of their low-temperature ultraviolet spectral data for [18]annulene. They have not offered an alternative explanation for the position, or the intensity, of the ultraviolet absorption except to suggest that these effects, as well as the nuclear magnetic resonance spectrum of [18]annulene (Jackman, Sondheimer, Amiel, Ben-Efraim, Gaoni, Wolovsky & Bothner-By, 1962), may all be due to some unknown factor that reduces the mobility of the π electrons around the aromatic ring. If their suggestion is accepted, the observed variation in bond lengths may, perhaps, fill the role of the postulated unknown factor. Qualitatively, this is the behavior we should expect; the π electrons will tend to be localized in the six pairs of shorter, inner bonds as a result of the smaller resonance integral of the outer bonds, which acts as a slight barrier between neighboring inner-bond pairs. We have not attempted a quantitative estimate of this effect in view of the uncertainty as to the reason, or reasons, for the bond-length variation.

The problems just considered, as well as the inconclusive result of the calculation of the out-of-plane deformation, point to the need for further theoretical study of this most challenging molecule.

We are grateful to Professor Franz Sondheimer and Dr Reuven Wolovsky for their encouragement of this investigation. We also benefited from stimulating discussions with Professor C. A. Coulson and, by correspondence, with Mr C. W. Haigh. Mr Reuben Cohen prepared the diagrams.

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The Crystal Structure of the Red Potassium Molybdenum Bronze, $K_{0\cdot26}MoO_3$

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$K_{0\cdot26}MoO_3$ crystallizes in the monoclinic system, space group $C2/m$, with the unit-cell dimensions $a=14\cdot278$, $b=7\cdot723$, $c=6\cdot387$ Å, $\beta=92°\ 34'$. Its structure, determined by image-seeking and refined by three-dimensional differential Fourier syntheses and also by least squares, contains distorted Mo–O octahedra grouped by edge-sharing into units of six. These units share corners and form layers, with potassium ions occupying irregular eight-coordinated interlayer positions. Similarities to molybdenum oxides and oxyacids are discussed.

Introduction

The term *bronze* is used as a trivial name to describe a class of transition-metal oxide incorporating variable amounts of a third element, which is usually an alkali metal. Although the alkali tungsten bronzes were first prepared by Wöhler about 1824, it was not until recent years that the class was widened to include certain oxides of titanium, vanadium, niobium, platinum and palladium instead of tungsten. The crystal structures they adopt are not necessarily similar to one of the three known classes of tungsten bronze, and altogether the category is a wide one, with a classification more appropriately based on physical properties than upon crystal structure (Andersson & Wadsley, 1962).

Wold, Kunnmann, Arnott & Ferretti (1964) recently succeeded in preparing two potassium molybdenum bronzes by electrolysing fused mixtures of K_2MoO_4 and MoO_3 under rigidly restrictive conditions. The first, with the empirical composition $K_{0\cdot26}MoO_3$, was a typical semi-conductor, and the determination of its crystal structure is now reported. The second, $K_{0\cdot28}MoO_3$, behaved as a metal above −100 °C, and will be described shortly (Graham & Wadsley, 1965).

Experimental

The crystals, kindly donated by Professor Aaron Wold, Brown University, Rhode Island, U.S.A., were thin monoclinic reddish plates, elongated along *b*, with {100} the predominant form. The unit-cell data, listed in Table 1, were obtained from a powder photograph taken with a Guinier-type focusing camera. An internal potassium chloride standard was used for calibration, and indices were assigned on the basis of preliminary lattice constants obtained from precession photographs, which were then refined by a least-squares treatment (Cohen, 1936) with the final values not differing by more than 0·5% from the preliminary estimates.

Table 1. *Crystallographic data for* $K_{0\cdot26}MoO_3$

Symmetry:	monoclinic
Unit-cell dimensions:	$a = 14{\cdot}278 \pm 0{\cdot}008$ Å $b = 7{\cdot}723 \pm 0{\cdot}005$ $c = 6{\cdot}387 \pm 0{\cdot}004$ $\beta = 92°34' \pm 5'$
Absent reflexions:	$h+k \neq 2n$
Possible space groups:	$C2$, Cm, $C2/m$
D_x	4·36 g.cm^{-3}
D_m	4·32 g.cm^{-3}
μ	542 cm^{-}

The X-ray data were all collected from the one crystal with the dimensions 0·45 × 0·06 × 0·02 mm. Intensities for the reciprocal lattice layers $k = 0, 1, 2 \cdots 6$, were recorded on multifilms, the equi-inclination Weissenberg technique being used with Cu $K\alpha$ radiation, and were estimated by eye against a standard scale prepared in the usual manner. Correlation intensity data were measured photometrically from zero layer ($hk0$) precession photographs ($\mu = 30°$, Mo $K\alpha$ radiation) and corrected for Lorentz and polarization effects with the use of a transparent overlay based upon the chart prepared by Waser (1957). The resulting scaling factors for layers $k = 0$ to 6 were later adjusted as structure parameters during refinement.

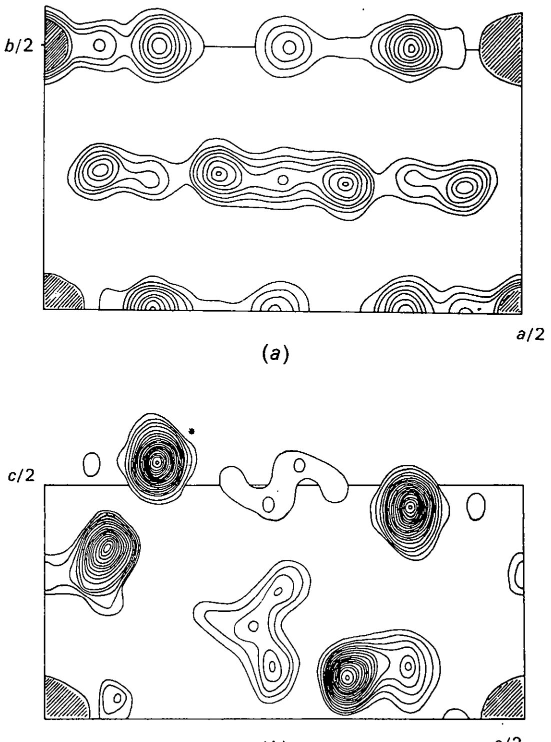
Absorption corrections, A, in the expression $I_{corr} = AI_{obs}$ ranging from 3·4 to 50·0 were applied to the intensities by Lovell's method (1961), a procedure based upon that of Busing & Levy (1957). Subsequently it was estimated that these corrections resulted in an overall decrease of 5% in the reliability index R. Scattering curves for K^+, O^- and Mo were obtained from *International Tables for X-ray Crystallography* (1962), with the real dispersion correction applied to Mo. All calculations were made on UTECOM, a Deuce electronic digital computer at the University of New South Wales, with programs written by Drs J. S. Rollett and J. Sime.

A total of 652 non-symmetry-related reflexions *hkl* were examined. These observed data, scaled by comparison with structure factors calculated for one-eighth the unit cell contents, are listed in Table 2.

Structure determination

The statistical distribution test of Howells, Phillips & Rogers (1950) was applied to the intensities of the zones *h*0*l* and *hk*0, and the results favoured the centrosymmetric space group $C2/m$. The projection $P(u, v)$ [Fig. 1(*a*)] consisted essentially of strong positive regions parallel to the **z** direction and centred in the sections $y/b = 0$, $\frac{1}{4}$ and $\frac{1}{2}$. All the atoms comprising the structure are therefore situated in, or close to planes normal to the y axis and $b/4$ Å apart, confirming $C2/m$ as the most probable space group.

Octahedra may share corners to form an endless linear string, or edges to form a zigzag string, and the



(*a*)

(*b*)

Fig. 1. (*a*) Patterson function, $P(u, v)$. (*b*) Patterson function $P(u, w)$. The vector marked with the asterisk was used to plot the (010) minimum function in Fig. 2(*a*).

Table 2. *Structure factor data*

Within each group of constant *l*, the columns contain, from left to right: *h*, *k*, 1·25 F_o and 1·25 F_c. Missing reflexions are omitted.

l = 0

4	0	178	-147
6	0	154	-146
8	0	229	-217
10	0	174	-146
12	0	92	-96
14	0	48	41
16	0	197	201
18	0	92	92
3	1	149	-139
5	1	180	-156
7	1	121	103
9	1	135	127
11	1	103	-104
13	1	43	-25
15	1	31	35
17	1	30	26
2	2	295	-297
4	2	139	-153
6	2	194	407
8	2	285	335
10	2	132	121
12	2	104	-94
14	2	104	-102
16	2	58	-42
1	3	175	180
3	3	62	-65
5	3	169	-122
7	3	70	49
9	3	73	61
11	3	115	-114
13	3	33	-19
15	3	55	61
17	3	54	57
4	4	128	-110
6	4	115	-114
8	4	150	-159
10	4	129	-116
12	4	75	-81
14	4	36	31
16	4	123	166
3	5	146	-107
5	5	125	-100
7	5	119	107
9	5	143	134
11	5	65	-57
13	5	33	-23
2	6	160	-151
4	6	82	-90
6	6	101	116
8	6	220	208
10	6	86	87
12	6	68	-58
14	6	60	-70

l = 1

0	0	155	-164
2	0	151	-181
-2	0	32	49
4	0	203	-257
-4	0	427	484
6	0	231	-220
-6	0	526	563
8	0	153	-129
-8	0	64	23
10	0	188	211
-10	0	159	-170
12	0	236	268
-12	0	113	-117
14	0	60	61
-14	0	85	-99
-16	0	-73	-64
-18	0	13	-23
1	1	13	-12
-3	1	53	-40
3	1	281	221
-5	1	88	85
5	1	32	-14
-7	1	117	75
7	1	128	-115
9	1	26	17
-9	1	159	-170
-11	1	17	-24
11	1	71	79
-13	1	117	113
13	1	17	-10
13	1	54	-51
-17	1	59	-55
17	1	31	-37
0	2	61	-59
-4	2	138	-137
4	2	156	158
-6	2	131	-147
6	2	67	68
-8	2	180	-176
8	2	107	-98
-10	2	69	48
10	2	102	-97
-12	2	179	190
12	2	65	-40
-14	2	170	188
14	2	144	-171
-16	2	33	15
16	2	74	-78
-1	3	82	-83
1	3	65	-36
3	3	175	117
-5	3	177	154
5	3	107	63
-7	3	448	115
7	3	160	-129
9	3	47	46
-9	3	154	-149
-11	3	51	-44
11	3	118	123
-13	3	84	72
13	3	35	33
-15	3	18	-27
15	3	33	-23
-17	3	52	-51
17	3	30	-37
-4	4	285	338
4	4	222	-186
-6	4	351	386
6	4	203	-174
-8	4	25	6
8	4	109	-99
-10	4	106	-136
10	4	147	163
-12	4	99	-97
12	4	190	217
-14	4	65	-80
14	4	47	46
-1	5	118	-140
1	5	16	15
-3	5	85	-80
5	5	53	40
-7	5	25	7
7	5	73	-64
-9	5	99	[illegible]
-11	5	17	3
-13	5	113	113
13	5	45	-42
15	5	43	-57
0	6	[illegible]	-27
-2	6	182	[illegible]
2	6	203	[illegible]
-4	6	87	-77
4	6	156	131
-6	6	69	-74
6	6	51	50
8	6	78	-60
-8	6	84	-103
-10	6	36	33
10	6	56	-57
-12	6	116	127
12	6	41	-23
-14	6	141	128

l = 2

0	0	364	-371
2	0	339	[illegible]
-2	0	116	-115
4	0	58	61
-4	0	39	-32
6	0	335	336
-6	0	117	-73
8	0	358	337
-8	0	213	214
10	0	65	47
-10	0	309	316
12	0	26	25
-12	0	90	129
-14	0	57	-53
16	0	139	-148
-16	0	65	-134
-1	1	164	172
1	1	124	-126
-3	1	65	73
3	1	117	-118
-5	1	41	-37
5	1	152	141
-7	1	130	-106
7	1	26	33
9	1	69	-75
-11	1	97	91
11	1	78	-81
-13	1	25	-27
13	1	58	43
-15	1	90	-95
15	1	76	64
-17	1	51	48
17	1	36	-45
0	2	198	225
-2	2	144	189
2	2	53	30
-4	2	98	140
4	2	90	-76
-6	2	236	-261
6	2	46	-18
-8	2	237	-240
8	2	192	-199
-10	2	56	-36
10	2	217	-286
-12	2	57	-84
12	2	44	37
-14	2	28	-22
14	2	153	165
-16	2	78	73
16	2	88	82
-1	3	76	75
1	3	177	-166
-3	3	23	28
3	3	96	-86
-5	3	45	-29
5	3	176	173
-7	3	54	-29
7	3	93	91
-9	3	63	75
-11	3	123	122
11	3	59	-55
13	3	35	29
-15	3	104	-103
15	3	45	33
-17	3	12	23
0	4	272	-268
-2	4	76	-89
2	4	195	-244
-4	4	20	-25
4	4	45	39
-6	4	80	-56
6	4	280	258
-8	4	163	152
8	4	253	249
-10	4	193	249
10	4	43	29
-12	4	76	96
12	4	14	19
-14	4	44	-48
-16	4	75	-112
-1	5	145	161
1	5	43	-37
-3	5	89	90
3	5	92	-78
-5	5	39	-35
5	5	84	57
-7	5	140	-120
7	5	28	-27
9	5	93	-99
-9	5	54	-44
11	5	71	-71
-11	5	46	36
-13	5	20	-30
13	5	54	39
-15	5	37	-58
0	6	102	136
-2	6	127	150
2	6	28	22
-4	6	88	88
4	6	52	-38
6	6	33	-12
-6	6	149	-160
-8	6	132	-146
8	6	117	-121
-10	6	35	-19
10	6	143	-182
12	6	28	29
-12	6	32	-52
-14	6	11	-11

l = 3

0	0	[illegible]	182
2	0	515	543
-2	0	133	-149
4	0	200	+195
-4	0	369	-379
6	0	46	48
-6	0	251	-236
8	0	117	55
-8	0	57	52
10	0	114	-144
-10	0	41	-8
12	0	239	-240
-12	0	54	48
14	0	87	-77
-14	0	161	186
16	0	49	36
-16	0	110	108
-1	1	43	30
1	1	148	168
-3	1	130	-171
3	1	89	-94
-5	1	21	4
5	1	136	-134
-7	1	128	129
7	1	22	19
9	1	104	76
-11	1	48	-42
11	1	32	18
-13	1	81	-58
13	1	93	-105
-15	1	49	52
15	1	23	24
-17	1	32	42
0	2	19	22
-2	2	96	63
2	2	177	-150
-4	2	107	104
4	2	393	-393
-6	2	205	241
6	2	170	-176
-8	2	156	153
8	2	155	152
-10	2	143	-130
10	2	182	188
12	2	63	52
-12	2	192	-200
-14	2	106	-93
14	2	13	23
-16	2	21	-14
-1	3	38	42
1	3	172	200
-3	3	161	-167
3	3	17	-4
-5	3	47	-53
-7	3	69	71
7	3	45	36
9	3	69	54
11	3	20	-20
-13	3	36	-9
13	3	107	-110
-15	3	74	82
0	4	117	137
-2	4	88	-117
4	4	144	137
-6	4	160	-181
6	4	36	32
-8	4	34	39
8	4	80	74
10	4	108	-116
-10	4	19	-9
12	4	173	-197
-12	4	37	36
-14	4	126	152
14	4	62	-64
-1	5	28	16
1	5	67	67
-3	5	-84	-95
3	5	128	-122
-5	5	53	50
5	5	127	-128
-7	5	139	128
9	5	88	70
11	5	50	46
-11	5	65	-50
13	5	45	-49
-13	5	87	-80
-2	6	65	41
2	6	94	-81
-4	6	68	67
4	6	246	-233
-6	6	140	153
6	6	136	-113
-8	6	117	105
8	6	107	106
10	6	124	125
-10	6	89	-84
-12	6	113	-135
12	6	33	36

l = 4

0	0	94	113
2	0	92	124
-2	0	206	262
4	0	27	5
-4	0	278	338
6	0	263	-274
-6	0	72	25
8	0	262	-222
-8	0	243	-251
10	0	63	-51
-10	0	285	-235
12	0	101	96
-12	0	34	-31
14	0	108	108
-14	0	56	53
-16	0	37	11
1	1	33	-31
-1	1	133	-159
-3	1	16	10
3	1	91	83
5	1	67	52
-7	1	85	85
7	1	78	62
9	1	68	-46
-9	1	76	-75
11	1	89	79
-11	1	53	46
-13	1	59	50
13	1	43	43
15	1	68	-71
0	2	322	-323
-2	2	172	-255
2	2	53	-55
-4	2	64	-62
4	2	202	248
-6	2	84	103
6	2	47	64
-8	2	121	84
8	2	59	50
-10	2	122	99
10	2	85	87
-12	2	159	174
14	2	84	-75
-14	2	23	[illegible]
-1	3	73	-78
1	3	22	27
-3	3	57	67
3	3	73	[illegible]
-5	3	168	150
5	3	[illegible]	12
-7	3	93	-95
7	3	115	-98
-9	3	34	-99
9	3	100	-75
11	3	80	72
-13	3	39	32
13	3	66	65
-15	3	13	7
0	4	63	80
-2	4	138	197
2	4	76	94
-4	4	193	249
-6	4	49	17
6	4	205	[illegible]
-8	4	209	-203
8	4	211	[illegible]
10	4	44	[illegible]
-10	4	150	-134
-12	4	25	-23
12	4	71	77
-14	4	34	44
1	5	66	-64
-1	5	144	-162
3	5	67	55
-3	5	29	-37
-5	5	110	96
5	5	86	69
-7	5	35	-44
-11	5	[illegible]	63
11	5	62	62
-13	5	49	49
0	6	208	-205
-2	6	148	-155
2	6	40	-10
4	6	171	161
-4	6	39	-10
-6	6	66	69
6	6	49	45
-8	6	84	57
8	6	33	37
10	6	54	61
-10	6	66	63

l = 5

0	0	58	-73
2	0	243	-312
-2	0	125	114
4	0	178	-208
-4	0	83	108
-6	0	145	136
6	0	56	50
8	0	105	89
-8	0	165	154
10	0	137	108
-10	0	106	117
12	0	133	92
-12	0	56	-62
-14	0	153	-209
-1	1	40	54
-3	1	79	78
3	1	55	-72
-5	1	111	-105
5	1	24	17
-7	1	[illegible]	-79
7	1	[illegible]	115
9	1	59	-45
-9	1	105	83
11	1	89	-84
-11	1	52	38
-13	1	62	-66
13	1	23	24
0	2	95	92
-2	2	51	92
2	2	53	45
-4	2	173	-204
4	2	147	127
-6	2	254	-254
6	2	136	114
-8	2	104	-90
8	2	58	-31
10	2	171	-159
-10	2	74	44
-12	2	92	101
12	2	146	-171
-14	2	44	35
-1	3	26	37
1	3	56	-46
-3	3	93	99
3	3	112	-116
-5	3	48	-35
-7	3	45	-25
7	3	122	119
-9	3	111	103
-11	3	33	29
11	3	40	-38
-13	3	75	-86
0	4	59	-60
-2	4	117	93
2	4	214	-255
-4	4	65	83
4	4	139	-167
-6	4	104	107
6	4	43	39
-8	4	118	122
8	4	83	71
-10	4	71	91
10	4	93	86
-12	4	31	-52
-1	5	55	50
1	5	23	29
-3	5	42	34
-5	5	140	-125
5	5	40	30
-7	5	111	-99
7	5	75	75
9	5	55	-61
-9	5	53	50
11	5	86	-96
0	6	54	69
-2	6	46	63
2	6	35	29
-4	6	126	-135
4	6	93	88
-6	6	151	-164
6	6	83	80
-8	6	50	-57
8	6	26	-21

l = 6

0	0	73	-56
2	0	40	39
-2	0	284	-297
4	0	136	106
-4	0	203	-184
6	0	157	127
-6	0	99	101
8	0	167	149
-8	0	147	106
10	0	109	114
-10	0	89	92
-12	0	48	73
1	1	85	83
-3	1	55	-58
3	1	57	55
5	1	113	-122
-7	1	75	70
7	1	44	-35
9	1	79	78
-11	1	101	-97
0	2	209	195
-2	2	82	69
2	2	87	100
-4	2	69	55
4	2	143	-135
-6	2	38	54
6	2	191	-232
-8	2	112	-82
8	2	97	-89
-10	2	148	-168
10	2	37	39
-12	2	97	-130
-1	3	52	-59
1	3	66	65
-3	3	92	-95
3	3	69	68
5	3	78	-69
-7	3	86	77
-9	3	40	37
9	5	101	92
-11	3	51	-50
0	4	53	-45
-2	4	198	-243
2	4	33	30
4	4	102	82
-4	4	157	-151
-6	4	83	83
6	4	102	101
-8	4	111	86
8	4	101	118
-10	4	53	74
1	5	85	72
-1	5	27	8
3	5	31	27
-5	5	14	25
5	5	106	-127
-7	5	45	44
7	5	48	-57
0	6	137	136
-2	6	53	45
2	6	54	67
-4	6	34	36
4	6	77	-89
-6	6	19	43

l = 7

0	0	81	75
2	0	187	163
-2	0	71	47
4	0	194	172
6	0	31	23
-6	0	174	-157
8	0	143	-170
-8	0	185	-202
-10	0	15	-13
-1	1	54	-55
1	1	115	-99
-3	1	90	85
3	1	61	54
-5	1	36	28
5	1	66	52
7	1	57	-53
-9	1	44	-46
0	2	182	-198
-2	2	45	-34
2	2	169	-146
-4	2	194	202
4	2	60	-51
-6	2	149	125
6	2	38	39
-8	2	37	19
-1	3	27	-24
1	3	69	-53
-3	3	74	74
3	3	98	88
5	3	80	66
-7	3	36	-57
0	4	51	58
-2	4	43	34
2	4	115	131
-6	4	79	-131
-1	5	44	-62
1	5	114	-109
-3	5	44	68

l = 8

0	0	95	102
-2	0	133	178
2	0	42	55
-4	0	74	93
-1	1	74	86
1	1	25	-18
-3	1	29	-25

structures of many metallic oxides contain these two kinds of simple unit grouped together in various ways. If the metal–oxygen bond distance is assumed to be approximately 2·0 Å, one would expect heavy Mo–Mo vectors to appear within a distance of 4 Å from the origin of the Patterson function. In the projection $P(u, w)$ a very heavy peak [marked with an asterisk in Fig. 1(*b*)] corresponds to octahedra sharing a corner, and this vector was subsequently used to plot a (010) minimum function [Fig. 2(*a*)], the symmetry indicating that a simple centrosymmetric vector had been chosen for the origin shift. The peak heights and distribution of the electron density projection $\varrho(x, z)$ [Fig. 2(*b*)] confirmed this model, where the atoms could all be placed in the four- and eightfold positions of $C2/m$.

The contents of the unit cell are $K_4Mo_{12}O_{36}$ when the sites are fully occupied. The empirical formula of the bronze is more nearly $K_3Mo_{12}O_{36}$, and the fourfold potassium site evidently is only partially occupied. In the calculation of structure factors the atomic scattering curve for potassium was therefore scaled down to three-quarters of its normal value, giving a statistical distribution of three atoms over four positions. This led to a reasonable agreement between observed and calculated peak heights (Table 3).

The proposed structure gave an initial reliability index R, of 30% for all observed reflexions. Successive cycles of differential syntheses and structure factors, in which the positional and isotropic thermal parameters of all atoms were allowed to vary, reduced this value to 16%. After each cycle the scaling factors for layers $k=0$ to 6 were adjusted by comparison with the calculated structure amplitudes. Further refinement was carried out by a diagonalized least-squares procedure in which $\Sigma w(|F_o|-|F_c|)^2$ was minimized. The weight w, assigned to each reflexion was:

$$|F_o| \le 5|F_{min}|,\ w=(F_o/5F_{min})^2;$$
$$|F_o| > 5|F_{min}|,\ w=(5F_{min}/F_o)^2.$$

Owing to the limited storage capacity of the computer only the molybdenum atomic parameters were refined and at a scale which was one-eighth absolute. After two cycles the reliability index reduced to 13·4%. The final shifts in the heavy atom positions were only 0·001 Å. Further refinement extended to the remaining atoms together with the introduction of an occupancy factor for the potassium atom in the least-squares program would be desirable, but the computing facilities did not enable this procedure to be followed.

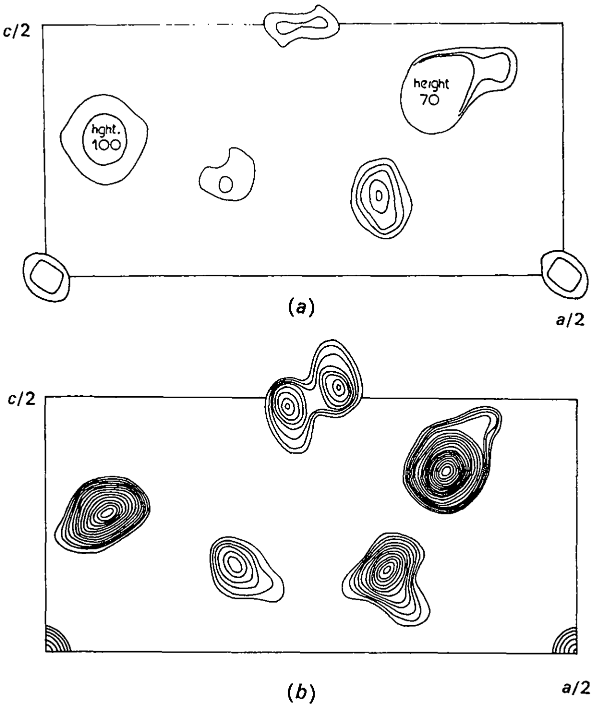


Fig. 2. (*a*) Minimum function $M(u, w)$ based upon the peak marked with an asterisk in Fig. (1*b*). (*b*) Electron density projection (x, z); contours at equal but arbitrary intervals, zero contour omitted.

Table 3. *Atomic peak heights and curvatures*

Atom		Height (e.Å^{-3})	Curvature (e.Å^{-5})					
			$-A(HH)$	$-A(KK)$	$-A(LL)$	$A(HK)$	$A(HL)$	$A(KL)$
K	obs.	43·5	921	606	1114	−4	+39	−560
	calc.	37·3	838	555	934	−31	+8	−489
Mo(1)	obs.	125·0	2973	1823	3121	−126	+106	−1559
	calc.	127·6	3122	1937	3034	−88	+132	−1606
Mo(2)	obs.	125·4	2911	1942	3236	−82	+147	−1604
	calc.	132·0	3234	2109	3261	−45	+196	−1709
O(1)	obs.	11·5	300	75	494	−60	−161	−129
	calc.	12·5	318	106	448	−60	−129	−152
O(2)	obs.	11·6	135	97	381	−62	−35	−136
	calc.	12·0	137	92	371	− 45	−27	−136
O(3)	obs.	10·2	147	70	311	+154	−2	−56
	calc.	12·5	209	124	371	+155	−26	−112
O(4)	obs.	12·2	215	34	332	−26	−39	−42
	calc.	10·7	155	67	324	−35	−46	−44
O(5)	obs.	11·2	180	65	265	−25	−69	−67
	calc.	11·6	213	76	267	−59	−120	−70
O(6)	obs.	8·4	333	108	126	−3	+30	−81
	calc.	10·9	424	137	204	−1	+52	−103
O(7)	obs.	19·2	60	337	495	−8	+9	−201
	calc.	18·1	38	297	412	+1	−39	−173

The final atomic coordinates are listed in Table 4 and the parameters of the temperature factor expression

$$T = 2^{-(b_{11}h^2+b_{22}k^2+b_{33}l^2+b_{23}kl+b_{13}hl+b_{12}hk)}$$

in Table 5. The estimated standard deviations in atomic positional parameters were calculated according to Cruickshank (1949). The structure in projection is illustrated by Fig. 3.

Description

The preliminary description is made easier if the molybdenum coordination is considered to be regular and octahedral. Two octahedra are centred about each of the levels $y=\frac{1}{4}$, $\frac{1}{2}$, and $\frac{3}{4}$ (as well as $y=\frac{3}{4}$, 0, $\frac{1}{4}$) where they join in pairs with common edges. These pairs form compact groups of six by additional edge-sharing [Fig. 4(*a*)], which then join up with similar groups above and below by corner-sharing [the atoms O(4)], and run throughout the structure in the [010] direction. The infinite linear groups are next linked together by additional corner sharing [the atoms O(1)], forming infinite two-dimensional sheets, each of which is centred around (100) [Fig. 4(*b*)]. Identical sheets are separated by a distance of *a*/2, but displaced relative to each other by a distance of *b*/2 in the [010] direction, a consequence of the side-centring. Finally the layers are joined together by the large potassium ions which are in an irregular eightfold coordination with four oxygens from each of two adjacent sheets.

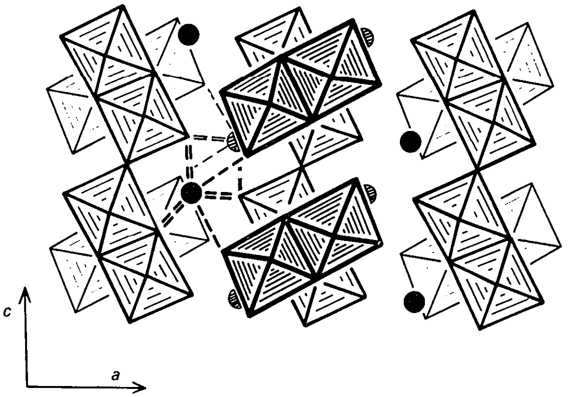


Fig. 3. The octahedral structure of $K_{0\cdot26}MoO_3$ projected on to (010). The black and hatched circles are potassium ions at $y=\frac{1}{2}$ and 0 respectively, with their bonds to oxygen drawn as broken lines.

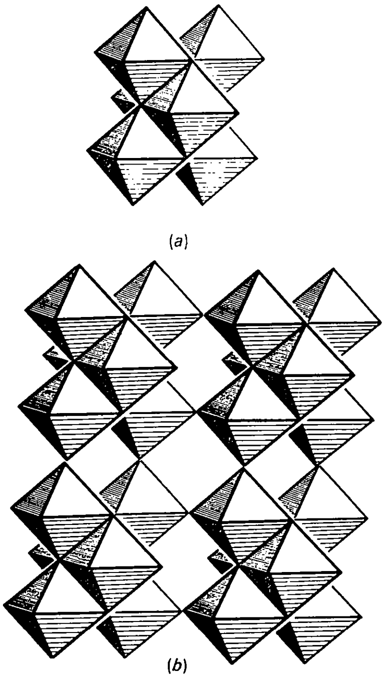


Fig. 4. (*a*) Group of six idealized octahedra forming the basis of the octahedral structure. A hypothetical polyanion $(Mo_6O_{22})^{8-}$. (*b*) The groups of Fig. 4(*a*) join by common corners giving the sheets in the structure of $K_{0\cdot26}MoO_3$.

Table 4. *Fractional atomic coordinates and standard deviations* (Å)

Space group *C*2/*m*, (0, 0, 0) ($\frac{1}{2}$, $\frac{1}{2}$, 0)+

Atom	Point position	*x*	*y*	*z*	σ(*x*)	σ(*y*)	σ(*z*)
$\frac{3}{4}$ K	4(*i*)	0·3167	0	0·1634	0·004	0	0·003
Mo(1)	4(*i*)	0·1235	0	0·6393	0·001	0	0·001
Mo(2)	8(*j*)	0·0597	0·2610	0·2699	0·001	0·001	0·001
O(1)	4(*h*)	0	0·278	0	0	0·03	0
O(2)	4(*i*)	0·225	0	0·521	0·02	0	0·02
O(3)	4(*i*)	0·155	0	0·929	0·02	0	0·02
O(4)	4(*i*)	0·542	0	0·290	0·02	0	0·02
O(5)	4(*i*)	0·052	0	0·293	0·02	0	0·02
O(6)	8(*j*)	0·182	0·259	0·179	0·02	0·02	0·03
O(7)	8(*j*)	0·086	0·242	0·572	0·05	0·02	0·02

Table 5. *Thermal parameters used for the final calculations of structure amplitudes*

Atom	b_{11}	b_{22}	b_{33}	b_{23}	b_{13}	b_{12}
Mo(1)	0·0024	0·0100	0·0059	0·0000	0·0005	0·0000
Mo(2)	0·0029	0·0082	0·0073	0·0010	0·0010	−0·0006

K	$B=1\cdot35$ Å^2
Oxygen atoms	$B=2\cdot60$ Å^2

The interatomic distances are summarized in Table 6. Both of the molybdenum–oxygen octahedra are irregular. There are five Mo(2)–O bonds varying between 1·87 and 2·02 Å with a sixth at 2·35 Å, and four Mo(1)–O bonds 1·67 to 1·99 Å with two more at 2·39 and 2·56 Å.

Table 6. *Interatomic distances* (Å)

Mo(1)–O(2)	1·67	Mo(2)–O(6)	1·87
–O(3)	1·89	–O(1)	1·89
–O(7)	1·99 (2)	–O(7)	1·96
–O(5)	2·39	–O(7′)	2·35
–O(7′)	2·56	–O(4)	1·87
O(3)–O(5)	3·22	–O(5)	2·02
O(5)–O(5′)	3·09	O(7)–O(7′)	2·58
O(5′)–O(2)	2·81	O(7′)–O(1)	3·06
O(2)–O(3)	2·83	O(1)–O(6)	2·80
O(2)–O(7)	2·76	O(6)–O(7)	2·92
O(2)–O(7′)	2·81	O(6)–O(4)	2·84
O(3)–O(7)	3·08 (2)	O(6)–O(5)	2·85
O(5)–O(7)	2·61 (2)	O(7)–O(5)	2·61
O(5)–O(7′)	2·88 (2)	O(7)–O(4)	2·74
		O(7′)–O(5)	2·88
K–O(6)	2·78 (2)	O(7′)–O(4)	2·74
–O(6′)	2·87 (2)	O(1)–O(5)	2·92
–O(7)	2·92 (2)	O(1)–O(4)	2·57
–O(3)	2·69		
–O(2)	2·68		

This appears to be typical for molybdenum oxides. Kihlborg (1963*a*) showed that the octahedral distances in MoO_3 ranged from 1·67 to 2·33 Å, and considered an alternative tetrahedral coordination by discarding the two oxygen atoms forming the longest bonds. The structure described in this way lent support to the proposal of polymeric gaseous species $(MoO_3)_n$ formed at high temperatures (Berkowitz, Inghram & Chupka, 1957). Kihlborg (1963*b*) has also discussed the structures of certain reduced molybdenum oxides, where the oxidation numbers for Mo are of the same order of magnitude as in the molybdenum bronze. In all acses there are considerable variations in bond distances, not only between compounds, but for crystallographically different quasi-octahedral metal atoms within the one structure. Although no satisfactory explanation can be found by favouring one kind of polyhedron, it is quite clear that Mo–O distances in oxides vary only between 1·73 and 1·82 Å where tetrahedral coordination is completely unambiguous (Ibers & Smith, 1964). This appears to be restricted to certain classes of compound where Mo is hexavalent.

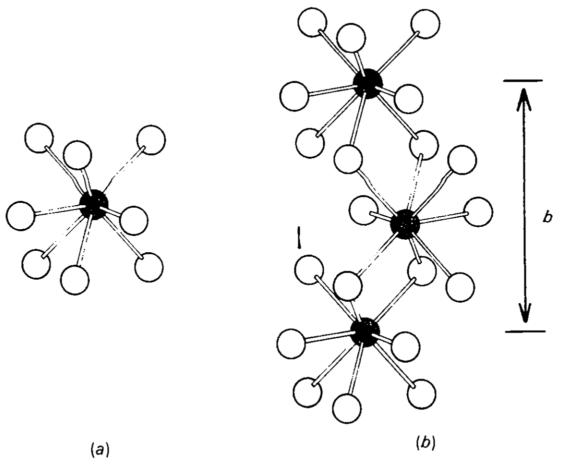
Any adjacent pair of metal atoms in a single group of six [Fig. 2(*a*)] will be separated by about 2·7 Å if the octahedra in the bronze are perfectly regular. Short distances of this order have been reported, but are confined to oxides of Mo^{5+} (McCarroll, Katz & Ward, 1957) or Mo^{4+} (Magnéli & Andersson, 1955) where they evidently reflect some form of bonding between the metal atoms. The structure of $Mo_{17}O_{47}$, on the other hand, which is predominantly octahedral, is the only higher oxide of molybdenum containing a short Mo–Mo distance of 2·62 Å (Kihlborg, 1960), and this could be due to bonding between localized metal atoms of lower valency.

The nearest neighbour Mo–Mo distances in the present case vary between 3·20 and 3·88 Å, and are in good agreement with the values for all other reduced molybdenum oxides with oxidation numbers intermediate between 5·5 and 6 (Kihlborg, 1963*b*). There are therefore no metal–metal bonds in the bronze, and the octahedra, particularly the one centered about Mo(1), are distorted simply because the metal ions carry a high charge and repel each other. These forces are evidently strong enough to increase the lengths of some Mo(1)–O bonds to such a degree that the environment of this atom becomes virtually tetrahedral.

Potassium is bonded to eight oxygen atoms, six at the corners of a trigonal prism at distances of 2·78, 2·87 and 2·92 Å (all twice) and two more at 2·68 and 2·69 Å situated beyond the centres of two prism faces [Fig. 5(*a*)]. An alternative description is a distorted square Archimedean antiprism. These polyhedra unite with a common edge forming zigzag chains [Fig. 5(*b*)], a modification of the type of coordination for the sodium ions in the vanadium bronze $Na_{2-x}V_6O_{15}$ (Wadsley, 1955). The alkali metals occupy the best positions available to them, their main function being to bind the octahedral layers together.

Discussion

The potassium molybdenum bronze is an example of a simple binary oxide adopting a structure entirely different from its normal one when it is crystallized in the presence of ions too large to be substituents. Although it has little formal resemblance to any particular molybdenum oxide, it can nevertheless be compared to the isopolyacids of molybdenum, tungsten and niobium. The octa- and heptamolybdates contain the discrete anions $(Mo_8O_{26})^{4-}$ and $(Mo_7O_{24})^{6-}$ built up of Mo–O octahedra sharing edges (Lindqvist, 1950*a*, 1950*b*), bearing a striking resemblance to the units of



(*a*) (*b*)

Fig. 5. (*a*) Eightfold oxygen environment of K. (*b*) Zigzag chains of K–O polyhedra.

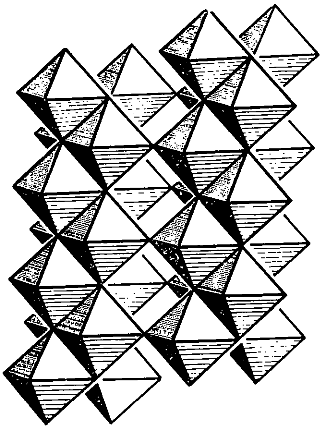


Fig. 6. Octahedral structure of $CoMoO_4$ (Smith & Ibers, 1965) containing octahedral strings, related to those in Fig. 4(*b*), joined by corners.

six octahedra in the bronze. Wells (1962) has drawn attention to a sub-unit of six octahedra common to both anions, and this is almost but not quite the same as Fig. 2(*a*). Both would have the formula $(Mo_6O_{22})^{8-}$. Although an anion with this formula has not been reported in the aqueous chemistry of molybdenum, to the best of our knowledge, it might nevertheless be present in the fused salt system K_2MoO_4–MoO_3 under the precise conditions at which the bronze was formed. Electrolysis of the melt would induce these ions to coalesce into sheets with the formula MoO_3, the presence of potassium ions assuring that they pack together repetitiously to form a crystalline solid.

The units of six octahedra can be expected to condense in a number of ways to give stable structures, related to but differing from that of the bronze. One, which was recently reported by Smith & Ibers for $CoMoO_4$ (1965) and shown in Fig. 6, contains endless doubled octahedral strings formed by these units sharing edges instead of corners which now are no longer recognizable as such. The way any two adjacent strings are joined by common corners is also shown in Fig. 6.

Like all known bronzes $K_{0 \cdot 26}MoO_3$ is chemically and structurally stable. The 'foreign' potassium ions, which are evidently so necessary for it to form, upset the charge distribution and create the anomalies of valency responsible for the characteristic appearance and physical properties of the crystals. As a general rule bronzes are not stoichiometric compounds, as the positions available to the alkali metal atoms are seldom, if ever, completely filled. On purely structural grounds there are no good reasons why this should be so, and $K_{0 \cdot 26}MoO_3$ could be expected from its space group to have a 'saturated' formula $K_{1/3}MoO_3$. It may well be that electrons liberated from the Mo ions by K are raised to energy levels, intermediate between valency and conduction bands, which are filled long before this formula is reached, an approach applied by Frueh (1955) to the problems of a similar kind posed by the electron-deficient mineral stromeyerite.

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