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A Refinement of the Structure of Disodium Di-μ-oxo-bis{[cysteinato(2−)]oxomolybdate}(*Mo–Mo*) Pentahydrate Based on X-ray and Neutron Diffraction Data

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Abstract. $Na_2[Mo_2O_4\{SCH_2CH(NH_2)CO_2\}_2].5H_2O$, orthorhombic, $P2_12_12_1$, $Z = 4$, $T = 295$ K, $a = 14.835$ (7), $b = 19.448$ (5), $c = 6.491$ (2) Å, $V = 1872.73$ Å^3, $D_c = 2.234$ Mg m^{-3}. All H-atom positions were determined using neutron diffraction data obtained at 50 K. A final residual of 0·052 was obtained over 1014 reflections and 190 variables. Atomic distances in the two halves of the molecule agree well, except for Mo—O(carboxyl).

Introduction. The role of Mo^V in enzyme catalysis has been widely studied (Wentworth, 1976) and a variety of Mo-containing species have been employed as models – particularly those of the nitrogenase system (Corbin, Pariyadath & Stiefel, 1976; Cramer, 1978). The title compound, $Na_2[Mo_2O_4cys_2].5H_2O$, one of the simpler of these, has been studied by X-ray crystallography (Knox & Prout, 1969), nuclear magnetic resonance and optical spectroscopic techniques (Liu, 1981). In order to provide a firm basis for the interpretation of these latter data a low-temperature neutron diffraction study was performed.

The compound was prepared by the method of Kay & Mitchell (1970). Suitable crystals were grown by vapor diffusion of ethanol into an aqueous solution in about one week. Both needle- and plate-like crystals were obtained, shown to be isomorphous, and used for the X-ray and neutron diffraction measurements.

X-ray diffraction data were collected on an Enraf–Nonius CAD-4 diffractometer using standard room-temperature techniques. Neutron diffraction data were collected with the pin-mounted sample inside an aluminum can which was filled with He gas and attached to a Displex® closed-cycle refrigeration system and mounted on the H6S spectrometer at the High Flux Beam Reactor of Brookhaven National Laboratory. Crystal and experimental data for both measurements are shown in Table 1.

Table 1. *Crystal and experimental data*

	X-ray	Neutron
Crystal dimensions (mm)	0·31 × 0·12 × 0·37	2·0 × 0·4 × 3·0
Crystal faces: common	(010)(0$\bar{1}$0)(011)(0$\bar{1}$1)(00$\bar{1}$)(120) (1$\bar{2}$0)($\bar{1}$20)($\bar{1}\bar{2}$0)	
different	(101)($\bar{1}$01)	(30$\bar{1}$)($\bar{3}$0$\bar{1}$)
λ (Å)	0·7107	1·1621
Temperature (K)	295	50
a (Å)	14·835 (7)	14·788 (4)
b (Å)	19·448 (5)	19·283 (15)
c (Å)	6·491 (2)	6·457 (6)
V (Å^3)	1872·73	1841·26
D_c (Mg m^{-3})	2·234	2·272
μ (mm^{-1})*	1·665	0·170
Scattering factors	Doyle & Turner (1968); Stewart, Davidson, Simpson (1965)	Shull (1972)
Absorption-correction range	1·20–1·58	1·07–1·31
$\sin\theta/\lambda$ limit (Å^{-1})	0·02–0·66	0·02–0·46
Total number of reflections	5054	1014
Number of unique reflections	2527	1014
Total number of variables	245	190
Number of atomic positions refined	27	47
Temperature-factor model (non-H)	Anisotropic	Isotropic
$R(F^2)$	0·063	0·052
$wR(F^2)$	0·093	0·059
$S\,[\sum w\Delta^2/(m-n)]^{1/2}$	2·26	1·23

All programs used in this analysis are described in the *CRYSNET* manual (Berman, Bernstein, Bernstein, Koetzle & Williams, 1976).

* Values for the absorption coefficients were those in *International Tables for X-ray Crystallography* (1968, 1974), except for μ/ρ for H in the neutron case, for which a value of 23·9 × 10^2 mm^2 g^{-1} was used.

Using the atomic coordinates of Knox & Prout (1969), refinement was initiated against the 2363 reflections obtained by averaging symmetry-related X-ray diffraction observations with $F_o^2 > 3\sigma$. Final agreement indices, calculated with all reflections, are given in Table 1 and the refined positional parameters with standard deviations are listed in Table 2. Using these results in conjunction with the neutron diffrac-

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Table 2. *Fractional atomic coordinates* ($\times 10^5$) *and equivalent isotropic mean-square amplitudes of vibration* ($\times 10^3$) $[U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})]$ *for the non-hydrogen atoms determined by X-ray diffraction at* 295 K

	x	y	z	U_{eq} (Å^2)
MO(1)	60837(4)	69371(3)	80630(10)	201(1)
MO(2)	43945(4)	69854(3)	71882(10)	206(1)
S(1)	70224(13)	66982(11)	111553(33)	265(5)
S(2)	33726(15)	67550(12)	42176(32)	316(6)
O(1)	54241(36)	67432(29)	55017(89)	280(17)
O(2)	50346(34)	68268(27)	97949(84)	238(16)
O(3)	63406(35)	77809(27)	79335(107)	342(17)
O(4)	42629(37)	78433(27)	70343(105)	357(17)
O(5)	72011(36)	49246(28)	84657(98)	323(17)
O(6)	62045(31)	57714(25)	79928(101)	252(15)
O(7)	41275(30)	58256(26)	76367(93)	255(15)
O(8)	30205(35)	50572(27)	73627(120)	404(21)
N(1)	73462(42)	66413(35)	64650(113)	271(19)
N(2)	31051(42)	68205(34)	88531(110)	256(19)
C(1)	70117(48)	55350(39)	80487(140)	266(21)
C(2)	77485(48)	60632(41)	77116(135)	270(22)
C(3)	80210(49)	63394(43)	98212(139)	282(24)
C(4)	32946(51)	56458(39)	76093(134)	286(23)
C(5)	26396(48)	62443(42)	78214(138)	273(22)
C(6)	23668(55)	64874(47)	56885(138)	310(25)
O(9)	54798(42)	43728(33)	96521(127)	476(23)
O(10)	43308(48)	41043(38)	63453(166)	680(30)
O(11)	91400(40)	46927(38)	86654(123)	508(23)
O(12)	11409(38)	48025(37)	73976(127)	559(25)
O(13)	821(56)	69272(43)	75057(111)	726(30)
NA(1)	50706(26)	55692(25)	104722(75)	607(16)
NA(2)	787(28)	57334(24)	81423(88)	638(16)

Table 3. *Fractional atomic coordinates* ($\times 10^4$) *and isotropic B values* ($\times 10$) *for all atoms determined by neutron diffraction at* 50 K

	x	y	z	B (Å^2)
MO(1)	6136(2)	6934(2)	8117(7)	5(1)
MO(2)	4441(2)	6988(2)	7209(7)	5(1)
S(1)	7062(6)	6679(4)	11263(16)	3(2)
S(2)	3413(6)	6738(5)	4238(16)	5(2)
O(1)	5475(3)	6715(2)	5570(7)	5(1)
O(2)	5070(3)	6839(2)	9876(8)	5(1)
O(3)	6412(3)	7784(2)	7974(9)	6(1)
O(4)	4324(3)	7858(2)	6996(9)	7(1)
O(5)	7222(3)	4900(2)	8606(8)	7(1)
O(6)	6234(3)	5760(2)	8068(8)	4(1)
O(7)	4146(3)	5823(2)	7685(8)	7(1)
O(8)	3003(3)	5066(2)	7458(8)	9(1)
N(1)	7411(2)	6612(1)	6566(5)	5(1)
N(2)	3142(2)	6845(2)	8902(5)	6(1)
C(1)	7035(3)	5506(2)	8161(6)	3(1)
C(2)	7793(3)	6036(2)	7830(7)	5(1)
C(3)	8053(3)	6324(2)	9940(7)	6(1)
C(4)	3309(3)	5663(2)	7703(7)	5(1)
C(5)	2648(3)	6273(2)	7899(7)	4(1)
C(6)	2389(3)	6502(2)	5687(7)	6(1)
O(9)	5449(4)	4406(2)	9810(9)	7(1)
O(10)	4297(4)	4106(3)	6578(8)	11(1)
O(11)	9164(3)	4690(3)	8725(9)	7(1)
O(12)	1171(3)	4817(3)	7538(8)	9(1)
O(13)	50(3)	6897(3)	7479(10)	11(1)
NA(1)	5101(5)	5594(4)	10561(13)	11(2)
NA(2)	93(6)	5711(4)	8344(13)	12(2)
H(1)	7291(6)	6461(4)	5039(15)	18(2)
H(2)	7849(6)	7017(4)	6509(15)	19(2)
H(3)	8363(6)	5794(4)	7054(14)	14(2)
H(4)	8327(6)	5908(4)	10917(15)	20(2)
H(5)	8572(6)	6726(4)	9759(14)	18(2)
H(6)	3244(6)	6749(4)	10451(15)	18(2)
H(7)	2738(6)	7291(4)	8823(14)	16(2)
H(8)	2046(6)	6116(4)	8773(14)	17(2)
H(9)	1929(5)	6940(4)	5793(13)	16(2)
H(10)	2057(7)	6082(5)	4874(15)	22(2)
H(11)	6019(7)	4521(5)	9270(15)	20(2)
H(12)	5071(7)	4251(5)	8685(17)	26(2)
H(13)	3826(6)	4452(5)	6874(15)	22(2)
H(14)	4055(6)	3658(5)	6827(16)	22(2)
H(15)	9299(7)	4348(5)	9690(18)	29(2)
H(16)	8524(6)	4691(4)	8580(15)	19(2)
H(17)	1208(6)	4399(5)	8380(17)	26(2)
H(18)	1788(6)	4928(4)	7343(13)	15(2)
H(19)	-105(7)	6977(5)	6174(21)	33(2)
H(20)	99(6)	7326(5)	8166(16)	25(2)

tion data obtained from the sample at 50 K we were able to locate the H atoms and refine the coordinates of all atoms to yield the positions shown in Table 3.* Because of the very small size of the neutron crystal used it was not possible to obtain an extensive high-precision data set which would justify an anisotropic model for thermal motion. However, because of the low temperature the thermal motions are substantially smaller and more isotropic than at room temperature and we believe that no serious inadequacy of our model is imposed by this.

Discussion. There is no phase transition between 295 and 50 K, but the cell parameters undergo a slight and normal contraction. Because of the greater overall precision of the results from the neutron diffraction experiment these are used as the basis for discussion. The bond lengths, which are shown with the atomic nomenclature for the non-H atoms in Fig. 1, deviate slightly from those determined by Knox & Prout (1969). Atomic distances in the two halves of the molecule agree well except for the bonds Mo(1)—O(6) and Mo(2)—O(7) which differ in both our X-ray and neutron diffraction determinations; this may be due to the different patterns of C—O bonds adopted by the two carboxyl groups. In both our neutron and X-ray analyses the two Mo—N distances are equivalent, 2·223 (5) and 2·226 (5) Å (neutron), and 2·217 (7) and 2·221 (6) Å (X-ray), contrary to the result of Knox & Prout (1969) who obtained 2·26 (2) and 2·20 (2) Å.

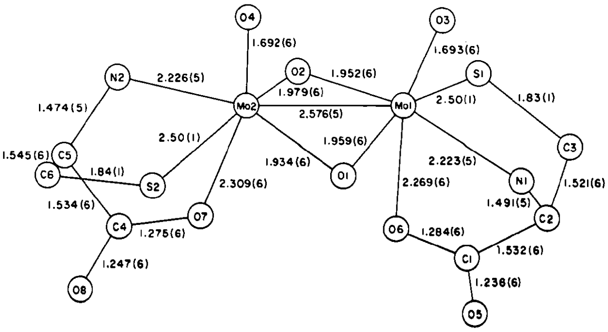

Fig. 1. Atomic nomenclature (following Knox & Prout, 1969) and bond distances (Å) for the non-hydrogen atoms from the neutron diffraction experiment at 50 K. This figure is based on a computer-produced drawing (McCandlish, Andrews & Bernstein, 1976).

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* Lists of the anisotropic temperature factors (X-ray case) and observed and calculated structure factors for both X-ray and neutron experiments have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36167 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The bond lengths within each cysteine ligand agree quite well with those of free L-cysteine (Kerr, Ashmore & Koetzle, 1975), except for the S—C and O—C bonds which are lengthened about 0·03 Å in comparison with those of free L-cysteine. The interior angles of the chelating rings decrease about 2–4° in comparison with the corresponding angles of free cysteine and approach the tetrahedral value.

All H positions were determined and the geometry of their linkages is given in Table 4. Four water molecules hydrogen bond with the main molecule, but both H atoms of the water oxygen atoms O(9) and O(10) form hydrogen bonds. These are presumed to be the more stable waters of hydration which remain in the material when it is heated to 393 K (Huang & Haight, 1970) or held under vacuum (Liu, 1981). Good internal agreement and accord with published values from other neutron diffraction studies (Ferraris & Franchini-Angela, 1972) indicate that the hydrogen bonds of this structure fall within the normal range. Only one sodium ion, Na(1), binds directly to the binuclear complex, see Fig. 2. This metal ion is octahedrally coordinated by three O atoms of the complex and three water molecules. These waters in turn coordinate to Na(2) in a square-pyramidal array and thereby link the complex ions together.

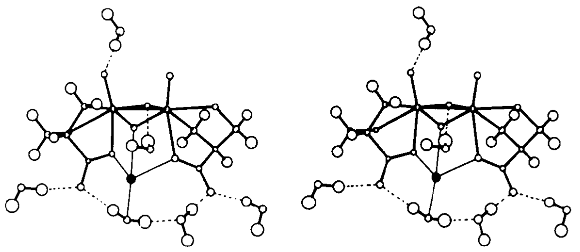

Fig. 2. A stereodrawing (Johnson, 1976) showing the molecular complex together with the single Na^+ ion (black) and the water molecules linked directly to it.

Table 4. *Geometry for the hydrogen atoms from the neutron diffraction experiment at* 50 K

Estimated standard deviations for the distances and angles average 0·01 Å and 0·08° respectively.

DISTANCES		ANGLES		TORSION ANGLES	
AMINO					
N(1)-H(1)	1.04	H(1)-N(1)-H(2)	106.8	H(1)-N(1)-C(2)-H(3)	49.7
N(1)-H(2)	1.02			H(2)-N(1)-C(2)-H(3)	-69.3
N(2)-H(6)	1.03	H(6)-N(2)-H(7)	106.2	H(6)-N(2)-C(5)-H(8)	48.4
N(2)-H(7)	1.05			H(7)-N(2)-C(5)-H(8)	-67.8
METHINE				H(3)-C(2)-C(3)-H(4)	-57.9
C(2)-H(3)	1.09			H(3)-C(2)-C(3)-H(5)	61.5
C(5)-H(8)	1.10			H(8)-C(5)-C(6)-H(9)	60.2
METHYLENE				H(8)-C(5)-C(6)-H(10)	-59.4
C(3)-H(4)	1.10	H(4)-C(3)-H(5)	108.6		
C(3)-H(5)	1.10			HYDROGEN BONDS	
C(6)-H(9)	1.09	H(9)-C(6)-H(10)	109.2	O(3) ..H(14)	1.86
C(6)-H(10)	1.08			O(5) ..H(11)	1.97
WATER				O(5) ..H(16)	1.97
O(9) -H(11)	.94	H(11)-O(9) -H(12)	108.2	O(8) ..H(13)	1.74
O(9) -H(12)	.97			O(8) ..H(18)	1.82
O(10)-H(13)	.98	H(13)-O(10)-H(14)	108.6	O(10)..H(12)	1.80
O(10)-H(14)	.95			O(9) -H(11)..O(5)	168.2
O(11)-H(15)	.93	H(15)-O(11)-H(16)	106.3	O(9) -H(12)..O(10)	170.5
O(11)-H(16)	.95			O(10)-H(13)..O(8)	178.6
O(12)-H(17)	.98	H(17)-O(12)-H(18)	102.0	O(10)-H(14)..O(3)	175.9
O(12)-H(18)	.94			O(11)-H(16)..O(5)	166.7
O(13)-H(19)	.89	H(19)-O(13)-H(20)	108.3	O(13)-H(20)..O(8)	168.9
O(13)-H(20)	.94				

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References

BERMAN, H. M., BERNSTEIN, F. C., BERNSTEIN, H. J., KOETZLE, T. F. & WILLIAMS, G. J. B. (1976). *CRYSNET Manual.* Informal Report BNL 21714. Brookhaven National Laboratory, New York.

CORBIN, J. L., PARIYADATH, N. & STIEFEL, E. I. (1976). *J. Am. Chem. Soc.* **98**, 7862–7864.

CRAMER, S. P. (1978). NATO Advanced Study Institute Conference. *Synchrotron Radiation Applied to Biophysical and Biochemical Research*, Frascati, Italy, edited by A. CASTELLANI & I. F. QUERCIA. New York, London: Plenum.

DOYLE, P. A. & TURNER, P. S. (1968). *Acta Cryst.* A**24**, 390–397.

FERRARIS, G. & FRANCHINI-ANGELA, M. (1972). *Acta Cryst.* B**28**, 3572–3583.

HUANG, J. T. & HAIGHT, G. P. JR (1970). *J. Am. Chem. Soc.* **92**, 2336–2342.

International Tables for X-ray Crystallography (1968). Vol. III, 2nd ed., Table 3.2.5. Birmingham: Kynoch Press.

International Tables for X-ray Crystallography (1974). Vol. IV, Table 2.1C. Birmingham: Kynoch Press.

JOHNSON, C. K. (1976). *ORTEP* II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.

KAY, A. & MITCHELL, P. C. H. (1970). *J. Chem. Soc. A*, pp. 2421–2428.

KERR, K. A., ASHMORE, J. P. & KOETZLE, T. F. (1975). *Acta Cryst.* B**31**, 2022–2026.

KNOX, J. R. & PROUT, C. K. (1969). *Acta Cryst.* B**25**, 1857–1866.

LIU, H. (1981). To be published.

MCCANDLISH, L., ANDREWS, L. & BERNSTEIN, H. (1976). Program *PRJCTN*, described in Berman *et al.* (1976).

SHULL, C. G. (1972). Personal communication.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

WENTWORTH, R. A. D. (1976). *Coord. Chem. Rev.* **18**, 1–27.