000)=1240$, orthorhombic, $a=14{\cdot}83\pm0{\cdot}01$, $b=19{\cdot}45\pm0{\cdot}01$, $c=6{\cdot}48\pm0{\cdot}01$ Å. $D_m=2{\cdot}201$ g.cm^{-3} (by flotation), $z=4$, $D_c=2{\cdot}238$ g.cm^{-3}, Mo $K\alpha$ radiation, $\lambda=0{\cdot}7107$ Å, $\mu=15$ cm^{-1}. Space group $P2_12_12_1$ (D_2^4, No. 19).

Intensity data were collected with a PAILRED* linear diffractometer from a crystal measuring $0{\cdot}08\times0{\cdot}16\times0{\cdot}44$ mm mounted along the rod axis c. Crystal-monochromatized (Si) Mo $K\alpha$ radiation was used with a scintillation counter. The moving-crystal stationary-counter procedure employed an ω-scan speed of 2·5° per minute. A peak count was rejected if the two 20-second background counts differed by more than three times the standard error of their total count. Of 3910 hkl and $\bar{h}kl$ ($1\leq8$) reflexions within the region 0·1–1·0 reciprocal lattice units, the 1417 intensities with background-corrected counts greater than three times the standard error of the total count were used in the structure analysis. Corrections for Lorentz and polarization effects, but not for absorption, were made.

* Philips Automatic Indexing Linear Reciprocal Space Exploring Diffractometer.

Solution and refinement of the structure

Positions for the two molybdenum atoms were obtained from an unsharpened three-dimensional Patterson function. A Fourier synthesis phased on these atoms revealed two oxygen atoms bridging between two molybdenum atoms. In addition, two oxo ligands, sulphur and nitrogen atoms and carboxyl groups from the cysteine ligand were found to be arranged octahedrally around each metal atom. Remaining carbon atoms of cysteine, five lattice water molecules, and two sodium ions were not distinguished with certainty at this stage, but were easily identified in the next synthesis. A difference synthesis with phases from all 27 atoms and with refined molybdenum positions was checked for additional water molecules, but none were found. No attempt was made to locate hydrogen atoms. The reliability index $\Sigma\,|F_o-F_c|/\Sigma F_o$ was 0·177 for 1417 observed reflexions.

In the full-matrix refinenement the quantity minimized was $\Sigma w|F_o-F_c|^2$ where w is $\{1+[(F_o-a)/b]^2\}^{-1}$ with $a=b=51$ on an absolute scale. Scattering curves were taken from *International Tables for X-ray Crystallography* (1962); the curve for neutral Mo was cor-

Table 1. *Observed and calculated structure factors (X5)*

Each h, k group gives, from left to right, l, F_o, F_c and phase angle.
Two reflections marked* were not used in refinement.

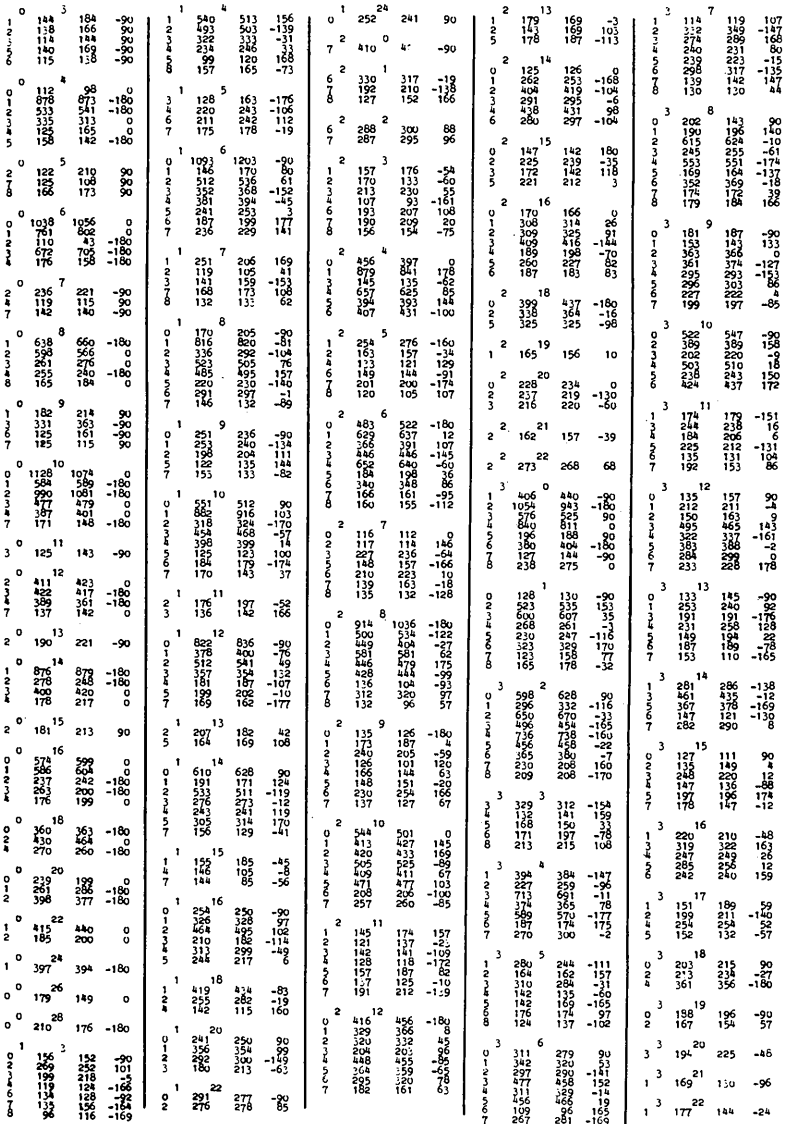
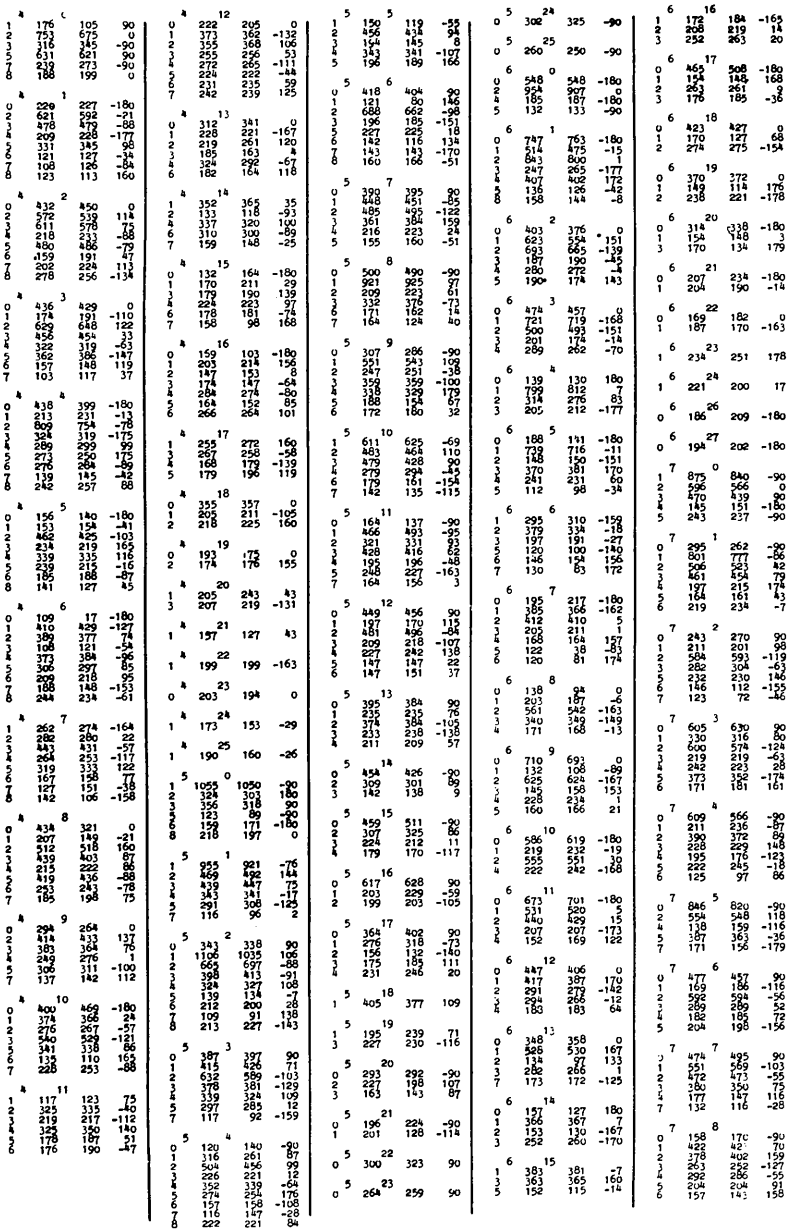


Table 1 (*cont.*)



rected for the real part of the dispersion effect ($\Delta f' = -1{\cdot}7$). Unobserved reflexions were omitted from the refinement and the two strong reflexions 080 and 140 given zero weight. With isotropic temperature factors the refinement proceeded smoothly through four cycles until the parameter shifts were less than $0{\cdot}070\sigma_i$. The R index was 0·066.

The molybdenum atoms were assigned anisotropic temperature factors and a block-diagonal refinement was continued for three cycles until all shifts were less than $0{\cdot}45\sigma_i$. The final R index was 0·062. A test of the R ratio showed that the anisotropic refinement led to a significant improvement in R (Hamilton, 1965). A final difference map did not show any unusual features. Observed and calculated structure factors are listed in Table 1. Positional parameters (L-configuration) and temperature factors are shown in Table 2 together with the standard errors from the least-squares procedure. Selected interatomic distances, bond angles and dihedral angles are given in Table 3, and the anion is sketched in Fig. 1.

Discussion

Molybdenum coordination

Two tridentate cysteine ligands, two *cis* terminal oxo ligands, and two bridging oxygen atoms are coordi-

Table 1 (*cont.*)

nated with the molybdenum atoms to form two distorted octahedra sharing a common edge of oxygen atoms. The whole is a binuclear anion the two halves of which are related by a non-crystallographic twofold axis perpendicular to the common edge of oxygen atoms.

In solution the sulphur and amino groups, the stronger σ donors, most likely coordinate first and leave the carboxyl group to compete with a water molecule for the position *trans* to the $p\pi$–$d\pi$ system of the Mo=O (terminal) bond. Though the infrared frequency at 1590 cm^{-1} had been assigned (Kay & Mitchell, 1968) to the asymmetric stretch of an uncoordinated ionized carboxyl group, this study shows that the carboxyl group has coordinated to the metal, replacing the water molecule. This is presumably because the larger $-CO_2$ group is better able to delocalize any build-up of charge density on the metal resulting from oxygen-to-metal $p\pi$-$d\pi$ bonding in the *trans* Mo=O bond. The two Mo–O (carboxyl) distances do not differ significantly and their average value is 2·30Å. Because the carboxyl is *trans* to Mo=O we expect some lengthening of the Mo–O (carboxyl) bond as a result of the '*trans* effect' (Cotton & Wing, 1965) of the multiple-bonded system.

Table 1 (*cont.*)

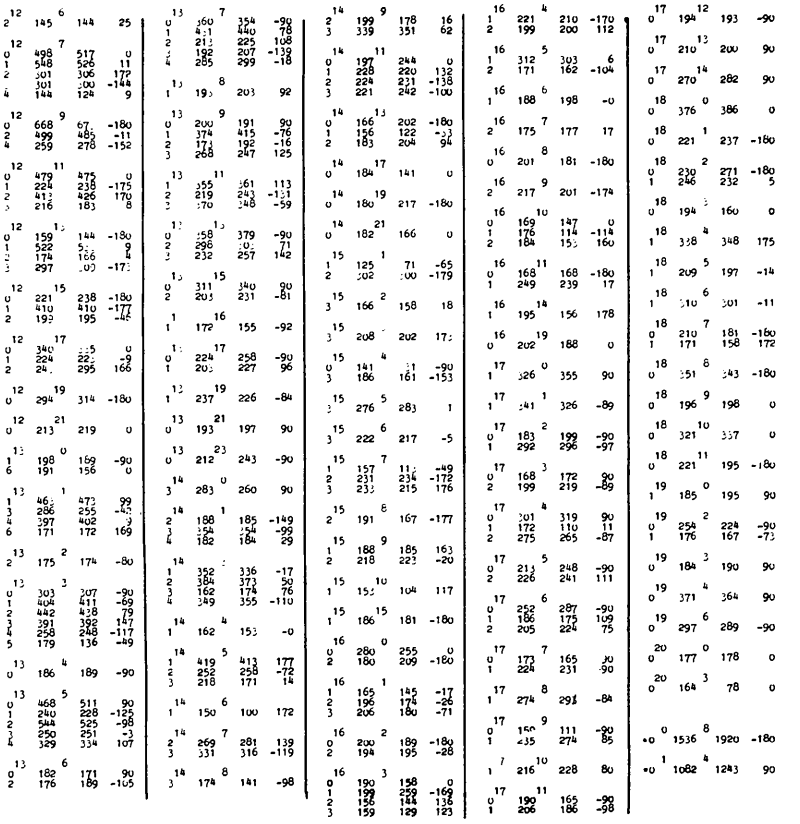


Table 2. *Fractional atomic coordinates* ($\times 10^4$) *and thermal parameters* ($\times 10^3$) *with standard deviations in parentheses*

	x	y	z	U (Å^2)
Mo(1)	6072 (1)	6933 (1)	8056 (2)	*
Mo(2)	4384 (1)	6984 (1)	7184 (2)	*
S(1)	7018 (4)	6698 (3)	11150 (8)	24 (1)
S(2)	3358 (4)	6762 (3)	4214 (8)	26 (1)
N(1)	7372 (10)	6636 (8)	6470 (24)	16 (3)
N(2)	3107 (11)	6818 (8)	8837 (26)	22 (3)
O(1)	5403 (10)	6752 (7)	5531 (23)	25 (3)
O(2)	5030 (10)	6827 (7)	9769 (22)	25 (3)
O(3)	6340 (9)	7785 (7)	7958 (27)	31 (3)
O(4)	4265 (9)	7859 (7)	7068 (25)	30 (3)
O(5)	7206 (9)	4923 (7)	8411 (22)	24 (3)
O(6)	6197 (9)	5757 (6)	7942 (24)	24 (3)
O(7)	4118 (9)	5830 (7)	7602 (22)	25 (3)
O(8)	3012 (10)	5058 (7)	7399 (23)	29 (3)
C(1)	7003 (12)	5514 (9)	8075 (33)	21 (4)
C(2)	7754 (12)	6048 (9)	7666 (30)	20 (4)
C(3)	8029 (15)	6328 (11)	9766 (35)	29 (5)
C(4)	3278 (14)	5640 (10)	7581 (33)	26 (4)
C(5)	2607 (13)	6244 (9)	7754 (34)	24 (4)
C(6)	2362 (15)	6465 (12)	5659 (37)	29 (5)
Na(1)	5084 (8)	5552 (6)	10386 (22)	59 (3)
Na(2)	0086 (10)	5748 (7)	8085 (26)	75 (4)
O(9)	5456 (12)	4358 (9)	9556 (30)	44 (4)
O(10)	4336 (17)	4097 (13)	6271 (44)	78 (7)
O(11)	9146 (12)	4675 (10)	8646 (34)	50 (5)
O(12)	1154 (13)	4788 (9)	7454 (33)	55 (5)
O(13)	0050 (15)	6964 (11)	7439 (36)	73 (6)

* Coefficients ($\times 10^4$) have the form:

$$\exp\left[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{23}klb^*c^*+2U_{31}lhc^*a^*+2U_{12}hka^*b^*)\right].$$

	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
Mo(1)	0140 (6)	0182 (7)	0183 (7)	0014 (15)	0039 (13)	—0041 (13)
Mo(2)	0150 (6)	0198 (7)	0174 (6)	0034 (15)	0029 (13)	0022 (14)

However, a comparison with the 2·12 Å Mo–O (oxalato) bond in $BaMo_2O_4(C_2O_4)_2(H_2O)_2$ (Cotton & Morehouse, 1965), also *trans* to Mo=O, indicates that the Mo–O (carboxyl) bond is longer than expected. We shall later attempt to show how the $-CO_2$ group is sterically unable to form a strong link with the metal.

The average terminal oxo distance (1·71 Å) compares with 1·70 Å in the oxalato structure There are two types of bridging Mo–O bonds, either *trans* to $-NH_2$ or *trans* to sulphur, with average values 1·91 and 1·95 Å. This shows that the strongest of the three bonds to cysteine is from the sulphur atom. The average

Table 3. *Distances* (Å, $\sigma \times 10^3$) *and angles* (deg., $\sigma \times 10$) *with standard errors in parentheses*

Distances and angles involving molybdenum

Mo(1)–O(1)	1·946 (15)	Mo(2)–O(1)	1·907 (15)
Mo(1)–O(2)	1·915 (15)	Mo(2)–O(2)	1·954 (15)
Mo(1)–O(3)	1·706 (18)	Mo(2)–O(4)	1·712 (16)
Mo(1)–S(1)	2·490 (6)	Mo(2)–S(2)	2·491 (6)
Mo(1)–N(1)	2·260 (16)	Mo(2)–N(2)	2·200 (17)
Mo(1)–O(6)	2·295 (16)	Mo(2)–O(7)	2·295 (14)
Mo(1)–Mo(2)	2·569 (2)		
N(1)—Mo(1)–S(1)	80·7 (4)	N(2)—Mo(2)–S(2)	79·9 (5)
N(1)—Mo(1)–O(1)	90·4 (6)	N(2)—Mo(2)–O(2)	88·9 (6)
S(1)—Mo(1)–O(2)	88·2 (5)	S(2)—Mo(2)–O(1)	90·5 (5)
O(1) —Mo(1)–O(2)	93·2 (6)	O(1) —Mo(2)–O(2)	93·2 (6)
O(3) —Mo(1)–O(1)	105·2 (7)	O(4) —Mo(2)–O(1)	107·0 (7)
O(3) —Mo(1)–O(2)	108·3 (7)	O(4) —Mo(2)–O(2)	104·1 (7)
O(3) —Mo(1)–S(1)	94·4 (6)	O(4) —Mo(2)–S(2)	94·3 (6)
O(3) —Mo(1)–N(1)	91·9 (7)	O(4) —Mo(2)–N(2)	94·5 (7)
O(6) —Mo(1)–O(1)	80·4 (6)	O(7) —Mo(2)–O(1)	88·4 (6)
O(6) —Mo(1)–O(2)	88·6 (6)	O(7) —Mo(2)–O(2)	80·2 (6)
O(6) —Mo(1)–S(1)	78·3 (4)	O(7) —Mo(2)–S(2)	79·4 (4)
O(6) —Mo(1)–N(1)	70·3 (6)	O(7) —Mo(2)–N(2)	69·5 (6)
O(1) —Mo(1)–S(1)	158·7 (5)	O(1) —Mo(2)–N(2)	157·1 (6)
O(2) —Mo(1)–N(1)	157·7 (6)	O(2) —Mo(2)–S(2)	159·2 (5)
O(3) —Mo(1)–O(6)	161·5 (7)	O(4) —Mo(2)–O(7)	163·6 (7)
Mo(2)–Mo(1)–O(3)	100·4 (6)	Mo(1)–Mo(2)–O(4)	98·6 (6)
Mo(2)–Mo(1)–O(6)	96·3 (4)	Mo(1)–Mo(2)–O(7)	96·0 (4)
Mo(1)–O(1) —Mo(2)	83·6 (6)	Mo(1)–O(2) —Mo(2)	83·2 (6)

Distances, angles and dihedral angles in chelated and free cysteine

$L_1 = S(1)H_2C(3)HC(2).H_2N(1).O(5)C(1)O(6)–Mo(1)$
$L_2 = S(2)H_2C(6)HC(5).H_2N(2).O(8)C(4)O(7)–Mo(2)$

	In L_1	In L_2	In L-cysteine
S—Cβ	1·89 (23)	1·84 (25)	1·86 (12)
Cβ–Cα	1·52 (30)	1·47 (33)	1·51 (14)
Cα–C	1·55 (29)	1·54 (31)	1·51 (13)
Cα–N	1·49 (25)	1·51 (27)	1·50 (12)
C—O	1·21 (26)	1·21 (26)	1·27 (12)
C—O*	1·29 (26)	1·30 (26)	1·24 (12)
O···S	3·03 (16)	3·06 (15)	3·71 (8)
O···N	2·62 (22)	2·56 (22)	2·65 (11)
N···S	3·08 (17)	3·02 (18)	3·37 (9)
S—Cβ–Cα	110·4 (15)	111·3 (17)	114·4 (8)
Cβ–Cα–C	106·3 (17)	108·4 (18)	113·2 (9)
Cβ–Cα–N	107·0 (16)	109·5 (18)	111·0 (9)
C—Cα–N	109·3 (16)	106·2 (17)	109·1 (9)
Cα–C—O	119·4 (18)	120·7 (19)	115·8 (9)
Cα–C—O*	114·3 (18)	113·7 (18)	120·7 (9)
O—C—O	126·3 (20)	125·6 (20)	123·4 (9)
O*—C—Cα–N	−21·0	−25·1	−3·0
O*—C—Cα–Mo	11·4	8·8	—
O*—C—Cα–S	62·0	59·3	93·6
O*—C—Cα–Cβ	94·0	92·4	121·1
O*—C—Cα–O	177·7	181·6	179·4
N—Cα–Cβ–Mo	41·2	38·8	—
N—Cα–Cβ–S	60·0	54·5	72·6
N—Cα–Cβ–O*	85·9	84·0	95·6
N—Cα–Cβ–C	116·6	115·4	123·1
N—Cα–Cβ–O	143·7	141·9	148·0

* Oxygen *cis* to $-NH_2$ with respect to C–Cα bond.

Table 3 (*cont.*)

Hydrogen bonds		
O(5)–O(9)		2·91 (26)
O(5)–O(11)		2·92 (27)
O(8)–O(10)		2·81 (26)
O(8)–O(12)		2·81 (25)
O(9)–O(10)		2·75 (34)
N(1)—S(1)	(x, y, $z-1$)	3·49 (16)
N(1)—S(2)	($\frac{1}{2}+x$, $\frac{3}{2}-y$, $1-z$)	3·47 (18)
N(2)—S(1)	($x-\frac{1}{2}$, $\frac{3}{2}-y$, $2-z$)	3·31 (18)
N(2)—S(2)	(x, y, $z+1$)	3·51 (18)
O(12)–S(2)	($\frac{1}{2}-x$, $1-y$, $z-\frac{1}{2}$)	3·30 (17)
O(10)–O(3)	($1-x$, $y-\frac{1}{2}$, $\frac{3}{2}-z$)	2·79 (33)
O(9)—O(5)—O(11)		143·3 (16)
O(10)–O(8)—O(12)		124·5 (16)
C(1)—O(5)—O(9)		100·5 (14)
C(1)—O(5)—O(11)		114·3 (15)
C(4)—O(8)—O(10)		115·0 (14)
C(4)—O(8)—O(12)		119·7 (14)
O(5)—O(9)—O(10)		114·2 (9)
O(8)—O(10)–O(9)		95·6 (10)
Mo(1)–N(1)—S(1)	(x, y, $z-1$)	108·1 (4)
Mo(1)–N(1)—S(2)	($\frac{1}{2}+x$, $\frac{3}{2}-y$, $1-z$)	100·8 (4)
Mo(2)–N(2)—S(1)	($x-\frac{1}{2}$, $\frac{3}{2}-y$, $2-z$)	107·1 (4)
Mo(2)–N(2)—S(2)	(x, y, $z+1$)	113·4 (4)
O(8) —O(10)–O(3)	($1-x$, $y-\frac{1}{2}$, $\frac{3}{2}-z$)	108·1 (11)
O(9) —O(10)–O(3)	($1-x$, $y-\frac{1}{2}$, $\frac{3}{2}-z$)	104·3 (11)
Sodium–oxygen distances		
Na(1)–O(2)		2·51 (20)
Na(1)–O(6)		2·32 (21)
Na(1)–O(7)		2·37 (20)
Na(1)–O(9)		2·45 (28)
Na(1)–O(11)	($\frac{3}{2}-x$, $1-y$, $\frac{1}{2}+z$)	2·44 (27)
Na(1)–O(12)	($\frac{1}{2}-x$, $1-y$, $\frac{1}{2}+z$)	2·37 (28)
Na(2)–O(9)	($\frac{1}{2}-x$, $1-y$, $z-\frac{1}{2}$)	2·43 (29)
Na(2)–O(10)	($\frac{1}{2}-x$, $1-y$, $\frac{1}{2}+z$)	2·26 (27)
Na(2)–O(11)	($x-1$, y, z)	2·53 (28)
Na(2)–O(12)		2·48 (27)
Na(2)–O(13)		2·40 (29)

metal–sulphur distance (2·49 Å) is shorter than the distances in the singly-oxo-bridged $Mo_2O_3[S_2P(OC_2H_5)_2]_4$ (Knox & Prout, 1968*b*) and $Mo_2O_3(S_2COC_2H_5)_4$ (Blake, Cotton & Wood, 1964), in which the Mo–S bonds *trans* to the bridge are 2·55 and 2·54 Å.

In the two halves of the anion the Mo–N distances differ by 0·06 Å. Reasons for this are not clear, but it may be that the Mo–N(2) bond is shortened by its stronger polarization interaction with the sulphur atom of the type $Mo–N^{\delta-}–H^{\delta+}\cdots S$ (3·31 Å), compared with 3·47 Å for the N(1)···S distance. Nevertheless, the average value 2·23 Å compares favourably with 2·21 Å in $(\pi\text{-}C_5H_5)_2MoS(CH_2)_2NH_2^+I^-$ (Knox & Prout, 1968*b*), in which there is a similar $N^{\delta-}–H^{\delta+}\ldots I^-$ interaction. The N–Mo–S angle in this cysteine chelate (80·4°) is near the 78·4° value in the aminoethanethiol compound while the N–Mo–O angle (69·9°) falls at the lower end of the 68°–85° range defined by thirteen first transition metal α-amino acid chelates (Freeman, 1967). This agrees with Freeman's observation that N–M–O angles decrease as the average of the M–N and M–O distances increases, owing to the constancy of the N···O contact.

The bonding to molybdenum may be described as seven-coordination, for there is a direct Mo–Mo bond (2·569 Å) between adjacent atoms, not unlike the 2·54 Å bond in $BaMo_2O_4(C_2O_4)_2(H_2O)_2$ (Cotton & Morehouse, 1965). Together with the two oxo-bridges, this metal–metal bond permits spin coupling and accounts for the diamagnetism of the compound (Kay & Mitchell, 1968). The Mo_2O_4 bridge system is folded along O(1)···O(2) with an angle of 151° between the two MoO_2 planes. A similar folding is present in the oxalato compound and was said to allow the formation of the Mo–Mo bond without distorting the angles in the bridge. However, the four Mo–Mo–O angles are forced to enlarge, especially the two angles involving the π-bonded terminal oxygen atoms. The Mo atoms are displaced out of the O–O–S–N planes by 0·38 Å in the direction of the terminal oxygen ligands. This tetragonal distortion is quite common in systems containing the Mo=O bond, whether singly or doubly bridged, or

non-bridged, as in $Mo_2O_3[S_2P(OC_2H_5)_2]_4$ (Knox & Prout, 1968*b*), $BaMo_2O_4(C_2O_4)_2(H_2O)_2$ (Cotton & Morehouse, 1965) or $[(C_6H_5)_4As]^+[MoOBr_4(H_2O)]^-$ (Scane, 1967).

The cysteine ligands

Fig. 2 shows bond conformations as viewed along the C–Cα, Cα–Cβ and N–Cα bonds of chelated cysteine. The ψ,χ,φ notation follows Edsall (Edsall, Flory, Kendrew, Liquori, Nemethy, Ramachandran & Scheraga, 1966). From derived hydrogen angles one sees that the $-CH_2$ and $-NH_2$ groups are within 2° and 10° of being staggered with respect to the CH bond. As there are no reported metal–cysteine structures, we examine the effects of chelation on the cysteine molecule by means of a comparison with free L-cysteine* (Harding & Long, 1968) and with the unsubstituted aminoethanethiol chelate $(\pi\text{-}C_5H_5)_2MoS(CH_2)_2NH_2^+I^-$ (Knox & Prout, 1968*b*). Upon the preferential formation in solution of the Mo–S and Mo–N bonds, the dihedral angle S–C–C–N of the chelated cysteine (57°) is considerably decreased from its value in L-cysteine (73°) and becomes nearly equal to the angle in $(\pi\text{-}C_5H_5)_2MoS(CH_2)_2NH_2^+I^-$ (55°). This dihedral angle is then unaffected by the presence of $-CO_2$ at the α-carbon. In the absence of other effects (to be discussed below), this decrease of the S–C–C–N angle would cause the $-CO_2$ group to rotate *away* from the molybdenum atom. However, it can approach the remaining bonding position by two means. First, there is rotation of the cysteine molecule around the S···N axis until intramolecular contacts between bridging and carboxyl oxygen atoms (2·75 Å) prevent further necessary rotation. The Cα and Cβ atoms are 0·92 and 0·30 Å to one side of the S–Mo–N plane. Second, the carboxyl group must undergo a ψ rotation about C–Cα, and thereby twist out of the plane it formed with the Cα–N bond. In the chelate the magnitude of the O–C–Cα–N dihedral angle ($\psi = -23°$) is greater than in L-cysteine (−3°), but is less than the 30–40° rotation required for maximum in-plane bonding. Continued rotation of $-CO_2$ about C–Cα is made impossible by the close 3·04 Å intraligand approach of the oxygen atom towards the sulphur atom; the corresponding contact in L-cysteine is 3·71 Å. After these two rotations further movement of the carboxyl plane towards molybdenum is permitted by: (1) a decrease in the skeletal angle C–Cα–Cβ from 113° in the free acid to 107° in the chelate; (2) a decrease in the interior angle O–C–Cα from 121° to 114°. Nevertheless, upon completion of the conformational changes just described, the metal atom is still 0·51 Å from the Cα–CO_2 plane, and a rather weak Mo–O (carboxyl) bond results.

* A brief report of the cysteine.HCl.H_2O structure appeared in 1965 (Ramachandra Ayyar & Srinivasan, 1965) but as the refinement was incomplete, we use the more recent results of Harding & Long. Their structure contains two types of molecule, with the sulphur and nitrogen atoms either *cis* or *trans* to the Cα–Cβ bond. We quote their results for the *cis* form, since the chelated ligand is *cis* also.

The individual distances and angles in the two cysteine ligands are equal within 2σ. The more easily deformed dihedral angles show slightly greater differences but all are less than 6°. While the average bond angles and dihedral angles of the free and chelated amino acids differ according to the requirements of tridentate co-

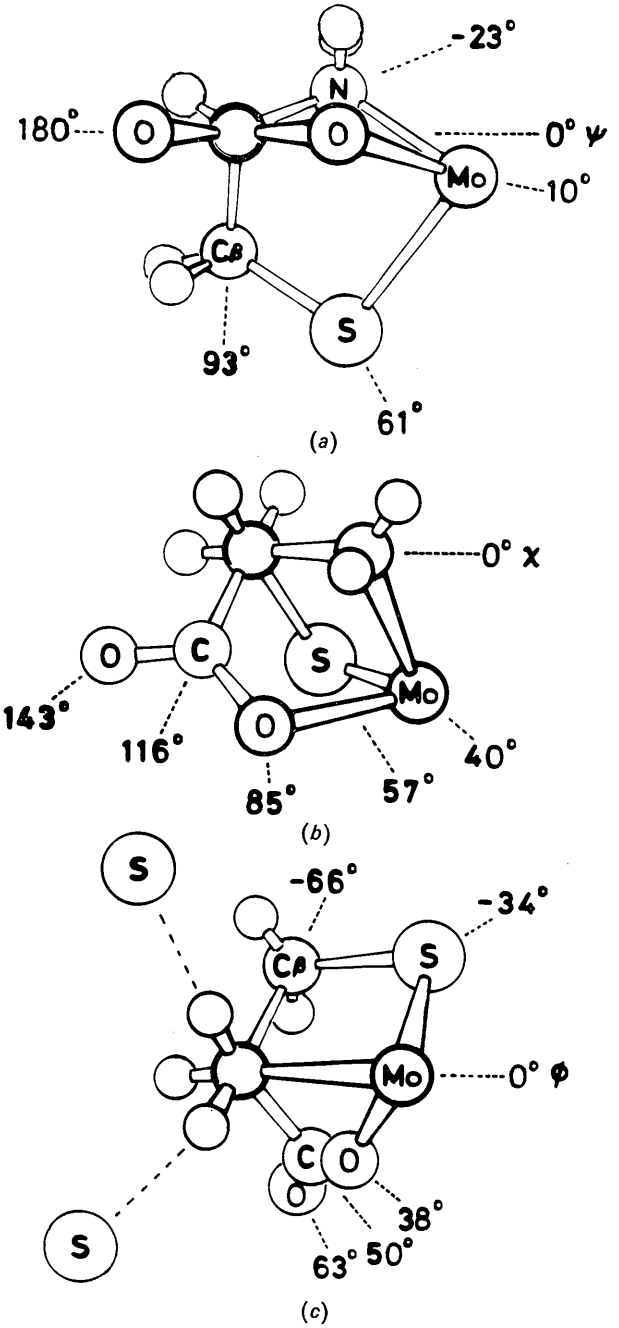


Fig. 2. Average dihedral angles. View along bond: (*a*) from C to Cα, (*b*) from Cα to Cβ, (*c*) from N to Cα. Values are positive as far atom rotates clockwise relative to near atom. Bond distances not to scale. Values for free L-cysteine given in Table 3.

ordination, the average C–C, C–N and C–S distances are little changed by chelation. The largest difference is in the C–Cα bond, which is 0·035 Å longer in the chelate. In both the ligand and in the free acid a somewhat long Cβ–S bond is observed; the values are 1·87 and 1·86 Å against the single-bond value 1·81 Å (Pauling, 1960). Upon chelation the C–O bond *cis* to $-NH_2$ lengthens from 1·24 to 1·29 Å and the uncoordinating C–O bond contrasts from 1·27 to 1·21 Å, as a result of charge delocalization into the bond.

Crystal structure

Each outer carboxyl atom participates in hydrogen bonding with two molecules of water. The four bonds involve $H_2O(9,10,11,12)$ and range from 2·8 to 2·9 Å. Each pair is roughly planar with, and trigonally related to, the C–O bond (Fig. 3). The fifth molecule $H_2O(13)$ links anions along **c** by weaker bonds (3·0 to 3·2 Å) between terminal and bridging oxygen atoms. Accepting a hydrogen bond from $H_2O(9)$ (2·75 Å) $H_2O(10)$ bridges across terminal and carboxyl oxygen atoms to join anions along **b** by means of the sequence, Mo=O(3)...H–O–H...O(8)-C–O–Mo=O(4). There is little interaction of water molecules with the sulphur or amino groups of cysteine, other than the single 3·3 Å bond between $H_2O(12)$ and S(2). Each amino sulphur forms intermolecular hydrogen bonds with two sulphur atoms [Fig. 2(*c*)] at distances from 3·3 to 3·5 Å, the expected range for N–H...S bonds (Srinivasan & Chacko, 1967).

Of the two sodium ions, Na(1) is nearer to the binuclear anion and is coordinated to it *via* the bridging oxygen atom O(2) and two carboxyl atoms O(6) and O(7). Three molecules of water complete its octahedral environment. The proximity of CH bonds allows only a distorted trigonal-bipyramidal coordination of five water molecules around the Na(2) ion.

Anisotropy in the molybdenum vibration is slight. The minimum and maximum root-mean-square displacements are 0·111 and 0·138 Å for Mo(1) and 0·119 and 0·145 Å for Mo(2). Major vibration is generally perpendicular to the Mo–Mo bond.

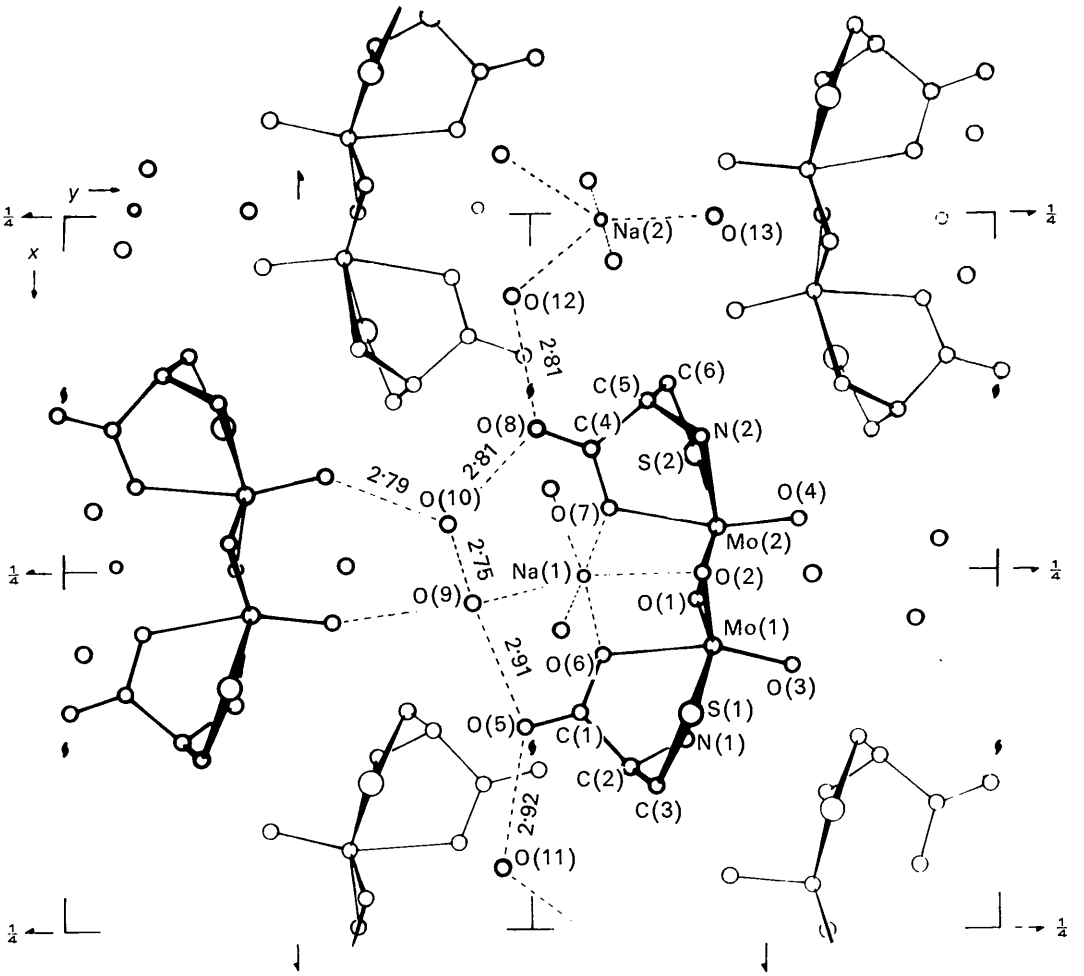


Fig. 3. Projection of structure down **c**.

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The Crystal and Molecular Structure of Bis-(1,4-diazacycloheptane)copper(II) Nitrate Hemihydrate*

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Bis-(1,4-diazacycloheptane)copper(II) nitrate hemihydrate,

$$[Cu(dach)_2NO_3]NO_3 . [Cu(dach)_2H_2O](NO_3)_2 ,$$

crystallizes in the monoclinic space group $P2_1/n$ with $a=20{\cdot}92$, $b=15{\cdot}79$, $c=10{\cdot}04$ Å and $\beta=91{\cdot}7°$. There are four formula units per unit cell. The structure was solved by Patterson and Fourier techniques and refined by least-squares calculations, based on 3845 reflections measured on a Picker automatic diffractometer; the final R index was 0·11. The copper atoms in the $[Cu(dach)_2NO_3]^+$ and $[Cu(dach)_2H_2O]^{2+}$ cations have approximately square pyramidal coordination with average equatorial Cu–N and average axial Cu–O bond lengths of 2·01 and 2·34 Å, respectively. The chelated 1,4-diazacycloheptane moieties are in double-boat conformation. This is the first structural analysis of a bis complex of a cyclic diamine with a transition metal.

Introduction

Pentacoordinated copper complexes may have either trigonal bipyramidal (D_{3h}) or square pyramidal (C_{4v}) structures. Copper(II) complexes of 6-methyl-2-picolylamine (Sutton, 1963; Utsuno & Sone, 1966) and tris-(2-dimethylaminoethyl)amine with Cl^-, Br^- or ClO_4^- ions occupying the fifth position (Ciampolini & Nardi, 1966) are examples of the former structure. The square pyramidal arrangement around copper(II) has been observed in *N,N'*-ethylene-bis(acetylacetoneiminato)-copper(II) monohydrate (Hall, Morgan & Waters, 1966), in *N,N'*-disalicylidenepropane-1,2-diaminecopper(II) monohydrate (Llewellyn & Waters, 1960) and in 4-methylpyridine-bis-(*o*-hydroxyacetophenonato)-copper(II) (Duckworth, Graddon, Mockler & Stephenson, 1967).

Recently the preparation and characterization of copper(II) complexes of 1,4-diazacycloheptane (dach) have been reported (Musker & Hussain, 1967). It was concluded that addition of tetraethylammonium chloride or bromide to bis-(1,4-diazacycloheptane)copper(II) perchlorate in nitromethane resulted in pentacoordinated species, in which the substituent at the assumed apical position could be varied systematically

* Abstracted from Ph.D. thesis of M. Sakhawat Hussain, University of California, Davis (1968).

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