

The Structure of a Cysteine Complex of Molybdenum(V): Na₂Mo₂O₄[SCH₂CH(NH₂)CO₂]₂·5H₂O

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(Received 4 October 1968)

Na₂Mo₂O₄[SCH₂CH(NH₂)CO₂]₂·5H₂O crystallizes in space group $P2_12_12_1$ with $a=14.83$, $b=19.45$, $c=6.48$ Å; $Z=4$. The structure was refined by the method of least squares to $R=0.062$ 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 Na₂Mo₂O₄(cysteine)₂(H₂O)₂·3H₂O 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, 1968a).

Experimental

Orange air-stable crystals were prepared and supplied by P. C. H. Mitchell of Reading University. The crystal data are: Na₂Mo₂O₄[SCH₂CH(NH₂)CO₂]₂·5H₂O; $M=630$, $F(000)=1240$, orthorhombic, $a=14.83 \pm 0.01$, $b=19.45 \pm 0.01$, $c=6.48 \pm 0.01$ Å. $D_m=2.201$ g.cm⁻³ (by flotation), $z=4$, $D_c=2.238$ g.cm⁻³, Mo $K\alpha$ radiation, $\lambda=0.7107$ 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 $0.08 \times 0.16 \times 0.44$ 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 hkl ($1 \leq 8$) 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.

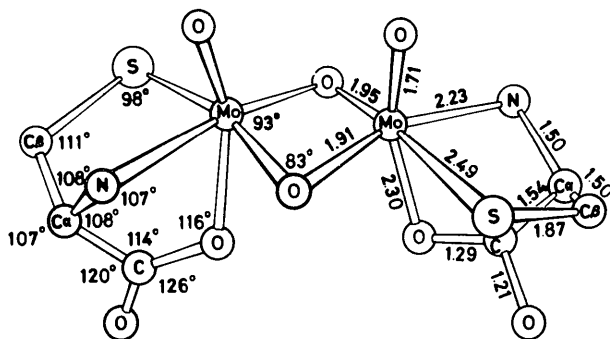


Fig. 1. The di- μ -oxobis{oxo[cysteinatomolybdenum(V)]} anion. Distances and angles are average values from both halves of the anion.

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* 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 refinement 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.

0	144	184	-90	1	540	513	185	0	252	241	90	1	2	179	169	-3	3	114	119	107		
1	138	166	-90	2	543	513	-139	1	2	410	0	4	-90	3	141	103	103	2	144	149	-147	
2	114	184	90	3	322	313	-31	2	2	330	1	317	-19	4	125	126	0	3	274	289	168	
3	140	166	-90	4	234	234	0	3	2	192	210	-135	0	5	178	187	-113	4	240	243	80	
4	158	158	-90	5	99	120	168	4	6	2	288	2	300	88	6	280	297	-104	5	239	231	-15
5				6	157	165	-73	5	8	2	287	295	96	7	130	130	0	6	290	317	-135	
6				7				6	8	2	128	163	-176	8	142	142	0	7	134	147	-147	
7				8				7	8	3	128	163	-176	9	142	142	0	8	130	130	44	
8				9				8	8	3	128	163	-176	10	142	142	0	9	130	130	-134	
9				10				9	8	3	128	163	-176	11	142	142	0	10	130	130	-134	
10				11				10	8	3	128	163	-176	12	142	142	0	11	130	130	-134	
11				12				11	8	3	128	163	-176	13	142	142	0	12	130	130	-134	
12				13				12	8	3	128	163	-176	14	142	142	0	13	130	130	-134	
13				14				13	8	3	128	163	-176	15	142	142	0	14	130	130	-134	
14				15				14	8	3	128	163	-176	16	142	142	0	15	130	130	-134	
15				16				15	8	3	128	163	-176	17	142	142	0	16	130	130	-134	
16				17				16	8	3	128	163	-176	18	142	142	0	17	130	130	-134	
17				18				17	8	3	128	163	-176	19	142	142	0	18	130	130	-134	
18				19				18	8	3	128	163	-176	20	142	142	0	19	130	130	-134	
19				20				19	8	3	128	163	-176	21	142	142	0	20	130	130	-134	
20				21				20	8	3	128	163	-176	22	142	142	0	21	130	130	-134	
21				22				21	8	3	128	163	-176	23	142	142	0	22	130	130	-134	
22				23				22	8	3	128	163	-176	24	142	142	0	23	130	130	-134	
23				24				23	8	3	128	163	-176	25	142	142	0	24	130	130	-134	
24				25				24	8	3	128	163	-176	26	142	142	0	25	130	130	-134	
25				26				25	8	3	128	163	-176	27	142	142	0	26	130	130	-134	
26				27				26	8	3	128	163	-176	28	142	142	0	27	130	130	-134	
27				28				27	8	3	128	163	-176	29	142	142	0	28	130	130	-134	
28				29				28	8	3	128	163	-176	30	142	142	0	29	130	130	-134	
29				30				29	8	3	128	163	-176	31	142	142	0	30	130	130	-134	
30				31				30	8	3	128	163	-176	32	142	142	0	31	130	130	-134	
31				32				31	8	3	128	163	-176	33	142	142	0	32	130	130	-134	
32				33				32	8	3	128	163	-176	34	142	142	0	33	130	130	-134	
33				34				33	8	3	128	163	-176	35	142	142	0	34	130	130	-134	
34				35				34	8	3	128	163	-176	36	142	142	0	35	130	130	-134	
35				36				35	8	3	128	163	-176	37	142	142	0	36	130	130	-134	
36				37				36	8	3	128	163	-176	38	142	142	0	37	130	130	-134	
37				38				37	8	3	128	163	-176	39	142	142	0	38	130	130	-134	
38				39				38	8	3	128	163	-176	40	142	142	0	39	130	130	-134	
39				40				39	8	3	128	163	-176	41	142	142	0	40	130	130	-134	
40				41				40	8	3	128	163	-176	42	142	142	0	41	130	130	-134	
41				42				41	8	3	128	163	-176	43	142	142	0	42	130	130	-134	
42				43				42	8	3	128	163	-176	44	142	142	0	43	130	130	-134	
43				44				43	8	3	128	163	-176	45	142	142	0	44	130	130	-134	
44				45				44	8	3	128	163	-176	46	142	142	0	45	130	130	-134	
45				46				45	8	3	128	163	-176	47	142	142	0	46	130	130	-134	
46				47				46	8	3	128	163	-176	48	142	142	0	47	130	130	-134	
47				48				47	8	3	128	163	-176	49	142	142	0	48	130	130	-134	
48				49				48	8	3	128	163	-176	50	142	142	0	49	130	130	-134	
49				50				49	8	3	128	163	-176	51	142	142	0	50	130	130	-134	
50				51				50	8	3	128	163	-176	52	142	142	0	51	130	130	-134	
51				52				51	8	3	128	163	-176	53	142	142	0	52	130	130	-134	
52				53				52	8	3	128	163	-176	54	142	142	0	53	130	130	-134	
53				54				53	8	3	128	163	-176	55	142	142	0	54	130	130	-134	
54				55				54	8	3	128	163	-176	56	142	142	0	55	130	130	-134	
55				56				55	8	3	128	163	-176	57	142	142	0	56	130	130	-134	
56				57				56	8	3	128	163	-176	58	142	142	0	57	130	130	-134	
57				58				57	8	3	128	163	-176	59	142	142	0	58	130	130	-134	
58				59				58	8	3	128	163	-176	60	142	142	0	59	130	130	-134	
59				60				59	8	3	128	163	-176	61	142	142	0	60	130	130	-134	
60				61				60	8	3	128	163	-176	62	142	142	0	61	130	130	-134	
61				62				61	8	3	128	163	-176	63	142	142	0	62	130	130	-134	
62				63				62	8	3	128	163	-176	64	142	142	0	63	130	130	-134	
63				64				63	8	3	128	163	-176	65	142	142	0	64	130	130	-134	
64				65				64	8	3	128	163	-176	66	142	142	0	65	130	130	-134	
65				66				65	8	3	128	163	-176	67	142	142	0	66	130	130	-134	
66				67				66	8	3	128	163	-176	68	142	142	0	67	130	130	-134	
67				68				67	8	3	128	163	-176	69	142	142	0	68	130	130	-134	
68				69				68	8	3	128	163	-176	70	142	142	0	69	130	130	-134	
69				70				69	8	3	128	163	-176	71	142	142	0	70	130	130	-134	
70				71				70	8	3	128	163	-176	72	142	142	0	71	130	130	-134	
71				72				71	8	3	128	163	-176	73	142	142	0	72	130	130	-134	
72				73				72	8	3	128	163	-176	74	142	142	0	73	130	130	-134	
73				74				73	8	3	128	163	-176	75	142	142	0	74	130	130	-134	
74				75				74	8	3	128	163	-176	76	142	142	0	75	130	130	-134	
75				76				75	8	3	128	163	-176	77	142	142	0	76	130	130	-134	
76				77				76	8	3	128	163	-176	78	142	142	0	77	130	130	-134	
77				78				77	8	3	128	163	-176	79	142	142	0	78	130	130	-134</	

Table 1 (cont.)

1	176	105	90	0	222	295	0	5	150	5	119	-55	0	5	302 ²⁴	325	-90	6	172	164	-169		
0	1	176	105	90	0	222	295	0	5	150	5	119	-55	0	5	302 ²⁴	325	-90	6	172	164	-169	
2	312	210	180	0	1	373	366	-132	0	1	456	434	94	0	0	260 ²⁵	250	-90	6	208	219	14	
3	438	315	-90	0	2	555	368	-106	0	2	154	145	8	0	0	0	0	0	0	6	252	263	20
4	564	420	-90	0	3	737	470	-132	0	3	343	34	-107	0	0	0	0	0	0	6	300	311	16
5	690	525	-90	0	4	919	572	-158	0	4	532	53	-132	0	0	0	0	0	0	6	348	359	32
6	816	630	-90	0	5	1101	674	-184	0	5	722	73	-158	0	0	0	0	0	0	6	396	407	58
7	942	735	-90	0	6	1283	776	-210	0	6	912	92	-184	0	0	0	0	0	0	6	444	455	84
8	1068	840	-90	0	7	1465	878	-236	0	7	1102	111	-210	0	0	0	0	0	0	6	492	503	110
9	1194	945	-90	0	8	1647	980	-262	0	8	1292	130	-236	0	0	0	0	0	0	6	540	551	136
10	1320	1050	-90	0	9	1829	1082	-288	0	9	1482	149	-262	0	0	0	0	0	0	6	588	599	162
11	1446	1155	-90	0	10	2011	1184	-314	0	10	1672	168	-288	0	0	0	0	0	0	6	636	647	188
12	1572	1260	-90	0	11	2193	1286	-340	0	11	1862	187	-314	0	0	0	0	0	0	6	684	695	214
13	1698	1365	-90	0	12	2375	1388	-366	0	12	2052	206	-340	0	0	0	0	0	0	6	732	743	240
14	1824	1470	-90	0	13	2557	1490	-392	0	13	2242	225	-366	0	0	0	0	0	0	6	780	791	266
15	1950	1575	-90	0	14	2739	1592	-418	0	14	2432	244	-392	0	0	0	0	0	0	6	828	839	292
16	2076	1680	-90	0	15	2921	1694	-444	0	15	2622	263	-418	0	0	0	0	0	0	6	876	887	318
17	2202	1785	-90	0	16	3103	1796	-470	0	16	2812	282	-444	0	0	0	0	0	0	6	924	935	344
18	2328	1890	-90	0	17	3285	1898	-496	0	17	3002	301	-470	0	0	0	0	0	0	6	972	983	370
19	2454	1995	-90	0	18	3467	2000	-522	0	18	3192	320	-496	0	0	0	0	0	0	6	1020	1031	396
20	2580	2100	-90	0	19	3649	2102	-548	0	19	3382	339	-522	0	0	0	0	0	0	6	1068	1079	422
21	2706	2205	-90	0	20	3831	2204	-574	0	20	3572	356	-548	0	0	0	0	0	0	6	1116	1127	448
22	2832	2310	-90	0	21	4013	2306	-600	0	21	3762	375	-574	0	0	0	0	0	0	6	1164	1175	474
23	2958	2415	-90	0	22	4195	2408	-626	0	22	3952	394	-600	0	0	0	0	0	0	6	1212	1223	500
24	3084	2520	-90	0	23	4377	2510	-652	0	23	4142	413	-626	0	0	0	0	0	0	6	1260	1271	526
25	3210	2625	-90	0	24	4559	2612	-678	0	24	4332	434	-652	0	0	0	0	0	0	6	1308	1319	552
26	3336	2730	-90	0	25	4741	2714	-704	0	25	4522	453	-678	0	0	0	0	0	0	6	1356	1367	578
27	3462	2835	-90	0	26	4923	2816	-730	0	26	4712	472	-704	0	0	0	0	0	0	6	1404	1415	604
28	3588	2940	-90	0	27	5105	2918	-756	0	27	4902	491	-730	0	0	0	0	0	0	6	1452	1463	630
29	3714	3045	-90	0	28	5287	3020	-782	0	28	5092	510	-756	0	0	0	0	0	0	6	1500	1511	656
30	3840	3150	-90	0	29	5469	3122	-808	0	29	5282	529	-782	0	0	0	0	0	0	6	1548	1559	682
31	3966	3255	-90	0	30	5651	3224	-834	0	30	5472	548	-808	0	0	0	0	0	0	6	1596	1607	708
32	4092	3360	-90	0	31	5833	3326	-860	0	31	5662	567	-834	0	0	0	0	0	0	6	1644	1655	734
33	4218	3465	-90	0	32	6015	3428	-886	0	32	5852	586	-860	0	0	0	0	0	0	6	1692	1703	760
34	4344	3570	-90	0	33	6197	3530	-912	0	33	6042	605	-886	0	0	0	0	0	0	6	1740	1751	786
35	4470	3675	-90	0	34	6379	3632	-938	0	34	6232	624	-912	0	0	0	0	0	0	6	1788	1799	812
36	4596	3780	-90	0	35	6561	3734	-964	0	35	6422	643	-938	0	0	0	0	0	0	6	1836	1847	838
37	4722	3885	-90	0	36	6743	3836	-990	0	36	6612	662	-964	0	0	0	0	0	0	6	1884	1895	864
38	4848	3990	-90	0	37	6925	3938	-1016	0	37	6802	681	-990	0	0	0	0	0	0	6	1932	1943	890
39	4974	4095	-90	0	38	7107	4040	-1042	0	38	6992	700	-1016	0	0	0	0	0	0	6	1980	1991	916
40	5100	4200	-90	0	39	7289	4142	-1068	0	39	7182	719	-1042	0	0	0	0	0	0	6	2028	2039	942
41	5226	4305	-90	0	40	7471	4244	-1094	0	40	7372	738	-1068	0	0	0	0	0	0	6	2076	2087	968
42	5352	4410	-90	0	41	7653	4346	-1120	0	41	7562	757	-1094	0	0	0	0	0	0	6	2124	2135	994
43	5478	4515	-90	0	42	7835	4448	-1146	0	42	7752	776	-1120	0	0	0	0	0	0	6	2172	2183	1020
44	5604	4620	-90	0	43	8017	4550	-1172	0	43	7942	795	-1146	0	0	0	0	0	0	6	2220	2231	1046
45	5730	4725	-90	0	44	8199	4652	-1198	0	44	8132	814	-1172	0	0	0	0	0	0	6	2268	2279	1072
46	5856	4830	-90	0	45	8381	4754	-1224	0	45	8322	833	-1198	0	0	0	0	0	0	6	2316	2327	1098
47	5982	4935	-90	0	46	8563	4856	-1250	0	46	8512	852	-1224	0	0	0	0	0	0	6	2364	2375	1124
48	6108	5040	-90	0	47	8745	4958	-1276	0	47	8702	871	-1250	0	0	0	0	0	0	6	2412	2423	1150
49	6234	5145	-90	0	48	8927	5060	-1302	0	48	8892	890	-1276	0	0	0	0	0	0	6	2460	2471	1176
50	6360	5250	-90	0	49	9109	5162	-1328	0	49	9082	909	-1302	0	0	0	0	0	0	6	2508	2519	1202
51	6486	5355	-90	0	50	9291	5264	-1354	0	50	9272	928	-1328	0	0	0	0	0	0	6	2556	2567	1228
52	6612	5460	-90	0	51	9473	5366	-1380	0	51	9462	947	-1354	0	0	0	0	0	0	6	2604	2615	1254
53	6738	5565	-90	0	52	9655	5468	-1406	0	52	9652	966	-1380	0	0	0	0	0	0	6	2652	2663	1280
54	6864	5670	-90	0	53	9837	5570	-1432	0	53	9842	985	-1406	0	0	0	0	0	0	6	2700	2711	1306
55	6990	5775	-90	0	54	10019	5672	-1458	0	54	10032	1004	-1432	0	0	0	0	0	0	6	2748	2759	1332
56	7116	5880	-90	0	55	10201	5774	-1484	0	55	10222	1023	-1458	0	0	0	0	0	0	6	2796	2807	1358
57	7242	5985	-90	0	56	10383	5876	-1510	0	56	10412	1042	-1484	0	0	0	0	0	0	6	2844	2855	1384
58	7368	6090	-90	0	57	10565	5978	-1536	0	57	10602	1061	-1510	0	0	0	0	0	0	6	2892	2903	1410
59	7494	6195	-90	0	58	10747	6080	-1562	0	58	10792	1080	-1536	0	0	0	0	0	0	6	2940	2951	1436
60	7620	6300	-90	0	59	10929	6182	-1588	0	59	10982	1099	-1562	0	0	0	0	0	0	6	2988	2999	1462
61	7746	6405	-90	0	60	11111	6284	-1614	0	60	11172	1118	-1588	0	0	0	0	0	0	6	3036	3047	1488
62	7872	6510	-90	0	61	11293	6386	-1640	0	61	11362	1137	-1614	0	0	0	0	0	0	6	3084	3095	1514
63	8000	6615	-90	0	62	11475	6488	-1666	0	62	11552	1156	-1640	0	0	0	0	0	0	6	3132	3143	1540
64	8126	6720	-90	0	63	11657	6590	-1692	0	63	11742	1175	-1666	0	0	0	0	0	0	6	3180	3191	1566
65	8252	6825	-90	0	64	11839	6692	-1718	0	64	11932	1194	-1692	0	0	0	0	0	0	6	3228	3239	1592
66	8																						

Table 1 (cont.)

7	663	9	638	86	8	270	265	82	9	1	390	47	10	1	811	0	11	1	416	90
2	205	1	201	-159	2	252	252	163	2	271	278	-6	0	661	644	-124	0	604	86	
3	313	314	-101	3	216	222	-120	1	176	185	176	0	2	299	291	159	2	216	268	
4	171	162	-11	4	330	331	96	2	617	601	159	0	4	44	281	-61	4	602	261	
5	226	226	-179	5	193	187	96	3	159	148	1	0	6	281	291	-87	5	179	147	
6	169	151	113	6	240	230	-2	4	473	482	-6	0	7	293	302	-87	6	162	175	
7	496	502	-84	7	212	212	04	5	119	125	177	0	8	246	238	97	7	198	-90	
8	417	231	35	8	396	389	-176	6	182	177	-55	0	9	171	146	0	8	217	216	
9	324	311	114	9	332	332	-104	7	209	197	-86	0	10	200	178	0	9	160	141	
0	166	166	-11	0	184	184	96	8	138	138	-123	0	11	141	144	158	0	153	-54	
1	253	250	-27	1	240	240	-2	9	418	412	-164	0	12	198	158	1	1	897	868	
2	526	545	-90	2	216	204	-180	0	418	412	-164	0	13	169	171	-32	2	356	350	
3	496	502	-84	3	212	212	04	1	274	260	-180	0	14	141	144	158	3	256	268	
4	417	231	35	4	396	389	-176	2	266	342	-5	0	15	141	144	158	4	319	314	
5	324	311	114	5	332	332	-104	3	304	313	-174	0	16	198	158	1	5	319	314	
6	166	166	-11	6	184	184	96	4	304	313	-174	0	17	169	171	-32	6	189	192	
7	496	502	-84	7	212	212	04	5	201	227	-171	0	18	169	171	-32	7	161	121	
8	417	231	35	8	396	389	-176	6	182	177	-55	0	19	169	171	-32	8	145	153	
9	324	311	114	9	332	332	-104	7	209	197	-86	0	20	161	134	-56	9	173	135	
0	166	166	-11	0	184	184	96	8	138	138	-123	0	21	141	144	158	0	163	140	
1	253	250	-27	1	240	240	-2	9	418	412	-164	0	22	141	144	158	1	622	636	
2	526	545	-90	2	216	204	-180	0	418	412	-164	0	23	157	172	173	2	367	364	
3	496	502	-84	3	212	212	04	1	274	260	-180	0	24	157	172	173	3	226	199	
4	417	231	35	4	396	389	-176	2	266	342	-5	0	25	157	172	173	4	171	151	
5	324	311	114	5	332	332	-104	3	304	313	-174	0	26	157	172	173	5	155	136	
6	166	166	-11	6	184	184	96	4	304	313	-174	0	27	157	172	173	6	140	140	
7	496	502	-84	7	212	212	04	5	201	227	-171	0	28	157	172	173	7	164	111	
8	417	231	35	8	396	389	-176	6	182	177	-55	0	29	157	172	173	8	442	438	
9	324	311	114	9	332	332	-104	7	209	197	-86	0	30	157	172	173	9	347	347	
0	166	166	-11	0	184	184	96	8	138	138	-123	0	31	157	172	173	0	469	477	
1	253	250	-27	1	240	240	-2	9	418	412	-164	0	32	157	172	173	1	441	-71	
2	526	545	-90	2	216	204	-180	0	418	412	-164	0	33	157	172	173	2	222	239	
3	496	502	-84	3	212	212	04	1	274	260	-180	0	34	157	172	173	3	164	174	
4	417	231	35	4	396	389	-176	2	266	342	-5	0	35	157	172	173	4	197	188	
5	324	311	114	5	332	332	-104	3	304	313	-174	0	36	157	172	173	5	203	188	
6	166	166	-11	6	184	184	96	4	304	313	-174	0	37	157	172	173	6	195	158	
7	496	502	-84	7	212	212	04	5	201	227	-171	0	38	157	172	173	7	195	158	
8	417	231	35	8	396	389	-176	6	182	177	-55	0	39	157	172	173	8	195	158	
9	324	311	114	9	332	332	-104	7	209	197	-86	0	40	157	172	173	9	195	158	
0	166	166	-11	0	184	184	96	8	138	138	-123	0	41	157	172	173	0	195	158	
1	253	250	-27	1	240	240	-2	9	418	412	-164	0	42	157	172	173	1	195	158	
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3	496	502	-84	3	212	212	04	1	274	260	-180	0	44	157	172	173	3	195	158	
4	417	231	35	4	396	389	-176	2	266	342	-5	0	45	157	172	173	4	195	158	
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6	166	166	-11	6	184	184	96	4	304	313	-174	0	47	157	172	173	6	195	158	
7	496	502	-84	7	212	212	04	5	201	227	-171	0	48	157	172	173	7	195	158	
8	417	231	35	8	396	389	-176	6	182	177	-55	0	49	157	172	173	8	195	158	
9	324	311	114	9	332	332	-104	7	209	197	-86	0	50	157	172	173	9	195	158	
0	166	166	-11	0	184	184	96	8	138	138	-123	0	51	157	172	173	0	195	158	
1	253	250	-27	1	240	240	-2	9	418	412	-164	0	52	157	172	173	1	195	158	
2	526	545	-90	2	216	204	-180	0	418	412	-164	0	53	157	172	173	2	195	158	
3	496	502	-84	3	212	212	04	1	274	260	-180	0	54	157	172	173	3	195	158	
4	417	231	35	4	396	389	-176	2	266	342	-5	0	55	157	172	173	4	195	158	
5	324	311	114	5	332	332	-104	3	304	313	-174	0	56	157	172	173	5	195	158	
6	166	166	-11	6	184	184	96	4	304	313	-174	0	57	157	172	173	6	195	158	
7	496	502	-84	7	212	212	04	5	201	227	-171	0	58	157	172	173	7	195	158	
8	417	231	35	8	396	389	-176	6	182	177	-55	0	59	157	172	173	8	195	158	
9	324	311	114	9	332	332	-104	7	209	197	-86	0	60	157	172	173	9	195	158	
0	166	166	-11	0	184	184	96	8	138	138	-123	0	61	157	172	173	0	195	158	
1	253	250	-27	1	240	240	-2	9	418	412	-164	0	62	157	172	173	1	195	158	
2	526	545	-90	2	216	204	-180	0	418	412	-164	0	63	157	172	173	2	195	158	
3	496	502	-84	3	212	212	04	1	274	260	-180	0	64	157	172	173	3	195	158	
4	417	231	35	4	396	389	-176	2	266	342	-5	0	65	157	172	173	4	195	158	
5	324	311	114	5	332	332	-104	3	304	313	-174	0	66	157	172	173	5	195	158	
6	166	166	-11	6	184	184	96	4	304	313	-174	0	67	157	172	173	6	195	158	
7	496	502	-84	7	212	212	04	5	201	227	-171	0	68	157	172	173	7	195	158	
8	417	231	35	8	396	389	-176	6	182	177	-55	0	69	157	172	173	8	195	158	
9	324	311	114	9	332	332	-104	7	209	197	-86	0	70	157	172	173	9	195	158	
0	166	166	-11	0	184	184	96	8	138	138	-123	0	71	157	172	173	0	195	158	
1	253	250	-27	1	240	240	-2	9	418	412	-164	0	72	157	172	173	1	195	158	
2	526	545	-90	2	216	204	-180	0	418	412	-164	0	73	157	172	173	2	195	158	
3	496	502	-84	3	212	212	04	1	274	260	-180	0	74	157	172	173	3	195	158	
4	417	231	35	4	396	389	-176	2	266	342	-5	0	75	157	172	173	4	195	158	
5	324	311	114	5	332	332	-104	3	304	313	-174	0	76	157	172	173	5	195	158	
6	166	166	-11	6	184	184	96	4	304	313	-174	0	77	157	172	173	6	195	158	
7	496	502	-84	7	212	212	04	5	201	227	-171	0	78	157	172	173	7	195	158	
8	417	231	35	8	396	389	-176	6	182	177	-55	0	79	157	172	173	8	195	158	
9	324	311	114	9	332	332	-104	7	209	197	-86	0	80	157	172	173	9	195	158	
0	166	166	-11	0	184	184	96	8	138	138	-123	0	81	157	172	173	0	195	158	
1	253	250	-27	1	240	240	-2	9	418	412	-164									

Table 1 (cont.)

12 145 6 144 25	13 360 7 354 -90	14 199 9 178 16	16 221 4 210 -170	17 194 ¹² 193 -90
1 498 7 517 0	1 4:1 440 -78	3 339 351 62	1 199 200 112	0 17 210 ¹³ 200 90
0 548 526 11	2 21: 225 168	1 197 244 0	1 312 5 303 6	0 17 210 ¹⁴ 282 90
1 501 306 177	3 192 207 -139	1 228 220 132	2 171 162 -104	0 18 0 376 0 386 0
4 144 124 9	4 285 299 -18	2 224 221 -138	3 221 242 -100	0 221 1 237 -180
0 668 9 67 -180	1 19: 8 203 92	3 221 242 -100	1 188 6 198 -0	0 230 271 -180
1 522 481 -11	0 200 191 90	0 166 13 202 -180	2 175 7 177 17	1 246 232 -180
2 499 238 -175	1 174 415 -76	1 196 122 -33	0 201 8 181 -180	0 18 194 160 0
4 259 278 -152	2 171 192 -16	2 183 204 -94	1 217 9 201 -174	1 246 232 -180
0 479 478 0	3 268 247 125	0 184 17 141 0	2 217 9 201 -174	0 18 194 160 0
1 224 238 -175	1 13 11 361 113	1 184 19 217 -180	0 169 10 147 0	1 338 4 348 175
0 411 426 170	1 355 379 -90	0 180 19 217 -180	1 176 114 -114	1 209 5 197 -14
2 216 183 8	2 219 243 -131	1 15 1 71 -65	2 184 15 160	1 170 6 181 -180
0 159 144 -180	3 170 248 -59	2 202 200 -179	0 168 11 168 -180	0 210 7 181 -180
1 522 51 -9	0 298 0 71	1 125 1 71 -65	1 249 239 17	1 171 158 172
2 174 166 4	0 311 340 90	2 202 200 -179	0 168 11 168 -180	0 18 194 160 0
3 297 0 -17	2 205 231 -81	3 166 2 158 18	1 249 239 17	1 209 5 197 -14
0 221 238 -180	1 172 155 -92	1 15 2 158 18	1 195 14 156 178	1 170 6 181 -180
1 410 410 -177	0 224 258 -90	3 208 202 172	0 202 19 188 0	0 210 7 181 -180
2 192 195 -42	1 20: 227 96	0 181 4 31 -90	1 226 0 355 90	0 18 194 160 0
0 340 225 -9	1 237 226 -84	3 186 161 -153	1 241 1 326 -89	0 196 9 198 0
2 24 295 166	0 193 21 197 90	1 276 5 283 1	0 183 2 199 -90	0 321 10 337 0
0 294 314 -180	0 193 21 197 90	3 15 222 6 217 -5	1 292 296 -97	0 221 11 195 -180
0 213 219 0	0 212 243 -90	1 15 7 11 -49	0 168 3 172 90	0 254 224 -90
1 198 0 159 -90	3 14 283 0 260 90	2 231 234 -172	2 199 219 -89	1 185 0 195 90
6 191 156 0	2 188 1 185 -149	3 231 234 -172	0 301 4 319 90	1 176 167 -73
1 46 1 473 99	3 182 184 29	1 157 7 11 -49	1 172 110 11	0 19 184 3 190 90
3 286 255 -42	1 14 352 336 -17	2 231 234 -172	2 275 265 -87	0 371 4 364 90
4 297 406 3	2 188 1 185 -149	3 231 234 -172	0 211 5 248 -90	0 297 6 289 -90
6 171 172 169	3 182 184 29	1 15 10 104 117	2 226 241 111	0 177 0 178 0
2 175 2 174 -80	1 14 419 5 413 177	1 15 15 15 104 117	0 252 175 109	0 164 3 78 0
0 303 3 207 -90	2 188 1 185 -149	1 15 15 15 104 117	2 205 224 75	0 1536 8 1920 -180
1 404 411 -59	3 182 184 29	1 15 15 15 104 117	0 173 7 165 90	0 1 1082 4 1243 90
2 442 438 79	1 14 352 336 -17	1 15 15 15 104 117	1 224 231 -90	
3 391 382 147	2 188 1 185 -149	1 15 15 15 104 117	1 274 8 291 -84	
4 250 248 -117	3 182 184 29	1 15 15 15 104 117	0 160 9 111 90	
5 179 136 -49	1 14 419 5 413 177	1 15 15 15 104 117	1 235 274 -85	
0 186 4 189 -90	2 188 1 185 -149	1 15 15 15 104 117	1 216 10 228 80	
0 458 511 90	3 182 184 29	1 15 15 15 104 117	0 190 3 188 0	
1 240 228 -125	1 14 352 336 -17	1 15 15 15 104 117	1 199 229 -169	
2 544 525 -98	2 188 1 185 -149	1 15 15 15 104 117	2 186 184 26	
3 250 251 -3	3 182 184 29	1 15 15 15 104 117	3 206 180 -71	
4 249 334 107	1 14 150 6 100 172	1 15 15 15 104 117	0 200 2 189 -180	
0 182 171 90	2 188 1 185 -149	1 15 15 15 104 117	2 194 195 -28	
2 176 189 -105	3 182 184 29	1 15 15 15 104 117	0 190 3 188 0	
	1 14 150 6 100 172	1 15 15 15 104 117	1 199 229 -169	
	2 188 1 185 -149	1 15 15 15 104 117	2 186 184 26	
	3 182 184 29	1 15 15 15 104 117	3 206 180 -71	
	1 14 150 6 100 172	1 15 15 15 104 117	0 200 2 189 -180	
	2 188 1 185 -149	1 15 15 15 104 117	2 194 195 -28	
	3 182 184 29	1 15 15 15 104 117	0 190 3 188 0	
	1 14 150 6 100 172	1 15 15 15 104 117	1 199 229 -169	
	2 188 1 185 -149	1 15 15 15 104 117	2 186 184 26	
	3 182 184 29	1 15 15 15 104 117	3 206 180 -71	
	1 14 150 6 100 172	1 15 15 15 104 117	0 200 2 189 -180	
	2 188 1 185 -149	1 15 15 15 104 117	2 194 195 -28	
	3 182 184 29	1 15 15 15 104 117	0 190 3 188 0	
	1 14 150 6 100 172	1 15 15 15 104 117	1 199 229 -169	
	2 188 1 185 -149	1 15 15 15 104 117	2 186 184 26	
	3 182 184 29	1 15 15 15 104 117	3 206 180 -71	
	1 14 150 6 100 172	1 15 15 15 104 117	0 200 2 189 -180	
	2 188 1 185 -149	1 15 15 15 104 117	2 194 195 -28	
	3 182 184 29	1 15 15 15 104 117	0 190 3 188 0	
	1 14 150 6 100 172	1 15 15 15 104 117	1 199 229 -169	
	2 188 1 185 -149	1 15 15 15 104 117	2 186 184 26	
	3 182 184 29	1 15 15 15 104 117	3 206 180 -71	
	1 14 150 6 100 172	1 15 15 15 104 117	0 200 2 189 -180	
	2 188 1 185 -149	1 15 15 15 104 117	2 194 195 -28	
	3 182 184 29	1 15 15 15 104 117	0 190 3 188 0	
	1 14 150 6 100 172	1 15 15 15 104 117	1 199 229 -169	
	2 188 1 185 -149	1 15 15 15 104 117	2 186 184 26	
	3 182 184 29	1 15 15 15 104 117	3 206 180 -71	
	1 14 150 6 100 172	1 15 15 15 104 117	0 200 2 189 -180	
	2 188 1 185 -149	1 15 15 15 104 117	2 194 195 -28	
	3 182 184 29	1 15 15 15 104 117	0 190 3 188 0	
	1 14 150 6 100 172	1 15 15 15 104 117	1 199 229 -169	
	2 188 1 185 -149	1 15 15 15 104 117	2 186 184 26	
	3 182 184 29	1 15 15 15 104 117	3 206 180 -71	
	1 14 150 6 100 172	1 15 15 15 104 117	0 200 2 189 -180	
	2 188 1 185 -149	1 15 15 15 104 117	2 194 195 -28	
	3 182 184 29	1 15 15 15 104 117	0 190 3 188 0	
	1 14 150 6 100 172	1 15 15 15 104 117	1 199 229 -169	
	2 188 1 185 -149	1 15 15 15 104 117	2 186 184 26	
	3 182 184 29	1 15 15 15 104 117	3 206 180 -71	
	1 14 150 6 100 172	1 15 15 15 104 117	0 200 2 189 -180	
	2 188 1 185 -149	1 15 15 15 104 117	2 194 195 -28	
	3 182 184 29	1 15 15 15 104 117	0 190 3 188 0	
	1 14 150 6 100 172	1 15 15 15 104 117	1 199 229 -169	
	2 188 1 185 -149	1 15 15 15 104 117	2 186 184 26	
	3 182 184 29	1 15 15 15 104 117	3 206 180 -71	
	1 14 150 6 100 172	1 15 15 15 104 117	0 200 2 189 -180	
	2 188 1 185 -149	1 15 15 15 104 117	2 194 195 -28	
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	1 14 150 6 100 172	1 15 15 15 104 117	1 199 229 -169	
	2 188 1 185 -149	1 15 15 15 104 117	2 186 184 26	
	3 182 184 29	1 15 15 15 104 117	3 206 180 -71	
	1 14 150 6 100 172	1 15 15 15 104 117	0 200 2 189 -180	
	2 188 1 185 -149	1 15 15 15 104 117	2 194 195 -28	
	3 182 184 29	1 15 15 15 104 117	0 190 3 188 0	
	1 14 150 6 100 172	1 15 15 15 104 117	1 199 229 -169	
	2 188 1 185 -149	1 15 15 15 104 117	2 186 184 26	
	3 182 184 29	1 15 15 15 104 117	3 206 180 -71	
	1 14 150 6 100 172	1 15 15 15 104 117	0 200 2 189 -180	
	2 188 1 185 -149	1 15 15 15 104 117	2 194 195 -28	
	3 182 184 29	1 15 15 15 104 117	0 190 3 188 0	
	1 14 150 6 100 172	1 15 15 15 104 117	1 199 229 -169	
	2 188 1 185 -149	1 15 15 15 104 117	2 186 184 26	
	3 182 184 29	1 15 15 15 104 117	3 206 180 -71	
	1 14 150 6 100 172	1 15 15 15 104 117	0 200 2 189 -180	
	2 188 1 185 -149	1 15 15 15 104 117	2 194 195 -28	
	3 182 184 29	1 15 15 15 104 117	0 190 3 188 0	
	1 14 150 6 100 172	1 15 15 15 104 117	1 199 229 -169	
	2 188 1 185 -149	1 15 15 15 104 117	2 186 184 26	
	3 182 184 29	1 15 15 15 104 117	3 206 180 -71	
	1 14 150 6 100 172	1 15 15 15 104 117	0 200 2 189 -180	
	2 188 1 185 -149	1 15 15 15 104 117	2 194 195 -28	
	3 182 184 29	1 15 15 15 104 117	0 190 3 188 0	
	1 14 150 6 100 172	1 15 15 15 104 117	1 199 229 -169	
	2 188 1 185 -149	1 15 15 15 104 117	2 186 184 26	
	3 182 184 29	1 15 15 15 104 117	3 206 180 -71	
	1 14 150 6 100 172	1 15 15 15 104 117	0 200 2 189 -180	
	2 188 1 185 -149	1 15 15 15 104 117	2 194 195 -28	
	3 182 184 29	1 15 15 15 104 117	0 190 3 188 0	
	1 14 150 6 100 172	1 15 15 15 104 117	1 199 229 -169	
	2 188 1 185 -149	1 15 15 15 104 117	2 186 184 26	
	3 182 184 29	1 15 15 15 104 117	3 206 180 -71	
	1 14 150 6 100 172	1 15 15 15 104 117	0 200 2 189 -180	
	2 188 1 185 -149	1 15 15 15 104 117	2 194 195 -28	
	3 182 184 29	1 15 15 15 104 117	0 190 3 188 0	
	1 14 150 6 100 172	1 15 15 15 104 117	1 199 229 -169	
	2 188 1 185 -149	1 15 15 15 104 117	2 186 184 26	
	3 182 184 29	1 15 15 15 104 117	3 206 180 -71	
	1 14 150 6 100 172	1 15 15 15 104 117	0 200 2 189 -180	
	2 188 1 185 -149	1 15 15 15 104 117	2 194 195 -28	
	3 182 184 29	1 15 15 15 104 117	0 190 3 188 0	
	1 14 150 6 100 172	1 15 15 15 104 117	1 199 229 -169	
	2 188 1 185 -149	1 15 15 15 104 117	2 186 184 26	
	3 182 184 29	1 15 15 15 104 117	3 206 180 -71	
	1 14 150 6 100 172	1 15 15 15 104 117	0 200 2 189 -180	
	2 188 1 185			

However, a comparison with the 2.12 Å Mo—O (oxalato) bond in BaMo₂O₄(C₂O₄)₂(H₂O)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 —CO₂ 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 —NH₂ 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

L₁ = S(1)H₂C(3)HC(2).H₂N(1).O(5)C(1)O(6)—Mo(1)

L₂ = S(2)H₂C(6)HC(5).H₂N(2).O(8)C(4)O(7)—Mo(2)

	In L ₁	In L ₂	In L-cysteine
S—C β	1.89 (23)	1.84 (25)	1.86 (12)
C β —C α	1.52 (30)	1.47 (33)	1.51 (14)
C α —C	1.55 (29)	1.54 (31)	1.51 (13)
C α —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—C β —C α	110.4 (15)	111.3 (17)	114.4 (8)
C β —C α —C	106.3 (17)	108.4 (18)	113.2 (9)
C β —C α —N	107.0 (16)	109.5 (18)	111.0 (9)
C—C α —N	109.3 (16)	106.2 (17)	109.1 (9)
C α —C—O	119.4 (18)	120.7 (19)	115.8 (9)
C α —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—C α —N	—21.0	—25.1	—3.0
O*—C—C α —Mo	11.4	8.8	—
O*—C—C α —S	62.0	59.3	93.6
O*—C—C α —C β	94.0	92.4	121.1
O*—C—C α —O	177.7	181.6	179.4
N—C α —C β —Mo	41.2	38.8	—
N—C α —C β —S	60.0	54.5	72.6
N—C α —C β —O*	85.9	84.0	95.6
N—C α —C β —C	116.6	115.4	123.1
N—C α —C β —O	143.7	141.9	148.0

* Oxygen *cis* to —NH₂ with respect to C—C α 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 $\text{Mo}_2\text{O}_3[\text{S}_2\text{P}(\text{OC}_2\text{H}_5)_2]_4$ (Knox & Prout, 1968*b*) and $\text{Mo}_2\text{O}_3(\text{S}_2\text{COC}_2\text{H}_5)_4$ (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 $\text{Mo}-\text{N}^{\delta-}-\text{H}^{\delta+}\cdots\text{S}$ (3.31 Å), compared with 3.47 Å for the $\text{N}(1)\cdots\text{S}$ distance. Nevertheless, the average value 2.23 Å compares favourably with 2.21 Å in $(\pi\text{-C}_5\text{H}_5)_2\text{MoS}(\text{CH}_2)_2\text{NH}_2^+\text{I}^-$ (Knox & Prout, 1968*b*), in which there is a similar $\text{N}^{\delta-}-\text{H}^{\delta+}\cdots\text{I}^-$ 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 $\text{N}\cdots\text{O}$ 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 $\text{BaMo}_2\text{O}_4(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2$ (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 $\text{O}(1)\cdots\text{O}(2)$ 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 $\text{Mo}_2\text{O}_3[\text{S}_2\text{P}(\text{OC}_2\text{H}_5)_2]_4$ (Knox & Prout, 1968*b*), $\text{BaMo}_2\text{O}_4(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2$ (Cotton & Morehouse, 1965) or $[(\text{C}_6\text{H}_5)_4\text{As}]^+[\text{MoOBr}_4(\text{H}_2\text{O})]^-$ (Scane, 1967).

The cysteine ligands

Fig. 2 shows bond conformations as viewed along the C–C α , C α –C β and N–C α 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 –CH₂ and –NH₂ 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 $(\pi\text{-C}_5\text{H}_5)_2\text{MoS}(\text{CH}_2)_2\text{NH}_2^+\text{I}^-$ (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 $(\pi\text{-C}_5\text{H}_5)_2\text{MoS}(\text{CH}_2)_2\text{NH}_2^+\text{I}^-$ (55°). This dihedral angle is then unaffected by the presence of –CO₂ 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 –CO₂ 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 C α and C β 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–C α , and thereby twist out of the plane it formed with the C α –N bond. In the chelate the magnitude of the O–C–C α –N dihedral angle ($\psi = -23^\circ$) is greater than in L-cysteine (-3°), but is less than the 30–40° rotation required for maximum in-plane bonding. Continued rotation of –CO₂ about C–C α 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–C α –C β from 113° in the free acid to 107° in the chelate; (2) a decrease in the interior angle O–C–C α from 121° to 114°. Nevertheless, upon completion of the conformational changes just described, the metal atom is still 0.51 Å from the C α –CO₂ plane, and a rather weak Mo–O (carboxyl) bond results.

* A brief report of the cysteine.HCl.H₂O 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 C α –C β 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 2 σ . 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-

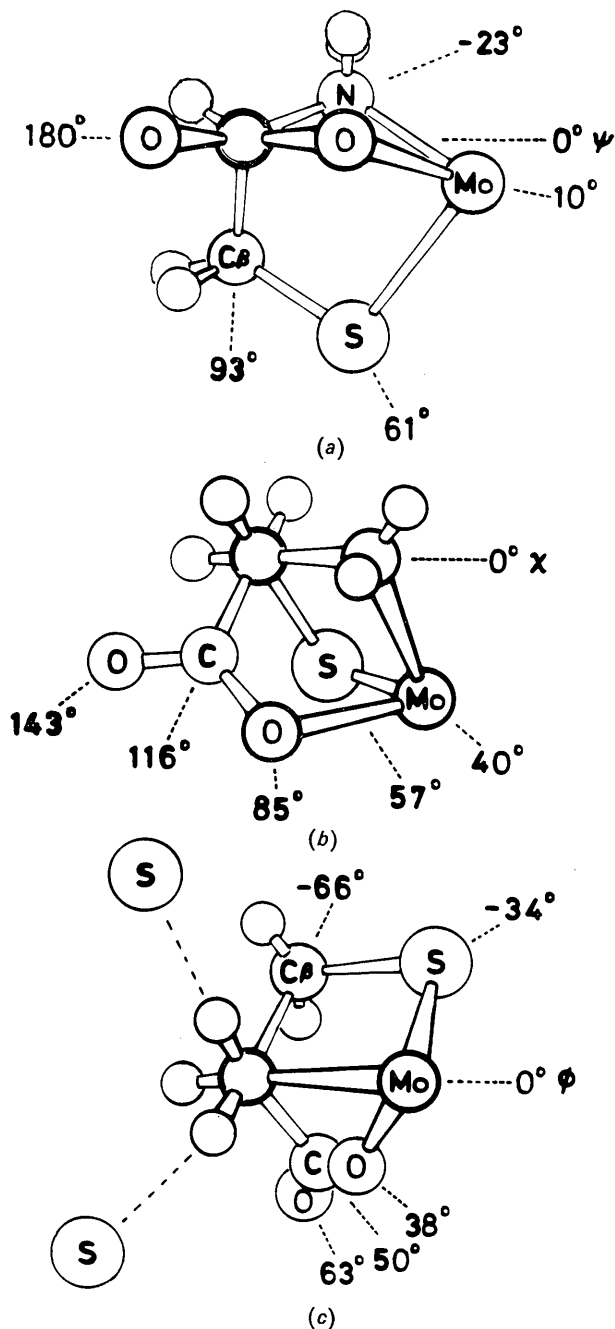


Fig. 2. Average dihedral angles. View along bond: (a) from C to C α , (b) from C α to C β , (c) from N to C α . Values are positive as far atom rotates clockwise relative to near atom. Bond distances not to scale. Values for free L-cysteine given in Table 3.

ordination, the average C-C, C-N and C-S distances are little changed by chelation. The largest difference is in the C-C α bond, which is 0.035 Å longer in the chelate. In both the ligand and in the free acid a somewhat long C β -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 -NH₂ 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 H₂O(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 H₂O(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 H₂O(9) (2.75 Å) H₂O(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 H₂O(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.

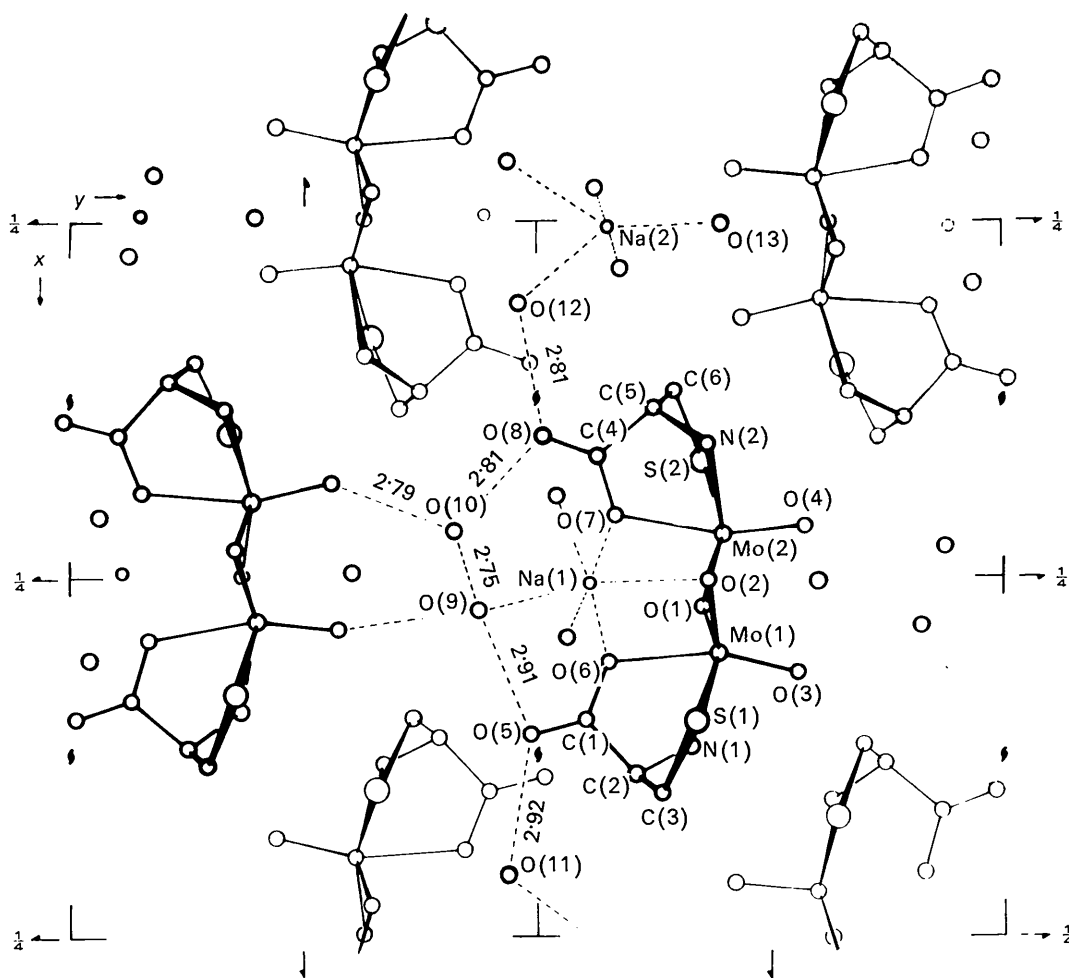


Fig. 3. Projection of structure down *c*.

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 a fellowship to J.R.K. Calculations were done on the Oxford University KDF9 computer with the *November Tape* programs written by Dr J.S. Rollett and modified by O.J.R. Hodder and G. Ford.

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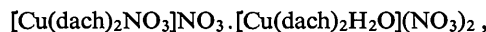
The Crystal and Molecular Structure of Bis-(1,4-diazacycloheptane)copper(II) Nitrate Hemihydrate*

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(Received 2 October 1968)

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



crystallizes in the monoclinic space group $P2_1/n$ with $a=20.92$, $b=15.79$, $c=10.04$ Å and $\beta=91.7^\circ$. 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 $[\text{Cu}(\text{dach})_2\text{NO}_3]^+$ and $[\text{Cu}(\text{dach})_2\text{H}_2\text{O}]^{2+}$ 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-picolyamine (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(acetylacetonimine)copper(II) monohydrate (Hall, Morgan & Waters, 1966), in N,N' -disalicylidene-propane-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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