

are an overestimate of the errors. Using the mean of σ_m and σ'_m as a measure of the accuracy, the final bond distances may be given as 1.514 ± 0.003 Å for the bonds joining the six-membered rings, and for the bonds in the six-membered rings, starting with the bond in the four-membered ring, 1.426 ± 0.003 Å, 1.372 ± 0.002 Å, 1.423 ± 0.003 Å, and 1.385 ± 0.004 Å. The mean valency angle in the four-membered ring is $90.0^\circ \pm 0.2^\circ$ (mean σ as for bond lengths), but the angles in the six-membered rings differ significantly from 120° . The angle adjacent to the four-membered ring is $122.6^\circ \pm 0.2^\circ$ (with the external angle being $147.4^\circ \pm 0.2^\circ$), and the other angles are $115.2^\circ \pm 0.2^\circ$ and $122.2^\circ \pm 0.2^\circ$. The differences between the various C-H bonds are not significant, and the mean C-H bond length is 1.06 ± 0.02 Å (no thermal oscillation correction). The final mean molecular dimensions are summarized in Fig. 2. The dimensions are very similar to (but much more accurate than) the values of the previous two-dimensional study; the largest difference is for bond *D*, which has increased from 1.38 Å to 1.426 Å.

The theoretical bond distances, derived with the use of standard correlations (Trotter, 1964) from the molecular-orbital bond-orders and from various valence-bond models (Mak & Trotter, 1962), are compared with the measured lengths in Table 4. As before, the molecular-orbital method gives a much closer estimation of

the bond distances in the molecule than does simple valence-bond theory (with all Kekulé structures given equal weight); the best valence-bond model is *d* (Mak & Trotter, 1962), which considers the molecule as predominantly a cyclobutane derivative, with a smaller amount of cyclobutene, but negligible cyclobutadiene, character. The individual agreement between measured and calculated bond lengths is quite good.

Grateful acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research under Grant PRF 1704-A5. All the computations were performed on the IBM 7040 computer with our own programs, and we thank the staff of the University of British Columbia Computing Centre for assistance.

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The Crystal Structure of the Blue Potassium Molybdenum Bronze, $K_{0.28}MoO_3$

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(Received 11 May 1965)

$K_{0.28}MoO_3$ crystallizes in the monoclinic system, space group $C2/m$, with unit-cell dimensions $a = 18.249$, $b = 7.560$, $c = 9.855$, $\beta = 117^\circ 32'$. Its structure was determined from two-dimensional Patterson projections and refined by three-dimensional Fourier methods and full-matrix least-squares. The layer structure is built up from subunits consisting of ten distorted octahedra sharing edges; the subunits are linked by corners. The octahedrally coordinated layers are joined solely by interlayer potassium ions which in this structure occupy two kinds of site, one seven- and the other ten-coordinated, the potassium sites being fractionally occupied. The bronze structure is discussed from the viewpoints of both close-packing and coordination polyhedra, and compared with that of the related bronze $K_{0.26}MoO_3$.

Introduction

Wold, Arnott, Kunnmann & Ferretti (1964) recently succeeded in making two potassium molybdenum oxide 'bronzes' by electrolyzing fused salt mixtures of K_2MoO_4 and MoO_3 . Unless the composition of the melt and the temperature were strictly confined to a

minute portion of the liquidus in the equilibrium phase diagram, the product was MoO_2 , and it is presumably for this reason that molybdenum bronzes, although sought on many previous occasions, have never before been found. The formulae of the bronzes were established by chemical analysis to be simply K_xMoO_3 , a red phase corresponding to $x = 0.26$, and a blue to

$x=0.28$. Although the compositions of the two are alike, their structures are nevertheless different (Graham, Stephenson, Wadsley & Wold, 1965). The red bronze was reported recently (Stephenson & Wadsley, 1965) while the blue forms the subject of the present paper.

Experimental

The specimen, kindly furnished by Professor Aaron Wold, Brown University, Rhode Island, U.S.A., consisted of metallic blue plate crystals with perfect mica-like cleavages, and secondary cleavages across the flakes. Lath-like fragments which were readily detached proved to be single crystals with monoclinic symmetry, the direction of maximum elongation corresponding to the unique axis, b . The lattice parameters listed in Table 1 were obtained from a Guinier film internally calibrated with potassium chloride and refined by a least-squares treatment. Intensity data for the layers $k=0, 1 \dots 4$ were collected from a crystal $0.40 \times 0.07 \times 0.01$ mm rotated about the b axis and recorded with Cu $K\alpha$ radiation on multiple films using the integrating Weissenberg technique. The $hk0$ layer, as well as a set of films taken around the $[10\bar{2}]$ axis, provided approximate interlayer scaling factors, which were later adjusted several times during refinement by comparing the observed data with calculated structure factors.

Table 1. *Crystallographic data for $K_{0.28}MoO_3$*

Symmetry	Monoclinic
Unit-cell dimensions	$a = 18.249 \pm 0.010$ Å $b = 7.560 \pm 0.005$ $c = 9.855 \pm 0.006$ $\beta = 117^\circ 32' \pm 5'$
Absent reflexions	hkl with $h+k \neq 2n$
Possible space groups	$C2, Cm, C2/m$
D_x	4.27 g.cm $^{-3}$
D_m	4.26 ± 0.05 g.cm $^{-3}$
μ	487 cm $^{-1}$

Intensities were measured by comparison with a standard scale and 769 out of a possible total of 923

reflexions were recorded. Absorption corrections were neglected. Scattering curves were those of Thomas & Umeda (1957) for Mo^{5+} , K^+ from *International Tables for X-ray Crystallography* (1962), both corrected for dispersion, and O^{2-} from Suzuki (1960). Calculations were made on the CSIRO Elliott 803 computer, except for several cycles of least squares with variable occupancy factors for K, using the ORFLS program of Busing & Levy on the IBM 7090 computer at Salisbury, South Australia.

Structure determination

The intensity statistics of Howells, Phillips & Rogers (1950) favoured the centrosymmetric space group $C2/m$. The projection of the Patterson function down the $[10\bar{2}]$ axis showed that the scattering matter was centred about the planes $y=0, \frac{1}{2}$ and $\frac{1}{2}$. The principal features of another projection $P(u, w)$ could be explained by placing two Mo atoms in $8(j)$ positions $\pm(x, y, z)$, (x, \bar{y}, z) , y being approximately $\frac{1}{2}$ for both, and one Mo in a fourfold site $4(i)$, $\pm(x, 0, z)$. Assuming octahedral coordination, the oxygen atoms were readily assigned to the special and general positions of $C2/m$ to give a complex layer structure with no atoms common to adjacent octahedral sheets. In this way, which will be described more fully below, the basic formula, disregarding potassium, was MoO_3 , the unit cell contained twenty formula units, while the structural proposition was consistent with the cleavages characteristic of the crystal specimens. One potassium atom was placed in a symmetry centre at $2(d)$, $(0, \frac{1}{2}, \frac{1}{2})$, but the other could not be deduced from Patterson or difference Patterson functions, or by refinement with two-dimensional data using electron density projections.

A three-dimensional Fourier synthesis confirmed the structure, and placed the additional potassium atom in a fourfold site $4(i)$, $\pm(x, 0, z)$ lying almost directly over one of the oxygen atoms in $8(j)$ in the projection onto (010) . Several cycles of least-squares refinement were run on the IBM 7090 computer to adjust the scale factors and to find values for the percentage occupancy

Table 2. *Fractional atomic parameters and standard deviations*

Space group $C2/m, (0,0,0) (\frac{1}{2}, \frac{1}{2}, 0) +$									
Atom	Point position	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$	B	$\sigma(B)$
K(1)	$2(d)$	0		$\frac{1}{2}$		$\frac{1}{2}$		3.7	0.6
K(2)	$4(i)$	0.8139	0.0012	0		0.2816	0.0022	1.7	0.4
Mo(1)	$4(i)$	0.2257	0.0003	0		0.1732	0.0005	0.95	0.08
Mo(2)	$8(j)$	0.4208	0.0002	0.2453	0.0007	0.0430	0.0004	0.92	0.06
Mo(3)	$8(j)$	0.1381	0.0002	0.2495	0.0007	0.3464	0.0004	1.15	0.06
O(1)	$4(f)$	$\frac{1}{2}$		$\frac{1}{2}$		$\frac{1}{2}$		0.8	0.7
O(2)	$4(i)$	0.2491	0.0031	0		0.0284	0.0054	2.2	1.0
O(3)	$4(i)$	0.3208	0.0028	0		0.3394	0.0050	1.7	0.9
O(4)	$4(i)$	0.4099	0.0027	0		0.0063	0.0048	1.7	0.9
O(5)	$4(i)$	0.9056	0.0024	0		0.0042	0.0044	0.9	0.8
O(6)	$4(i)$	0.1558	0.0028	0		0.3154	0.0051	1.8	0.9
O(7)	$4(i)$	0.6397	0.0029	0		0.3281	0.0052	2.7	1.0
O(8)	$8(j)$	0.3979	0.0019	0.2458	0.0054	0.1939	0.0034	1.0	0.6
O(9)	$8(j)$	0.1841	0.0018	0.2426	0.0055	0.1650	0.0034	1.1	0.6
O(10)	$8(j)$	0.0893	0.0021	0.2212	0.0061	0.4573	0.0039	1.8	0.7
O(11)	$8(j)$	0.0361	0.0017	0.2435	0.0053	0.1455	0.0052	0.9	0.5

Table 3. *Interatomic distances* (Å)

Mo(1) octahedron		Mo(2) octahedron		Mo(3) octahedron		K(2)-O(8)				
Mo(1)-O(2)	1.68 ± 0.05	Mo(2)-O(8)	1.73 ± 0.04	Mo(3)-O(10)	1.72 ± 0.04	K(2)-O(8)	2.84 ± 0.04 (2)			
-O(3)	1.75 ± 0.04	-O(11)	2.34 ± 0.03	-O(9)	2.31 ± 0.04	-O(9)	2.86 ± 0.04 (2)			
-O(5)	2.23 ± 0.04	-O(11')	1.87 ± 0.03	-O(1)	1.89 ± 0.01	-O(10)	2.89 ± 0.04 (2)			
-O(6)	2.30 ± 0.04	-O(4)	1.88 ± 0.04	-O(7)	1.90 ± 0.04	-O(2)	2.73 ± 0.04 (1)			
-O(9)	1.97 ± 0.04 (2)	-O(5)	1.96 ± 0.04	-O(6)	1.96 ± 0.04					
		-O(9)	2.06 ± 0.04	-O(4)	1.99 ± 0.03					
O(9)	-O(5)	2.59 ± 0.05 (2)	O(5)	-O(11)	2.85 ± 0.05	O(6)	-O(1)	2.63 ± 0.04	K(1)-O(8)	3.29 ± 0.04 (4)
	-O(2)	2.85 ± 0.06 (2)		-O(11')	2.90 ± 0.05		-O(10)	2.80 ± 0.06	-O(10)	2.82 ± 0.04 (4)
	-O(3)	2.93 ± 0.06 (2)		-O(9)	2.59 ± 0.05		-O(11)	2.75 ± 0.05	-O(3)	2.90 ± 0.04 (2)
	-O(6)	2.56 ± 0.06 (2)		-O(8)	2.74 ± 0.05		-O(9)	2.56 ± 0.06		
O(2)	-O(3)	2.73 ± 0.06	O(4)	-O(11)	2.77 ± 0.05	O(7)	-O(1)	2.71 ± 0.04		
	-O(5)	2.70 ± 0.06		-O(11')	2.83 ± 0.05		-O(10)	2.83 ± 0.06		
O(6)	-O(3)	2.92 ± 0.06		-O(9)	2.54 ± 0.05		-O(11)	2.72 ± 0.05		
	-O(5)	2.82 ± 0.06		-O(8)	2.71 ± 0.05		-O(9)	2.88 ± 0.06		
				O(8)	-O(11)	2.79 ± 0.05	O(1)	-O(9)	2.95 ± 0.04	
					-O(9)	3.15 ± 0.05	-O(10)	2.78 ± 0.04		
					O(11')-O(11)	2.55 ± 0.05	O(11)	-O(10)	2.77 ± 0.05	
					-O(9)	2.62 ± 0.05	-O(9)	2.62 ± 0.05		

Table 4. *Calculated and observed values of structure factors* (× 10)

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	0	-3745	-4129	0	0	0	-427	-3731	0	0	0	-325	-469	0	0	0	-293	-479
0	0	0	817	891	0	0	0	3365	823	0	0	0	691	857	0	0	0	691	857
0	0	0	-651	-462	0	0	0	-2376	-2849	0	0	0	1225	894	0	0	0	1225	894
0	0	0	-3455	-2871	0	0	0	-1015	-1293	0	0	0	727	512	0	0	0	727	512
0	0	0	-737	-343	0	0	0	-974	-1145	0	0	0	893	1043	0	0	0	893	1043
0	0	0	-1141	-1292	0	0	0	329	327	0	0	0	892	827	0	0	0	892	827
0	0	0	-1289	-847	0	0	0	855	1577	0	0	0	-175	-278	0	0	0	-175	-278
0	0	0	-1818	-3186	0	0	0	1146	1283	0	0	0	-671	-699	0	0	0	-671	-699
0	0	0	3356	4307	0	0	0	-1315	-1362	0	0	0	2631	2631	0	0	0	2631	2631
0	0	0	-251	-2817	0	0	0	2076	259	0	0	0	-491	-381	0	0	0	-491	-381
0	0	0	935	935	0	0	0	-977	-845	0	0	0	-1246	-676	0	0	0	-1246	-676
0	0	0	857	765	0	0	0	2076	4394	0	0	0	732	732	0	0	0	732	732
0	0	0	-1787	-2352	0	0	0	-1513	-1674	0	0	0	-1373	-1925	0	0	0	-1373	-1925
0	0	0	1242	1336	0	0	0	2576	3515	0	0	0	398	289	0	0	0	398	289
0	0	0	-1864	-1895	0	0	0	-2076	-259	0	0	0	-718	-734	0	0	0	-718	-734
0	0	0	-1156	-1339	0	0	0	2495	2897	0	0	0	-336	-337	0	0	0	-336	-337
0	0	0	-1147	-1271	0	0	0	-1333	-1266	0	0	0	589	471	0	0	0	589	471
0	0	0	315	347	0	0	0	2147	2468	0	0	0	-1265	-1199	0	0	0	-1265	-1199
0	0	0	339	311	0	0	0	-495	-384	0	0	0	199	289	0	0	0	199	289
0	0	0	755	813	0	0	0	-1649	-2822	0	0	0	1267	1535	0	0	0	1267	1535
0	0	0	648	715	0	0	0	465	447	0	0	0	982	1197	0	0	0	982	1197
0	0	0	-545	-343	0	0	0	669	616	0	0	0	429	422	0	0	0	429	422
0	0	0	1058	1058	0	0	0	223	228	0	0	0	179	799	0	0	0	179	799
0	0	0	-487	-388	0	0	0	377	383	0	0	0	366	344	0	0	0	366	344
0	0	0	-763	-873	0	0	0	-1303	-1267	0	0	0	683	683	0	0	0	683	683
0	0	0	-677	-726	0	0	0	325	356	0	0	0	1929	4191	0	0	0	1929	4191
0	0	0	1111	1195	0	0	0	-1366	1164	0	0	0	-2193	-2044	0	0	0	-2193	-2044
0	0	0	-655	-598	0	0	0	-559	-567	0	0	0	2101	2441	0	0	0	2101	2441
0	0	0	836	666	0	0	0	-437	-472	0	0	0	-737	-900	0	0	0	-737	-900
0	0	0	451	386	0	0	0	235	276	0	0	0	-567	-581	0	0	0	-567	-581
0	0	0	471	494	0	0	0	175	835	0	0	0	319	181	0	0	0	319	181
0	0	0	-1699	-1856	0	0	0	895	689	0	0	0	-992	-913	0	0	0	-992	-913
0	0	0	-1370	-1338	0	0	0	-757	-734	0	0	0	667	967	0	0	0	667	967
0	0	0	1499	1581	0	0	0	-325	-288	0	0	0	599	657	0	0	0	599	657
0	0	0	-571	-528	0	0	0	-175	-186	0	0	0	416	484	0	0	0	416	484
0	0	0	-479	-417	0	0	0	625	651	0	0	0	1319	1656	0	0	0	1319	1656
0	0	0	-319	-222	0	0	0	579	570	0	0	0	-976	-786	0	0	0	-976	-786
0	0	0	305	247	0	0	0	-390	-318	0	0	0	1895	1405	0	0	0	1895	1405
0	0	0	197	218	0	0	0	-427	-434	0	0	0	469	426	0	0	0	469	426
0	0	0	-1594	-1572	0	0	0	-199	-177	0	0	0	-184	-113	0	0	0	-184	-113
0	0	0	1931	2121	0	0	0	-299	-143	0	0	0	1709	1521	0	0	0	1709	1521
0	0	0	-1409	-1383	0	0	0	337	334	0	0	0	-1600	-1791	0	0	0	-1600	-1791
0	0	0	-1149	-950	0	0	0	423	-386	0	0	0	-565	-583	0	0	0	-565	-583
0	0	0	1579	1938	0	0	0	-1449	-1674	0	0	0	899	935	0	0	0	899	935
0	0	0	-722	-384	0	0	0	289	338	0	0	0	-861	-826	0	0	0	-861	-826
0	0	0	2198	1938	0	0	0	-1799	-1670	0	0	0	-861	-810	0	0	0	-861	-810
0	0	0	-901	-862	0	0	0	1345	1367	0	0	0	793	814	0	0	0	793	814
0	0	0	1277	1534	0	0	0	-326	-278	0	0	0	-466	-725	0	0	0	-466	-725
0	0	0	972	1479	0	0	0	751	761	0	0	0	501	481	0	0	0	501	481
0	0	0	-1027	-913	0	0	0	-1915	-1716	0	0	0	260	317	0	0	0	260	317
0	0	0	-1139	-1055	0	0	0	607	449	0	0	0	715	489	0	0	0	715	489
0	0	0	-866	-972	0	0	0	-1449	-1674	0	0	0	469	426	0	0	0	469	426
0	0	0	-2312	-3262	0	0	0	-1453	-1276	0	0	0	-523	-467	0	0	0	-523	-467
0	0	0	1889	2677	0	0	0	697	595	0	0	0	-507	-500	0	0	0	-507	-500
0	0	0	-1156	-3574	0	0	0	2676	2590	0	0	0	2076	2300	0	0	0	2076	2300
0	0	0	1699	1856	0	0	0	-2676	-2590	0	0	0	-1895	-1405	0	0	0	-1895	-1405
0	0	0	-1370	-1338	0	0	0	-2644	-3371	0	0	0	2188	2525	0	0	0	2188	2525
0	0	0	1499	1581	0	0	0	3633	4439	0	0	0	-461	-384	0	0	0	-461	-384
0	0	0	-571	-528	0	0	0	-617	-789	0	0	0	173	193	0	0	0	173	193
0	0	0	-479	-417	0	0	0	2769	3761	0	0	0	253	228	0	0	0	253	228
0	0	0	305	247	0	0	0	-683	-686	0	0	0	371	270	0	0	0	371	270
0	0	0	197	218	0	0	0	1246	1346	0	0	0	1246	1346	0	0	0	1246	1346
0	0	0	-1594	-1572	0	0	0	1211	1225	0	0	0	-263	-260	0	0	0	-263	-260
0	0	0	1931	2121	0	0	0	-489	-489	0	0	0	810	810	0	0	0	810	810
0	0	0	-1409	-1383	0	0	0	1143	976	0	0	0	709	590	0	0	0	709	590
0	0	0	-1149	-950	0	0	0	1575	1565	0	0	0	371	270	0	0	0	371	270
0	0	0	1579	1938	0	0	0	-346	-346	0	0	0	686	846	0	0	0	686	846
0	0	0	-722	-384	0	0	0	-1032	-1022	0	0	0	519	810	0	0	0	519	810
0	0	0	2198	1938	0	0	0	-215	-366	0	0	0	163	344	0				

Table 4 (cont.)

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
5			578	618															
5			576	495															
5			-191	-191															
5			-165	-165															
5			793	648															
5			-1343	-1666															
5			-1113	-1613															
5			-1578	-2287															
5			-1217	-1523															
5			327	-250															
5			-479	-389															
5			-447	-526															
5			-250	-276															
5			-565	-467															
5			-821	-449															
5			1525	475															
5			222	273															
5			1023	1142															
5			1131	1346															
5			1447	329															
5			359	291															
5			461	346															
5			399	414															
5			-1569	-1087															
5			652	-287															
5			329	-344															
5			-617	-930															
5			-495	-596															
5			-1197	-1124															
5			181	321															
5			-287	-284															
5			2334	3237															
5			-1801	-1875															
5			673	1075															
5			233	248															
5			295	326															
5			833	839															
5			657	557															
5			822	537															
5			-534	-383															
5			-397	-249															
5			-458	-397															
5			1197	1197															
5			-252	-252															
5			-252	-252															
5			1919	1879															
5			-188	-204															
5			181	626															
5			73	433															
5			107	497															
5			871	691															
5			-487	-413															
5			-349	-393															
5			1313	1118															
5			-182	-145															
5			1152	899															
5			627	368															
5			486	423															
5			1216	949															
5			-21	-423															
5			2329	3750															
5			-641	-654															
5			245	291															
5			417	446															
5			315	325															
5			455	444															
5			-1227	-1427															
5			-1779	-2522															
5			891	901															
5			-1515	-1423															
5			-629	-729															
5			-727	-729															
5			1663	1259															
5			1291	1953															

* Omitted from least squares calculations

of the two independent potassium atoms. Several more cycles with the block diagonal approximation were then computed with the Elliott computer, the observed data being weighted by Cruickshank's method (Cruickshank, Pilling, Bujosa, Lovell & Truter, 1961). A number of the strongest reflexions which were evidently affected by extinction were omitted from the final cycles, and a final *R* index of 0.17 was eventually reached. Further refinement was attempted by reducing the space group to *C2* and then to *Cm*, as each of the eightfold Mo and O atoms could be reduced in two different ways to two groups of four. These efforts met with no success, and we concluded that additional refinement was impractical, owing to the likelihood of double Bragg scattering usually associated with crystals not ideally imperfect, and also because the presence in any oxide bronze of domains of differing composition and even of structure is more than likely (Fig. 5). An analysis of observed *vs* calculated intensities throughout reciprocal space suggested that absorption

effects were not negligible, and this was confirmed by calculating absorption corrections for a few reflexions by an approximate method (Hargreaves, 1959). In view of the above uncertainties it was felt that the labour involved in making the corrections was not warranted.*

The fractional atomic parameters and individual isotropic temperature factors, interatomic distances, and a comparison of *F_o* and *F_c* are given in Tables 2, 3 and 4.

Description

It is often easiest to describe the structures of solid state compounds in two stages; the ideal case where

* Absorption corrections for the related molybdenum bronze $K_{0.26}MoO_3$ which had a similar crystal habit (Stephenson & Wadley, 1965) reduced the *R* index by approximately 5%, and a like improvement could be expected in the present case. A further slight improvement could be expected by the use of anisotropic temperature factors.

the coordination polyhedra are assumed to be regular, followed by the departures from regularity, their consequences and implications.

The structure can be broken down into fundamental groups of five octahedra sharing edges [Fig. 1(a)] which join up in pairs by additional edge-sharing into larger groups of ten [Fig. 1(b)]. Were these isolated complex ions, such as those of the isopolymolybdates which they closely resemble, they would have a formula $[\text{Mo}_{10}\text{O}_{36}]^{12-}$. Each block of ten octahedra, however, joins up with certain corners common to four identical blocks forming infinite two-dimensional sheets [Fig. 1(c)] centred about the planes perpendicular to $[10\bar{2}]$. Adjacent sheets have no oxygen atoms in common, being held together solely by the potassium ions coordinated to them and occupying irregular interlayer positions. Fig. 2 shows the structure in projection on to (010) .

The Mo atoms at the centres of any two regular octahedra with a common edge are about 2.7 Å apart.

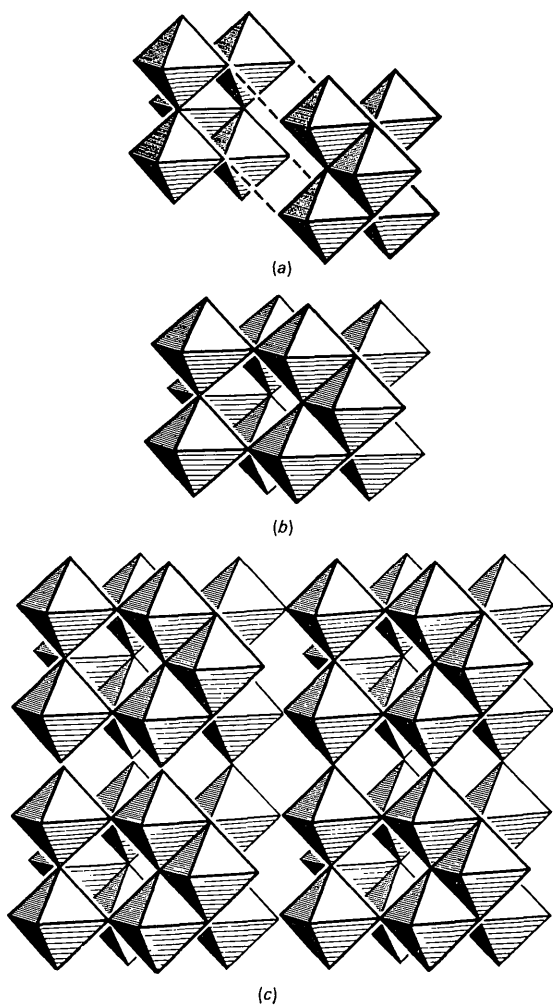


Fig. 1. (a) Groups of 5 octahedra link by sharing edges to form the compact subunit (b) of 10 octahedra. The subunits join by corners in two directions to form (c) the infinite sheets of formula MoO_3 that characterize the structure $\text{K}_{0.28}\text{MoO}_3$.

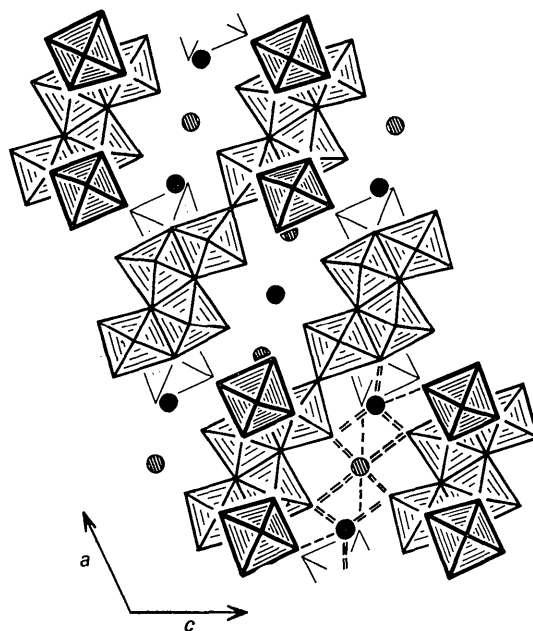


Fig. 2. Projection of the structure on (010) showing the octahedral sheets linked by inter-layer potassium ions. This projection shows the distortions of the oxygen lattice exaggerated somewhat. Potassium ions at the level $y=0$ are represented by hatched circles, at $y=1/2$ by solid circles.

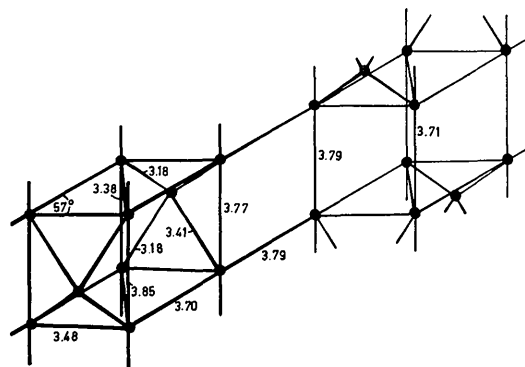


Fig. 3. Diagrammatic representation of the distribution of molybdenum atoms showing metal-metal distances. Inter-layer distances are much greater.

In the present case the metal atoms are strongly displaced from the ideal positions, as the minimum distance [between $\text{Mo}(1)$ and $\text{Mo}(2)$] is 3.18 ± 0.01 Å while distances for the others are even greater (Fig. 3). The shortest inter-sheet Mo-Mo distance is about 5.4 Å [between $\text{Mo}(1)$ and $\text{Mo}(1)$]. Evidently the molybdenum atoms prefer positions as far as possible from each other, and there are no metal-to-metal bonds in the structure. The oxygen atoms forming the octahedral framework are more or less close-packed, with distances between them ranging from 2.54 to 3.15 ± 0.05 Å. The shortest oxygen-oxygen distances between sheets are 3.1 and 3.4 Å.

The distortions are reflected strongly in the metal-oxygen distances which, within the limits of error for the three independent Mo atoms, range from about 1.7

to 2.3 Å in each case. These distances are in good agreement with those in other binary and ternary molybdenum oxides where the oxidation number of the metal is between 5 and 6 (Kihlberg, 1963). Although the four shorter distances in each case could be regarded as a distorted tetrahedron, there seems to be no valid reason to consider a tetrahedral rather than an octahedral coordination for Mo (Stephenson & Wadsley, 1965) as this introduces additional difficulties of description. There can be little doubt that solids, examined at room temperature, may not necessarily be identical with their precise forms at the temperature of formation, when the increase in thermal motions of the atoms can be expected to result in more regular interatomic distances in structures of higher symmetry. The structure described in this paper is probably not the equilibrium one, so that too much emphasis should not be placed on bonding schemes to explain the irregularities. In the next section, the ideal molybdenum coordination is shown to be fundamentally octahedral.

The potassium ions are of two kinds. K(1) is at the centre of an irregular cube of oxygen atoms not unlike the Na atom in the titanium dioxide bronze $Na_xTi_4O_8$ (Andersson & Wadsley, 1962). There are two additional oxygen atoms through the centres of opposing faces, and therefore it has ten nearest neighbours, four at 3.29 Å, four at 2.82 Å and two at 2.90 Å. K(2), on the other hand, is at the centre of a trigonal prism of oxygen atoms with K–O distances averaging 2.86 Å with a seventh oxygen atom at 2.73 Å through the centre of one prism face, closely resembling the Na coordination in the vanadium bronze $Na_xV_6O_{15}$ (Wadsley, 1955). These two K ions form an interconnected system with each other, illustrated in Fig. 4.

The formula of the blue bronze has a theoretical upper limit $K_{0.3}MoO_3$ without further distortion or disruption of the structure, in contrast to the red bronze where it is $K_{1/3}MoO_3$. The chemical analysis by Wold *et al.* (1964) gave the formula $K_{0.28}MoO_3$ while this crystallographic study, with potassium occupancy a variable, gave more nearly $K_{0.24}MoO_3$. Even this latter figure could perhaps be a little too high for potassium, as the temperature factor for K(1) [3.7 Å²] was much higher than that for K(2) [1.7 Å²]. (There is considerable interaction between temperature factor and occupancy parameters as their effects are much the same.) However, a higher temperature factor is not unexpected for K(1) since its bonding is much looser. Taking the occupancy figures at their face value, the ten-coordinated position is preferred.

As a general rule bronzes are non-stoichiometric compounds, with the interstitial positions of the host structure seldom, if ever, completely occupied by the alkali metal ions. In the present case there is no obvious reason for this fractional occupancy, but it may lie with the electronic structure of the transition metal octahedral framework. Furthermore there is no evidence of ordering in the vacant K positions, and these defects must therefore be random ones.

Discussion

The structure of the blue bronze described in this paper is similar in many ways to that of the red bronze already referred to. Both crystallize in the same space group, with their *b* axes corresponding to the height of two octahedra, and the side centering in each case is brought about by the alternating arrangement of single molybdenum octahedra between the two most populated levels of octahedra.

The description of the red and blue bronzes in terms of their coordination polyhedra emphasises the similarity of coordination of their metal atoms. The molybdenum atoms are all accommodated in similarly distorted octahedra, though a detailed study of interatomic distances reveals that the distortions are greater in the red bronze, the average distances also being greater (oxygen–oxygen distances average 2.82 Å in the red bronze and 2.75 in the blue). In both bronzes, O–O distances within each level of octahedra are longer than those between levels. This is due to the unscreened mutual repulsion of the molybdenum atoms in each level, and to screening by oxygen atoms between levels. The tendency of each molybdenum atom to assume a quasi-tetrahedral arrangement is also due to Mo–Mo repulsion, and the fact that this is most marked for the inter-level octahedra of the red bronze (Table 5) is because these octahedra are also arranged in pairs sharing an edge, thereby introducing an additional repulsion; for example Mo(1) is repelled by Mo(1) as well as by 4Mo(2).

The coordination around potassium ion K(2) in the blue bronze is virtually identical with that in the red, except that one of the oxygen ligands through the faces

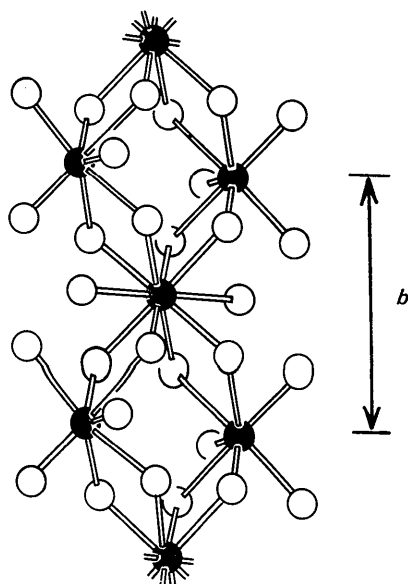


Fig. 4. Coordination scheme for potassium–oxygen, showing the two kinds of oxygen environment about the potassium. These infinite chains are not bridged laterally. White spheres: oxygen; black spheres: potassium. As in Fig. 2 the potassium sites are not fully occupied.

of the trigonal prism is missing in the former, and the distances are more nearly equal. There is no analogue in the red bronze for K(1), which has a higher coordination number but somewhat longer bonds.

New bronze structures can be devised by the addition of groups of four octahedra to the subunits. However the number of inter-sheet positions will increase, and the relative amount of potassium which can be inserted into them will in all likelihood decrease, so that these predictable structures might not be stable.

It is informative to consider the ideal structure of these bronzes from the viewpoint of a close-packed oxygen lattice. In the red bronze one tenth of the oxygen atoms are replaced by potassium ions which are of a comparable size. The molybdenum atoms between close-packed planes of oxygen atoms are distributed in groups of three among the octahedral positions (Fig. 5).

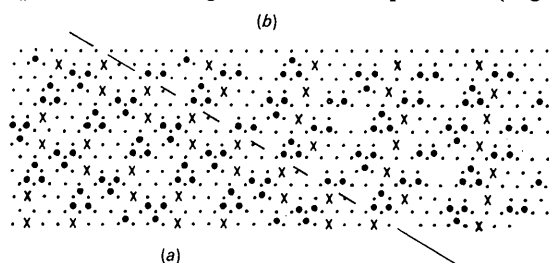


Fig. 5. The red (a) and blue (b) bronzes viewed as ideal close-packed oxygen lattices. All close-packed planes are similar but are displaced laterally. Black dots: oxygen; crosses: potassium; solid circles: molybdenum. The molybdenum atoms are above the plane of the other atoms.

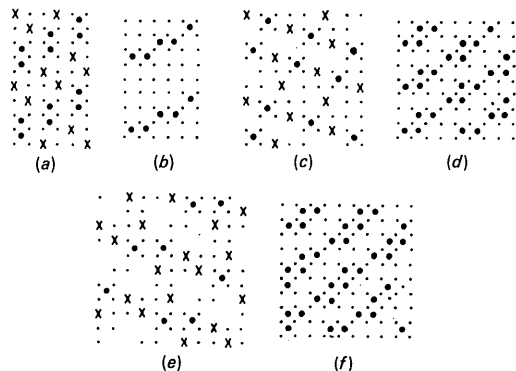


Fig. 6. Sections parallel to (010) of the various bronzes viewed as ideal close-packed lattices. (a) and (b), 'K₂Mo₆O₁₈', the red bronze; (c) and (d), 'K₃Mo₁₀O₃₀', the blue bronze; (e) and (f) the hypothetical 'K₄Mo₁₄O₄₂'. (a), (c) and (e), $y = \frac{1}{4}$; (b), (d) and (f), $y = 0$. Legend as Fig. 5.

The ideal cell dimensions of this bronze, assuming an oxygen radius of 1.40 Å, are shown in Table 6. The 2% changes in b and c have already been discussed. The 14% increase in a for the observed structure is due almost entirely to increased distances between sheets of the layer structure. Taking sections of the close-packed lattice parallel to (010) of the bronze (Fig. 6), we find that for $y = \frac{1}{4}$ and $\frac{3}{4}$ all oxygen positions are occupied and two-fifths of the octahedra are filled with Mo atoms; for the intermediate levels $y = 0$ and $\frac{1}{2}$, one-fifth of the oxygen atoms are replaced by potassium and only one-fifth of the octahedra are filled.

Table 6. *Ideal cell dimensions of potassium molybdenum bronzes*

		a	b	c	β	V
K ₂ Mo ₆ O ₁₈	obs.	14.28	7.72	6.39	92°34'	704
	(red) calc.	12.52	7.92	6.26	90°	621
K ₃ Mo ₁₀ O ₃₀	obs.	18.25	7.56	9.86	117°32'	1207
	(blue) calc.	16.80	7.92	8.85	118°24'	1118
K ₄ Mo ₁₄ O ₄₂	calc.	17.7	7.9	14.0	124°41'	1114

The blue bronze can be viewed in the same way, and the ideal cell dimensions are shown in Table 6. In this case both a and c are inter-sheet vectors and are considerably expanded; the percentage volume distortion, however, is less than for the simpler bronze, possibly because some of the atomic displacements can be accommodated by the vacant sites which are now present. Referring to Fig. 6(c) and (d), we see that all oxygen sites on the main levels $y = \frac{1}{4}$, $\frac{3}{4}$ are again occupied, four-ninths of the octahedra now being filled with Mo atoms. On the intermediate $y = 0$, $\frac{1}{2}$ levels, oxygen atoms occupy only two-thirds of the available sites, and one-third of the remainder contain potassium ions as in the red bronze, leaving vacant sites in pairs distributed over the level. Half of these double vacancies are occupied by the remaining potassium. The others are adjacent to potassium sites on the oxygen lattice and remain empty.

The hypothetical K₄Mo₁₄O₄₂ structure is shown in Fig. 6(e) and (f). Nearly half (6/13) of the octahedral positions of the main levels $y = \frac{1}{4}$ and $\frac{3}{4}$ are now filled with Mo atoms, but oxygen occupies only eight-thirteenths of the possible sites on the intermediate levels. A further two-thirteenths of the oxygen sites are occupied by potassium, leaving groups of three vacant sites distributed over the layer. These could contain additional potassium, but its coordination number

Table 5. *Comparison of interatomic distances in the two bronzes (Å)*

Standard deviations disregard errors in individual measurements.
Figures in brackets refer to the number of bonds included in the mean.

	Metal-oxygen		Oxygen-oxygen	
	Red	Blue	Red	Blue
Mo(1)	{ 1.89 ± 0.13 (4)	1.84 ± 0.13 (4)	2.83 ± 0.17 (8)	2.73 ± 0.16 (8)
	{ 2.48 ± 0.08 (2)	2.27 ± 0.03 (2)	2.99 ± 0.17 (4)	2.79 ± 0.09 (4)
Mo(2), (3)	{ 1.91 ± 0.06 (4)	1.86 ± 0.09 (2 × 4)	2.77 ± 0.12 (8)	2.74 ± 0.11 (2 × 8)
	{ 2.16 ± 0.20 (2)	2.18 ± 0.15 (2 × 2)	2.84 ± 0.18 (4)	2.78 ± 0.18 (2 × 4)
K(2)	2.81 ± 0.09 (8)	2.84 ± 0.05 (7)		
K(1)	—	3.02 ± 0.22 (10)		

would be low. Ideal unit-cell dimensions are shown in Table 6.

Finally it should be noted that Fig. 5, by emphasizing the similarities of packing, also offers a logical explanation for red and blue bronzes existing as parallel domains within certain crystals. We believe that this intergrowth between two or more structures could persist at the unit cell level, and perhaps for this reason a high degree of structure refinement is not achieved, and the questions of exact composition remain largely unresolved.

We wish to express our appreciation to Dr J.C.B. White for the use of his version of the ORFLS program on the IBM 7044 computer at Melbourne University.

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The Crystal and Molecular Structure of 3,3'-Bi-2-isoxazoline

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(Received 16 March 1965)

The structure of 3,3'-bi-2-isoxazoline, $C_6H_8N_2O_2$, a novel product of the reaction of ethylene and nitrogen dioxide, has been determined from three-dimensional scintillation-counter $Cu K\alpha$ diffraction data. The crystals are orthorhombic with space group $Iba2$; four molecules per unit cell. The unit cell constants are: $a = 8.92_2$, $b = 10.50_0$, $c = 7.04_2$ Å.

The positional and anisotropic thermal parameters were refined by full-matrix least-squares methods.

The molecule consists of two bridged five-membered isoxazoline rings. The conjugated bridging C-C bond was found to be 1.42 ± 0.02 Å. The molecule is essentially planar.

Introduction

One of the hitherto unreported products of the reaction of ethylene and nitrogen dioxide in anhydrous carbon tetrachloride is 3,3'-bi-2-isoxazoline, $C_6H_8N_2O_2$. In contrast to the previously known products of the reaction, which are all either unstable or explosive (Levy & Rose, 1947; Levy & Scaife, 1946; Levy, Scaife & Smith, 1946), the new product is most unusual for its inertness to common reagents and its marked thermal stability.

Although several substituted bi-isoxazolines are described in the literature (Quilico & Grunanger, 1952; Quilico, Grunanger & Mazzini, 1952), this appears to be the first parent compound prepared in any of the isomeric bi-isoxazoline series.

From the consideration of the chemical and physical properties, including infrared and ultraviolet absorption data, and nuclear magnetic resonance (Soffer, 1966), it is evident that the molecule is heterocyclic with both the oxygen and nitrogen in the ring. These data indicated either (I) or (II) as possible structures. Both satisfy the diffraction data requirements of a two-fold axis and near planarity. The preliminary X-ray structure analysis as reported by Bednowitz & Fan-

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