JOURNAL OF SOLID STATE CHEMISTRY **2**, 16–23 (1970)

The Crystal Structure of the Molybdenum Bronze Cs_xMoO_3 ($x \approx 0.25$)

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Received September 27, 1969

$Cs_{0.25}MoO_3$ crystallizes in the monoclinic system, space group $P2_{1/m}$ with unit cell dimensions $a = 6.425$, $b = 7.543$, $c = 8.169$, $\beta = 96°30'$. Its structure was determined from two-dimensional Patterson projections and refined by three-dimensional Fourier methods and also by least squares. It has a layer structure built up from subunits of six distorted octahedra sharing edges; the subunits are joined by corners to form layers. Cesium ions occupy irregular eight-coordinated interlayer sites. The bronze structure is compared with those of the related bronzes $K_{0.26}MoO_3$ and $K_{0.28}MoO_3$.

Introduction

In a recent review of oxide bronzes, Banks and Wold (*1*) discussed the preparative methods and the structural chemistry of the majority of transition-metal bronzes. For the preparation of many of these compounds they placed particular emphasis on electrolytic reduction, the method which was used by Wold et al. (*2*) to make the two first-known molybdenum bronzes. These were the red potassium molybdenum bronze $K_{0.26}MoO_3$ and the blue potassium molybdenum bronze $K_{0.28}MoO_3$, the structures of which were described by Graham, Stephenson, and Wadsley (*3*, *4*). Both contained clusters of MoO_6 octahedra in a frame-work that allowed the accommodation of K^+ ions by a reduction in the net valency of the Mo atoms.

In a recent study, electrolysis of molten titanate, molybdate, and vanadate melts has been used by Reid and Watts (*5*) to prepare single crystals of various new oxide phases. The present structural investigation shows that the product of electrolysis in the Cs_2MoO_4–MoO_3 system is a new cesium molybdenum bronze Cs_xMoO_3 ($x \approx 0.25$). Its relationship to the structures of the red and blue potassium molybdenum bronzes is described.

Experimental

A detailed description of the apparatus used for the preparation of this phase has been given elsewhere (*5*). Briefly, $Cs_{0.25}MoO_3$ was obtained by the electrolysis of a 30 mol % Cs_2MoO_4–70 mol % MoO_3 melt at 530°C. Small well-shaped copper coloured crystals were separated from the melt by treatment with dilute acid. Only a small amount of the phase (< 10 mg) could be isolated so that accurate chemical analysis was not possible, and the chemical composition has been derived from this structural investigation. Qualitative analysis of a small sample of 15 μg did indicate the presence of cesium.

The unit cell data listed in Table I were obtained using a Guinier-type focusing camera. Potassium chloride was used as an internal standard, and final parameters were obtained by a least-squares treatment of the powder data given in Table II.

The crystals examined were in the form of thin plates. X-ray data for the diffraction levels with $k = 0, 1 \ldots 6$, and the one additional layer $0kl$ were

TABLE I

CRYSTALLOGRAPHIC DATA FOR $Cs_{0.25}MoO_3$

Symmetry: Monoclinic
Unit cell: $a = 6.425\ (\pm\ 0.005)$ Å
$b = 7.543\ (\pm\ 0.005)$ Å
$c = 8.169\ (\pm\ 0.005)$ Å
$\beta = 96.50\ (\pm\ 0.05)°$
Absent reflections: $0k0$, $k \neq 2n$
Possible space groups: $P2_1$, $P2_{1/m}$
$D_x = 4.49$ gm/cm^3
$\mu = 675$ cm^{-1}

TABLE II

X-RAY POWDER DIFFRACTION DATA FOR $Cs_{0.25}MoO_3$

$\sin^2 \theta_{obsd}$	$\sin^2 \theta_{calc}$	$h\ k\ l$
0.01454	0.01456	1 0 0
0.05074	0.05071	0 2 1
0.05818	0.05823	2 0 0
0.06202	0.06205	2 0 $\bar{1}$
0.09152	0.09149	0 1 3
0.10370	0.10376	2 2 $\bar{1}$
0.17494	0.17491	0 3 3
0.20285	0.20286	0 4 2
0.30015	0.30013	4 1 2

obtained by the multiple film technique from a crystal measuring 0.05 × 0.05 × 0.02 mm. The integrated equiinclination method was used with $CuK\alpha_{1,2}$ radiation. Intensities were estimated visually against a standard scale, and the reduction to structure amplitudes and all subsequent computing was made with an Elliott 803 computer using the computing system devised by Daly, Stephens, and Wheatley (*6*). A total of 475 nonsymmetry-related reflections were recorded around *b* and the observed data, scaled by comparison with the structure factors calculated for the final model, are given in Table III.

The systematically absent reflections defined the space group alternatives as $P2_1$ and $P2_1/m$. It was assumed that the centro-symmetric space group $P2_1/m$ was the more probable, a choice which was later confirmed by the satisfactory solution and refinement of the structure.

Structure Determination

At the outset of the structure determination the composition of the crystals was unknown. However their bronze-like appearance, and the 7.6 Å repeat

TABLE III

H	K	L	F_O	F_C	H	K	L	F_O	F_C	H	K	L	F_O	F_C	H	K	L	F_O	F_C
0	0	1	797	1254	2	1	5	471	533	4	2	-7	289	-309	2	4	-4	517	525
0	0	2	187	-115	2	1	6	181	-196	4	2	-9	567	461	2	4	-5	644	767
0	0	3	187	-156	2	1	8	435	478	5	2	0	567	-475	2	4	-6	594	772
0	0	4	917	-1092	2	1	-1	648	-520	5	2	2	900	-798	2	4	-7	369	465
0	0	6	856	-952	2	1	-2	299	269	5	2	3	567	-516	2	4	-8	452	-578
0	0	7	346	-238	2	1	-3	431	-536	5	2	5	324	330	2	4	-9	268	-275
0	0	8	627	696	2	1	-5	743	890	5	2	6	922	968	3	4	0	363	418
0	0	9	501	444	2	1	-6	461	-467	5	2	7	179	240	3	4	1	1557	1594
0	0	10	627	628	2	1	-10	211	253	5	2	-2	509	491	3	4	2	654	678
1	0	0	359	-274	3	1	0	340	-355	5	2	-3	642	730	3	4	4	627	651
1	0	1	346	-325	3	1	1	1109	986	5	2	-4	1263	1159	3	4	5	388	-404
1	0	2	856	-1215	3	1	2	219	-135	5	2	-6	289	-349	3	4	6	569	-586
1	0	4	960	-1214	3	1	4	324	-363	5	2	-8	509	-478	3	4	7	701	-609
1	0	6	1385	1363	3	1	6	658	614	6	2	0	993	-1023	3	4	8	388	-376
1	0	7	336	379	3	1	7	396	-352	6	2	2	631	599	3	4	-1	199	101
1	0	-1	469	-296	3	1	8	179	-166	6	2	3	578	576	3	4	-2	1287	-1224
1	0	-2	1847	2124	3	1	-1	773	-707	6	2	4	642	662	3	4	-3	985	-1074
1	0	-3	1847	1865	3	1	-2	627	481	6	2	-2	377	-441	3	4	-5	343	-323
1	0	-4	842	1282	3	1	-4	406	405	6	2	-4	309	275	3	4	-6	313	346
1	0	-6	941	-1068	3	1	-5	229	-250	6	2	-5	301	201	3	4	-7	213	303
1	0	-8	421	-490	3	1	-6	369	-395	6	2	-6	763	897	3	4	-8	327	392
2	0	0	2142	-1896	3	1	-7	465	511	6	2	-7	457	413	4	4	0	343	326
2	0	1	593	-799	4	1	0	761	-752	7	2	0	737	614	4	4	1	289	228
2	0	2	476	-342	4	1	3	262	259	7	2	1	301	298	4	4	2	468	420
2	0	3	1081	1381	4	1	4	211	173	7	2	2	415	414	4	4	3	1005	-991
2	0	4	912	1458	4	1	5	644	-665	7	2	4	159	99	4	4	4	685	-714
2	0	5	402	422	4	1	6	143	129	7	2	-1	457	448	4	4	5	375	-415
2	0	6	635	588	4	1	7	196	183	7	2	-2	539	-608	4	4	7	569	521
2	0	9	582	-454	4	1	-1	623	595	7	2	-3	463	-390	4	4	-1	843	849
2	0	-1	495	-459	4	1	-2	421	432	7	2	-4	549	-523	4	4	-2	609	508
2	0	-2	433	479	4	1	-3	569	-547	8	2	0	309	417	4	4	-3	955	882
2	0	-3	767	-775	4	1	-5	231	-255	0	3	1	521	-557	4	4	-4	493	-448
2	0	-4	633	681	4	1	-6	287	336	0	3	2	712	-699	4	4	-5	999	-1010
2	0	-5	791	1043	4	1	-7	183	189	0	3	3	865	857	4	4	-6	251	-275
2	0	-6	741	869	4	1	-8	328	-431	0	3	5	315	-440	4	4	-7	257	-336
2	0	-7	595	572	5	1	3	509	-470	0	3	8	384	451	4	4	-8	222	203
2	0	-8	537	-650	5	1	4	542	542	1	3	0	479	-262	5	4	0	209	-180
2	0	-9	381	-320	5	1	6	189	-177	1	3	1	1047	873	5	4	1	1213	-1266
3	0	0	458	621	5	1	-1	627	544	1	3	2	667	-640	5	4	2	485	-473
3	0	1	2021	2384	5	1	-2	707	-736	1	3	3	249	-319	5	4	5	555	484
3	0	2	782	954	5	1	-4	363	396	1	3	4	425	528	5	4	6	169	178
3	0	4	856	893	5	1	-7	425	-428	1	3	6	336	352	5	4	-1	343	229
3	0	5	561	-449	6	1	2	623	557	1	3	7	413	-433	5	4	-2	409	340
3	0	6	793	-728	6	1	3	255	-243	1	3	8	268	-240	5	4	-3	536	593
3	0	7	749	-719	6	1	4	231	-251	1	3	9	271	289	5	4	-5	545	555
3	0	8	627	-413	6	1	5	198	238	1	3	-2	266	-244	5	4	-6	313	182
3	0	9	641	472	6	1	-1	175	-194	1	3	-3	439	-439	5	4	-7	421	-518
3	0	-1	287	144	6	1	-2	183	-177	1	3	-4	885	1177	6	4	2	241	212
3	0	-2	1203	-1433	6	1	-3	528	581	2	3	0	1158	-918	6	4	3	623	571
3	0	-3	1129	-1324	7	1	0	185	186	2	3	1	411	349	6	4	4	394	317
3	0	-5	425	-331	7	1	1	481	-414	2	3	2	837	798	6	4	5	289	578
3	0	-6	474	470	7	1	3	307	298	2	3	3	435	-461	6	4	-1	916	-930
3	0	-7	315	347	7	1	4	163	-181	2	3	5	419	-520	6	4	-2	576	-601
3	0	-8	495	475	7	1	-2	149	182	2	3	7	307	364	6	4	-4	268	185
					7	1	-4	421	-398	2	3	8	419	-459	6	4	-5	637	706

TABLE III—*continued*

3	0	9	593	472	7	1	-5	219	257	2	3	-1	461	252	7	4	0	243	231
4	0	0	495	488	8	1	0	313	283	2	3	-3	355	353	7	4	1	665	673
4	0	1	346	340	0	2	1	1851	1700	2	3	-5	613	-737	7	4	2	375	289
4	0	2	549	520	0	2	2	613	669	2	3	-6	441	542	7	4	-2	327	303
4	0	3	1017	-1185	0	2	3	662	-540	3	3	0	501	459	7	4	-3	381	-441
4	0	4	784	-820	0	2	4	667	-836	3	3	1	860	-802	7	4	-4	435	-438
4	0	5	549	-522	0	2	5	1519	-1701	3	3	4	192	261	0	5	1	127	65
4	0	7	962	640	0	2	7	509	436	3	3	6	557	-610	0	5	2	449	466
4	0	-1	945	1059	0	2	9	509	576	3	3	7	401	358	0	5	3	767	-777
4	0	-2	695	721	1	2	1	1793	-1571	3	3	8	220	171	0	5	4	233	-250
4	0	-3	1041	1250	1	2	2	309	-433	3	3	-1	689	618	0	5	5	330	330
4	0	-4	627	-534	1	2	3	819	-735	3	3	-2	505	-393	0	5	8	221	-307
4	0	-5	1034	-1232	1	2	4	509	527	3	3	-4	413	-418	1	5	0	281	-250
4	0	-7	411	-380	1	2	5	289	305	3	3	-6	287	331	1	5	1	1021	-861
4	0	-8	336	232	1	2	7	877	936	3	3	-7	469	-486	1	5	2	530	550
5	0	1	1829	-1559	1	2	8	334	400	4	3	0	708	663	1	5	3	277	249
5	0	2	617	-570	1	2	9	421	355	4	3	3	198	-250	1	5	4	327	-295
5	0	5	707	566	1	2	-1	2107	2005	4	3	5	602	618	1	5	6	237	-248
5	0	7	923	628	1	2	-3	831	886	4	3	-1	461	-454	1	5	7	227	255
5	0	-1	396	339	1	2	-4	697	812	4	3	-2	323	-371	1	5	-2	340	284
5	0	-2	474	413	1	2	-7	1063	-1283	4	3	-3	528	585	1	5	-3	301	307
5	0	-3	791	731	1	2	-8	662	-648	4	3	-6	317	-343	1	5	-4	658	-726
5	0	-5	687	667	2	2	0	491	-498	4	3	-8	323	343	1	5	-5	295	293
5	0	-7	635	-579	2	2	1	793	-588	5	3	3	559	479	1	5	-6	227	291
5	0	-8	346	-422	2	2	2	683	637	5	3	4	519	-479	2	5	0	858	736
6	0	2	421	302	2	2	4	429	612	5	3	-1	537	-532	2	5	2	559	-491
6	0	3	739	688	2	2	5	1479	1571	5	3	-2	541	572	2	5	3	315	344
6	0	4	631	369	2	2	8	578	-653	5	3	-4	274	-287	2	5	5	305	322
6	0	5	1041	699	2	2	9	497	-561	5	3	-7	373	435	2	5	6	269	-240
6	0	-1	1125	-1074	2	2	-1	970	-820	6	3	2	435	-448	2	5	7	396	-405
6	0	-2	751	-721	2	2	-2	793	-743	6	3	3	241	203	2	5	-1	491	-383
6	0	-5	838	857	2	2	-3	1113	1073	6	3	4	276	214	2	5	-3	381	-455
6	0	-7	321	269	2	2	-4	745	845	6	3	5	241	-248	2	5	-5	545	639
7	0	1	1041	813	2	2	-5	914	894	6	3	-3	667	-605	2	5	-6	237	-271
7	0	2	617	363	2	2	-6	384	413	7	3	1	407	399	3	5	0	199	-96
7	0	3	441	311	2	2	-8	497	431	7	3	3	357	-344	3	5	1	761	766
7	0	4	569	-485	2	2	-9	381	-492	7	3	-4	297	330	3	5	4	338	-321
7	0	-2	458	399	2	2	-10	509	-647	0	4	1	858	719	3	5	6	469	419
7	0	-3	633	-515	3	2	0	667	514	0	4	3	280	-298	3	5	7	251	-243
7	0	-4	651	-519	3	2	1	448	479	0	4	4	850	-906	3	5	-1	517	-445
7	0	-5	512	-402	3	2	2	1371	1491	0	4	6	693	-806	3	5	-2	355	377
8	0	-1	793	674	3	2	3	1263	1190	0	4	8	481	589	3	5	-4	255	243
8	0	-2	595	484	3	2	4	613	-628	0	4	9	291	368	3	5	-5	214	-275
0	1	2	813	804	3	2	5	387	-447	1	4	0	363	-303	3	5	-6	342	-342
0	1	3	1038	-1063	3	2	6	648	-703	1	4	1	327	-269	3	5	-7	287	364
0	1	5	421	482	3	2	9	359	-323	1	4	2	1118	-1039	4	5	0	555	-555
0	1	8	421	-459	3	2	-1	900	-780	1	4	3	335	-445	4	5	5	555	-466
0	1	10	253	299	3	2	-3	687	-701	1	4	4	916	-946	4	5	6	156	183
1	1	1	1329	-1197	3	2	-4	1451	-1433	1	4	8	335	422	4	5	-1	463	454
1	1	2	862	867	3	2	-5	359	376	1	4	-1	553	-391	4	5	-2	309	325
1	1	3	173	256	3	2	-6	387	462	1	4	-2	1734	1561	4	5	-3	239	-295
1	1	4	485	-542	3	2	-7	860	818	1	4	-3	1321	1285	4	5	-5	181	-199
1	1	6	359	-381	3	2	-8	602	631	1	4	-9	437	-428	4	5	-6	201	226
1	1	7	379	399	4	2	0	1428	1267	1	4	-6	716	-865	5	5	3	273	-300
1	1	8	194	220	4	2	1	369	349	1	4	-8	381	-426	5	5	4	415	444
1	1	9	355	-383	4	2	2	1141	-1109	1	4	-9	348	-428	5	5	-1	327	330
1	1	-2	255	413	4	2	4	369	-401	2	4	0	1624	-1424	5	5	-2	505	-608
1	1	-4	1227	-1251	4	2	5	497	-484	2	4	1	667	-653	5	5	-4	295	333
1	1	-5	225	214	4	2	8	797	746	2	4	2	415	-384	6	5	2	478	473
1	1	-6	773	364	4	2	-1	765	823	2	4	3	1083	1066	6	5	3	165	-193
1	1	-9	344	-404	4	2	-2	831	872	2	4	4	1061	1115	6	5	-1	152	-133
1	1	-10	211	208	4	2	-3	602	-489	2	4	-1	555	-512	6	5	-3	361	382
2	1	0	1133	1069	4	2	-5	328	-260	2	4	-2	291	192	6	5	-4	227	-215
2	1	2	821	-868	4	2	-6	900	-939	2	4	-3	713	-585					
2	1	3	475	472															

distance along b, a distance characteristic of MoO_6 octahedra joined by corners into vertical strings, led us to anticipate that the phase was a cesium molybdenum bronze.

Oxide compounds of molybdenum contain MoO_6 octahedra sharing corners and edges in a variety of differing configurations. In such structures, the usual molybdenum–oxygen distance of approximately 2.0 Å leads to strong Mo–Mo vectors appearing within a distance of 4 Å from the origin in the Patterson functions. Patterson projections $P(u,w)$ and $P(v,w)$ for the present compound are shown in Fig. 1(a) and (b). The strong peaks marked A and B in these projections were consistent with a group of four corner shared MoO_6 octahedra arranged with their Mo atoms almost at the corners of a square and lying close to $y = 0$ and $\frac{1}{2}$ in the general positions 4(*f*). A further strong peak marked C in the projection $P(u,w)$ could then be interpreted as an Mo–Mo interaction caused by an additional MoO_6 octahedron, edge sharing with these groups of four, with the molybdenum atom lying alternatively on either side of the groups at $y = \frac{1}{4}$ and $\frac{3}{4}$ in the position 2(*e*).

On this basis approximate coordinates for the octahedrally coordinated oxygen atoms were derived, two in the general positions 4(*f*), four in the twofold position 2(*e*) and one in the twofold position 2(*a*) at the origin. As this resulted in unit cell contents of Mo_6O_{18}, the further peak marked D in Fig. 1(a) was regarded as a possible Cs–Mo vector that located the cesium atom in the twofold site 2(*e*). If this site was partially occupied, the overall stoichiometry would then be Cs_xMoO_3 by analogy with the chemical composition of the potassium molybdenum bronzes.

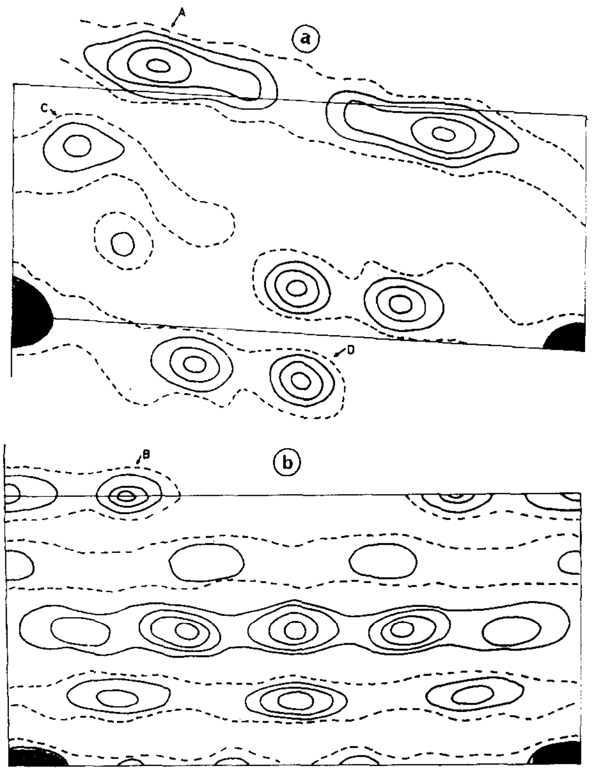

FIG. 1. (a) Patterson function, $P(u,w)$; (b) Patterson function, $P(u,v)$.

The contents of the unit cell are defined as $Cs_2Mo_6O_{18}$ when the sites are fully occupied. While the empirical formula was not known, it was felt that a partial occupancy factor for Cs close to that found satisfactory for the potassium molybdenum bronzes (*3*, *4*) would be suitable for the initial structure factor calculations. The atomic scattering curve for cesium was scaled down to three-quarters of its normal value, giving a statistical distribution of $1\frac{1}{2}$ atoms over two positions, in accord with a formula of $Cs_{0.25}MoO_3$.

A three dimensional Fourier synthesis confirmed this structure, and was used to obtain more accurate atomic positions. In repeated Fourier syntheses, the Cs (atomic number 55) peak was always of the same intensity as that for Mo (atomic number 42), confirming the 0.75 occupancy originally chosen. Refinement was continued for several least-squares cycles. The block diagonal approximation was used, and the observed data were weighted by Cruickshank's method (*7*). Individual isotropic temperature factors were varied for each atom, and refinement proceeded smoothly to give a final R value of 12.5. Refinement was stopped when the shift of each variable was less than one-quarter of its standard deviation. No attempt was made to reduce the symmetry to $P2_1$.

Atomic parameters, the temperature factors and their e.s.d.'s are given in Table IV. We had no facility in our computing procedures to vary the occupancy factor during the refinement of the structure. However, the temperature factor for the cesium atom behaved normally, and this was taken as strong evidence that the partial occupancy factor chosen originally was reasonably close to the correct value. The structure is shown in [010] projection in Fig. 2.

TABLE IV

FRACTIONAL ATOMIC COORDINATES AND THERMAL PARAMETERS
(e.s.d.'s are given in brackets.)

Atom	Point Position	x	y	z	$B(A^2)$
$\frac{3}{4}$ Cs	2 (*e*)	0.1785 (8)	$\frac{3}{4}$	0.6113 (6)	1.25 (8)
Mo (1)	2 (*e*)	0.3482 (8)	$\frac{1}{4}$	0.7753 (7)	1.74 (9)
Mo (2)	4 (*f*)	0.2715 (5)	0.0047 (5)	0.1060 (4)	1.71 (6)
O (1)	2 (*e*)	0	0	0	4.54 (95)
O (2)	2 (*e*)	0.2991 (65)	$\frac{1}{4}$	0.0405 (55)	1.22 (76)
O (3)	2 (*e*)	0.3043 (82)	$\frac{3}{4}$	0.0927 (68)	2.76 (1.03)
O (4)	2 (*e*)	0.4635 (77)	$\frac{1}{4}$	0.5958 (61)	1.79 (91)
O (5)	2 (*e*)	0.0942 (93)	$\frac{1}{4}$	0.7214 (76)	3.22 (1.13)
O (6)	4 (*f*)	0.3970 (53)	0.0085 (52)	0.8542 (47)	2.02 (65)
O (7)	4 (*f*)	0.2218 (54)	0.0397 (68)	0.3032 (46)	2.57 (73)

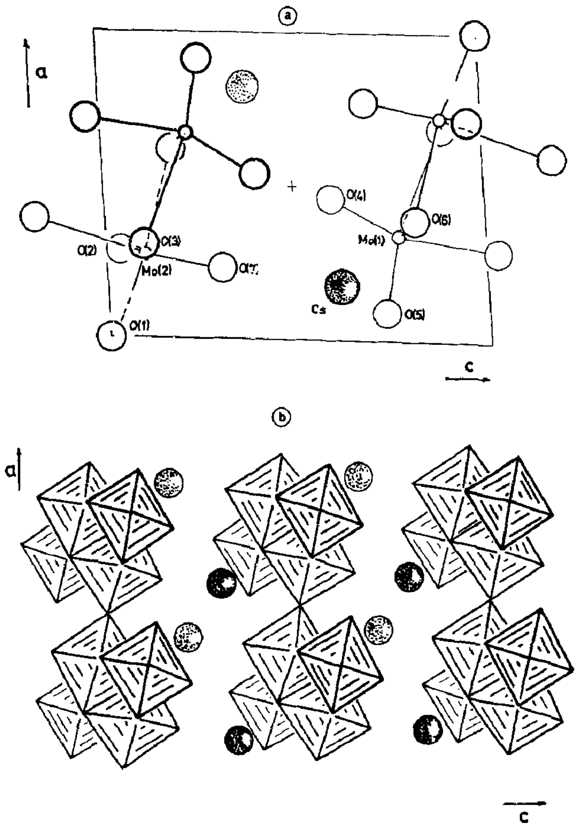

FIG. 2. (a) Ball and spoke representation of the structure of $Cs_{0.25}MoO_3$ projected onto (010). Small circles are molybdenum atoms; large open circles are oxygen atoms; large stippled circles are cesium atoms; light markings indicate atoms near $y = 0$; medium markings indicate atoms at $y = \frac{1}{4}$, $\frac{3}{4}$; heavy markings indicate atoms near $y = \frac{1}{2}$. (b) The structure of $Cs_{0.25}MoO_3$ as an assemblage of octahedra, projected down (010). Stippled circles are cesium ions.

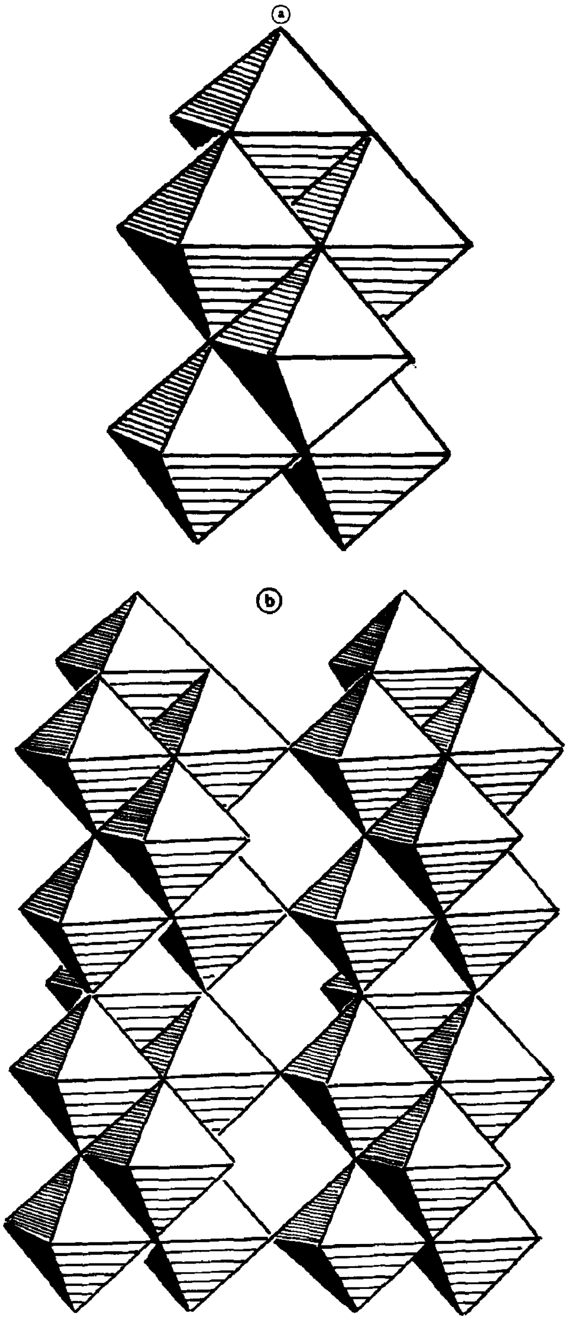

FIG. 3. (a) The group of six idealized octahedra forming the basis of the octahedral structure; (b) the groups of Fig. 3(a) join by common corners to give the sheets in the structure of $Cs_{0.25}MoO_3$.

Description

The structure is composed of pairs of octahedra centred about each of the levels $y = \frac{1}{4}$ and $\frac{3}{4}$. These pairs form groups of six by additional edge sharing [fig. 3(*a*)]. The groups then join up with similar groups above and below by corner sharing, and extend through the structure in the [010] direction. These infinite linear strings are linked together by additional corner sharing to form infinite two dimensional sheets centred about (100) [Fig. 2(b) and 3(b)]. Finally, the layers are joined together by the large cesium ions that have an irregular eightfold coordination. The inter-atomic distances are summarised in Table V.

Both of the molybdenum–oxygen octahedra are irregular. There are four Mo(1)–O distances between 1.59 and 1.99 Å, with two of 2.16 and 2.55 Å, and three Mo(2)–O bonds ranging from 1.64 to 1.96 Å with three further bonds between 2.14 and 2.19 Å in length. These large distortions of the octahedra are

TABLE V

BOND LENGTHS (e.s.d.'s in brackets)

Mo(1)-O(4)	1.59 (4)		
-O(5)	1.73 (5)		
-O(3)	2.55 (4)		
-O(2)	2.16 (3)		
-O(6)	2 × 1.99 (4)		
O(6)-O(4)	2 × 2.81 (5)		
-O(5)	2 × 2.95 (6)		
-O(3)	2 × 2.72 (6)		
-O(2)	2 × 2.44 (5)		
O(2)-O(5)	3.00 (6)		
O(4)-O(5)	2.52 (6)		
O(3)-O(4)	3.04 (6)		
O(2)-O(4)	3.70 (5)		
Mo(2)-O(7)	1.64 (4)		
-O(1)	2.01 (7)		
-O(6)	2.19 (4)		
-O(6)'	2.15 (4)		
-O(2)	1.96 (3)		
-O(3)	1.96 (4)		
O(2)-O(6)'	2.44 (5)		
-O(6)	2.95 (5)	O(6)'-O(6)	2.80 (5)
-O(7)	2.69 (5)	O(6)'-O(1)	2.74 (8)
-O(1)	2.75 (8)	O(1)-O(7)	2.96 (8)
O(3)-O(6)'	2.80 (6)	O(7)-O(6)	2.71 (6)
-O(6)	2.72 (6)		
-O(7)	2.83 (6)		
-O(1)	2.88 (8)		
Cs-O(6)	2 × 3.19 (4)		
-O(7)	2 × 3.34 (4)		
-O(7)'	2 × 3.07 (4)		
-O(4)'	2.76 (4)		
-O(5)'	3.34 (5)		

caused by the repulsion of the highly charged molybdenum atoms. Any adjacent pair of molybdenum atoms in a group of edge-shared octahedra would be separated by a distance of 2.7 Å if the octahedra were perfectly regular. In the present case, the nearest neighbour Mo–Mo distances vary between 3.29 and 3.90 Å. The molybdenum atoms evidently prefer positions as far as possible from each other. The metal–oxygen distances are similar to those found in MoO_3 (*8*) where the octahedral distances vary between 1.67 and 2.33 Å, while the Mo–Mo distances are in good agreement with the values for all other reduced molybdenum oxides with oxidation numbers between 5.5 and 6 (*9*). The Mo–Mo and Mo–O distances for this compound are compared with those of the two potassium molybdenum bronzes and the sodium molybdenum bronze $Na_{0.9}Mo_6O_{17}$ (*10*) in Table VI. It is seen that the tendency for the Mo(1) atom in $Cs_{0.25}MoO_3$ to adopt a tetrahedral coordination is less marked than it is in the red potassium molybdenum bronze, and distortions in the MoO_6 octahedra are more comparable with those in the blue potassium molybdenum bronze. This can be ascribed to the stepping of the Mo(1) octahedra on alternate sides of the group of four Mo(2) octahedra, an arrangement which gives each Mo(1) atom only four near neighbour Mo(2) atoms. In the red potassium molybdenum bronze, because the inter level octahedra

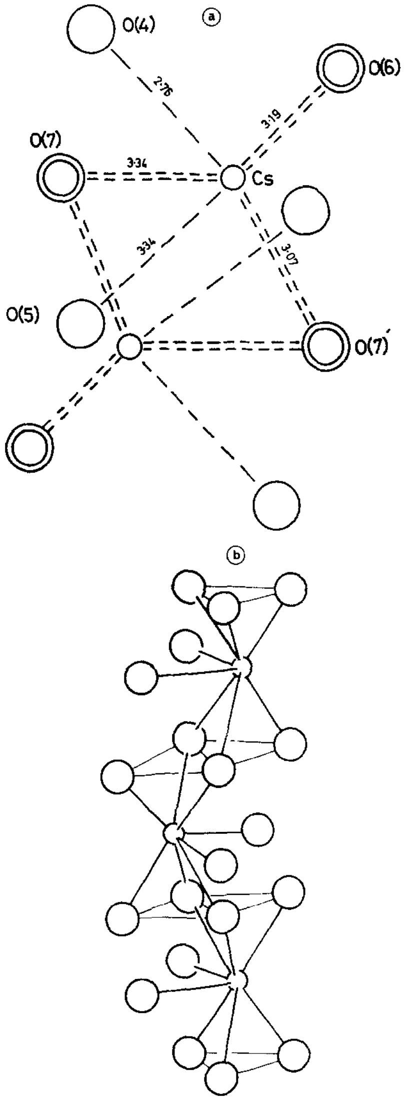

FIG. 4. (a) The eightfold coordination of Cs; (b) zigzag chains of Cs–O polyhedra.

TABLE VI

COMPARISON OF INTERATOMIC DISTANCES IN MOLYBDENUM BRONZES[a]

	Nearest Neighbour Mo–Mo Distances	Mo-Oxygen Distances	Alkali Metal–Oxygen Distances
$Cs_{0.25}MoO_3$	3.29–3.90	Mo(1) 1.82 (4) 2.35 (2)	3.16 (8)
		Mo(2) 1.89 (4) 2.17 (2)	
Red molybdenum bronze, $K_{0.26}MoO_3$	3.20–3.88	Mo(1) 1.89 (4) 2.48 (2)	2.81 (8)
		Mo(2) 1.91 (4) 2.16 (2)	
Blue molybdenum bronze, $K_{0.28}MoO_3$	3.18–3.85	Mo(1) 1.84 (4) 2.27 (2)	2.84 (7) 3.02 (10)
		Mo(2) 1.86 (2 × 4) 2.18 (2 × 2)	
$Na_{0.9}Mo_6O_{17}$	3.76–4.30 (corner sharing only)	Mo(1) 1.94 (3) 2.15 (3)	2.56 (12)
		Mo(2) 1.87 (3) 2.00 (3)	
		Mo(3) 1.90 (3) 2.05 (3)	

[a] Figures in brackets refer to the number of bonds included in the mean.

are arranged in pairs, an additional repulsion is introduced; for example, each Mo(1) is repelled by a near neighbour Mo(1), as well as by four Mo(2).

The cesium ions lie in interlayer positions and are each bonded to eight oxygen atoms, six at the corners of a trigonal prism with Cs–O separations of 3.20 (2), 3.34(2), and 3.08(2) Å, with two further oxygen atoms situated through the centres of the two prism faces at distances of 3.34 and 2.74 Å (Fig. 4). These polyhedra unite with a common edge to form zigzag chains similar to the coordination of potassium in the red potassium molybdenum bronze.

Discussion

The structure of the bronze described in this paper is similar in some respects to both of the potassium molybdenum bronzes, $K_{0.26}MoO_3$ and $K_{0.28}MoO_3$. The red potassium bronze has as a basic unit a cluster of six distorted MoO_6 octahedra [Fig. 5(a)], interlocked by edge sharing to give Mo_6O_{22} stoichiometry. Two K^+ ions are associated with each cluster and two valence electrons per cluster have been incorporated into the structure. The basic unit of the blue bronze is a cluster of ten distorted MoO_6 octahedra made up of two groups of five [Fig. 5(b)] that are interlocked by edge sharing to give a $Mo_{10}O_{36}$ unit. There are three K^+ ions and hence three valence electrons incorporated per cluster. In both the red and the blue potassium bronzes, clusters are connected by corner sharing of octahedra through oxygens. However, $Cs_{0.25}MoO_3$ is more closely related to the red potassium bronze, differing from it only in the manner in which the Mo(1) octahedra are stepped on alternate sides of the groups of four Mo(2) octahedra. This difference between the structures of the red potassium bronze and $Cs_{0.25}MoO_3$ probably is the result of the larger Cs^+ ion requiring more room in which to fit.

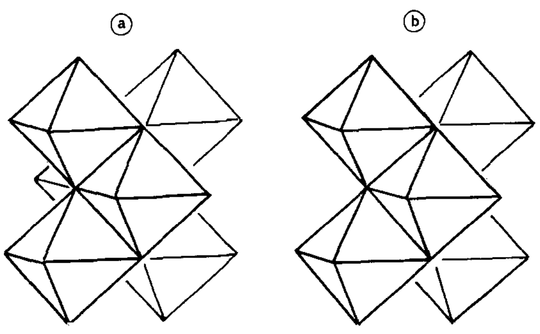

FIG. 5. (a) Cluster of octahedra in $K_{0.26}MoO_3$; (b) cluster of octahedra in $K_{0.28}MoO_3$.

In $Cs_{0.25}MoO_3$, as in other bronzes, a fraction of the Mo^{6+} ions are reduced to give in the host framework electrons which provide charge compensation for the Cs^+ ions, and thus allow the formation of a neutral crystal. It is probable that the electrons are not localized on any one Mo^{5+} ion, but are free to move within the host framework. Furthermore, because of the extended edge sharing along [010] due to the alternate stepping of the Mo(1) octahedron [Figure 3(b)], we feel that the compound may have a particularly high electrical conductivity in this [010] direction. We would expect the conductivity to be higher than in the potassium molybdenum bronzes where clusters are joined by corners only and there is no direction in which edge sharing is infinitely continued. Its conductivity may well approach that of the metallic-like MoO_2 (*11*), which has extended edge sharing as a predominant feature of its structure.

Stephenson and Wadsley (*4*) have already introduced the idea that large anions similar to the subunit of six octahedra, $(Mo_6O_{22})^{8-}$, found to be common to both the discrete anions in the octa- and hepta- molybdates of the isopolyacids of molybdenum might be present in the fused salt system K_2MoO_4-MoO_3 under reducing conditions. These polyanions would incorporate K^+ ions into the lattice upon crystallisation from the melt. The formation of similar types of polyanionic species during the formation of the bronze $K_3T_{18}O_{17}$ from alkali titanate melts has also been suggested (*12*). The general similarities of the basic units of MoO_6 octahedra in the three bronzes $K_{0.26}MoO_3$, $K_{0.28}MoO_3$, and $Cs_{0.25}MoO_3$ reinforces the idea that large anions may exist in the melts from which they crystallise. However, detailed differences between them are presumably determined by the conditions of electrolysis and the activity of the charged species in the melts.

Acknowledgment

The authors wish to express their thanks to Dr. A. F. Reid for helpful discussions during the preparation of this manuscript.

References

1. E. Banks and A. Wold, "Oxide Bronzes," *in* "Preparative Inorganic Reactions," (W. L. Jolly, Ed), Vol. 4, 1968.
2. A. Wold, W. Kunnmann, R. J. Arnott, and A. Ferretti, *J. Inorg. Chem.* **3**, 545 (1964).
3. J. Graham and A. D. Wadsley, *Acta Cryst.* **20**, 93 (1966).
4. N. C. Stephenson and A. D. Wadsley, *Acta Cryst.* **19**, 24 (1965).
5. A. F. Reid and J. A. Watts, *J. Solid State Chem.* (1970), in press.
6. J. J. Daly, F. S. Stephens, and P. J. Wheatley, Monsanto Research S.A., Final Report No. 52, 1963.
7. D. W. J. Cruickshank, D. E. Pilling, A. Bujosa, F. M. Lovell, and M. R. Truter, *in* "Computing Methods and the Phase Problem in X-Ray Crystal Analysis," p. 32, Pergamon Press, Oxford, 1961.
8. L. Kilborg, Ark. Kemi **21**, 357 (1963a).
9. L. Kilborg, Ark. Kemi **31**, 471 (1963b).
10. N. C. Stephenson, *Acta Cryst.* **20**, 59 (1965).
11. D. B. Rogers, R. D. Shannon, A. W. Sleight, and J. L. Gillson, *J. Inorg. Chem.* **8**, 841 (1969).
12. J. A. Watts, *J. Solid State Chem.* **1**, No. 3–4 (1970).