

The Crystal Structure of Na₂Ti₇O₁₅, an Ordered Intergrowth of Na₂Ti₆O₁₃ and 'Na₂Ti₈O₁₇'

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Crystals of Na₂Ti₇O₁₅ were isolated from a specimen of composition Na₂O·Al₂O₃·2TiO₂ heated in a sealed platinum capsule at 1300°C. Their symmetry is monoclinic, space group *C2/m*, with the unit-cell dimensions $a=14.9$, $b=3.74$, $c=20.9$ Å, $\beta=96.5^\circ$. The structure, deduced from the Patterson projection $P(u, w)$ by image-seeking and refined by three-dimensional difference Fourier methods, contains two kinds of condensed Ti–O octahedral group. One is three octahedra wide, joined by multiple edge-sharing to other units of three and forming an endless zigzag ribbon, whilst the other is four wide, but similarly joined. The groups unite with each other by corner-sharing to form a series of open tunnels containing the Na ions. The structure can be regarded as an ordered intergrowth, at the unit-cell level, of sodium hexatitanate Na₂Ti₆O₁₃, and a postulated sodium octatitanate Na₂Ti₈O₁₇.

Introduction

Recently we described the phase NaTi₂Al₅O₁₂ which resulted from an effort to synthesize a compound with the composition NaAlTi₂O₆ (Mumme & Wadsley, 1967). The two metals Ti and Al in the structure proved to be ordered, while the coordination of Al was of two kinds, octahedral and tetrahedral. The association of these same elements in a sodium-containing mixed oxide was reported for non-stoichiometric Na_{*x*}(Al_{*x*}Ti_{1–*x*})O₂, *x* approximately 0.2 (Bayer & Hoffman, 1965), but in this case the role of Al³⁺ was to replace Ti⁴⁺ by an amount necessary to maintain the balance of charge. The compound has the Na_{*x*}TiO₂ structure (Andersson & Wadsley, 1962*b*).

Attempts in this laboratory to prepare NaAlTiO₄, a possible member of an isomorphous group NaA³⁺B⁴⁺O₄ with the CaFe₂O₄ structure (Reid, Wadsley & Sienko, 1967) yielded a heterogeneous matrix containing a small number of colourless needle-like crystals. These were shown by the present structure analysis to be essentially Na₂Ti₇O₁₅, and not an aluminotitanate as originally supposed. This compound proved to be one of a series of structurally related alkali titanates, the already known members being Na₂Ti₃O₇ (Andersson & Wadsley, 1961) and Na₂Ti₆O₁₃ (Andersson & Wadsley, 1962*a*).

Experimental

Sodium oxalate, aluminum oxide and titanium dioxide (anatase) in the molar ratios 1:1:2 were intimately mixed, pre-fired at 900°C to remove carbon dioxide, reground, and heated for 24 hours at 1300°C in a sealed platinum capsule. The small needles were the only crystalline material large enough to manipulate, and no attempt was made to identify the remaining material. The Guinier powder pattern contained few lines, many having indexing ambiguities. The lattice parameters in Table 1 were therefore evaluated from single-crystal films; no greater accuracy than ± 0.1 Å for *a* and *c* could be obtained.

Table 1. Crystallographic constants for Na₂Ti₇O₁₅

Symmetry:	monoclinic
Unit-cell dimensions:	$a=14.9 \pm 0.1$ Å
	$b=3.74 \pm 0.01$
	$c=20.9 \pm 0.1$
	$\beta=96.5 \pm 0.5$
Systematically	
absent reflexions:	hkl with $h+k \neq 2n$
Possible space groups:	<i>C2/m</i> (no. 12), <i>Cm</i> (no. 8), <i>C2</i> (no. 5)
	$D_x=3.57$ g.cm ⁻³
	$Z=4$
	$\mu=322$ cm ⁻¹

Intensities were collected from a crystal measuring $0.05 \times 0.02 \times 0.01$ mm oriented for rotation about the *b* axis, the direction of elongation. The levels hkl , $k=0, 1$ and 2 were recorded on multiple film packs by the integrating Weissenberg method with copper $K\alpha$ radiation. Intensities were estimated visually with a standard scale, and specimen absorption was neglected. Only 167 reflexions, a small fraction of those in the copper sphere, were strong enough to be measurable. Scattering curves for the neutral atoms Ti and Na were taken from *International Tables for X-ray Crystallography* (1962) while Suzuki's (1960) values for O²⁻ were used for oxygen. Structure amplitudes were approximately scaled by Wilson's method, and the individual scale factors adjusted by comparing F_o and F_c before each successive refinement cycle. All calculations were made on the Division's Elliott 803 computer with the programming system of Daly, Stephens & Wheatley (1963), kindly made available by P.J. Wheatley and J.J. Daly.

Structure determination

The Patterson projection $P(u, w)$, consisted of parallel rows of well-defined peaks extending at angles of 80° from the positive direction of the *a* axis, and subdivided into a nearly rectilinear sub-lattice repeating itself fourteen times along *c* (Fig. 1). It could safely be assumed that the *b*-axis length, 3.74 Å, corresponded

to an octahedral body diagonal. Tentative models of the structure in cases such as this can be rapidly assessed by drawing an orthogonal grid of interconnected and overlapping squares each representing an ideal octahedron in projection, the centre being the metal together with the under- and overlying oxygen atoms, and the corners the remaining oxygen atoms. The orientation of the grid is determined by the relationship of the sub-cell to the unit cell, and the problem is one of finding a particular arrangement of edge- and corner-shared octahedra with the correct unit-cell size and space group, with suitable positions for the sodium atoms and with a balanced chemical composition.

By transferring the origin of a duplicate transparent map of the Patterson function to the strong peak marked *A* in Fig. 1, the major vector coincidences were represented on the grid as octahedra and not just the individual atoms. Separations of 3.0–3.1 Å were assumed to arise from octahedra sharing edges at the same level perpendicular to the *b* axis, while 2.5–2.6 Å corresponded to edges shared at different levels. In the latter case the squares on the model overlapped. This simple image-seeking procedure, which we have described in detail elsewhere (Gatehouse & Wadsley, 1964; Andersson, Mumme & Wadsley, 1966) led to a partial solution of the problem. The structure seemed to contain two identical but independent groups of three octahedra sharing edges in a plane and repeating *b*/2 downwards by additional edge-sharing, thereby forming two zigzag ribbons extending along the axis of symmetry. At this stage the manner of joining the groups could not be ascertained, nor could realistic positions for sodium be recognized. An electron-density projection on to (010), however, revealed an additional metal atom. Its position increased the size of one zigzag assemblage to four repetitive octahedra, so that the asymmetric unit contained seven metals – excluding sodium – a conclusion fully confirmed by the 14-fold periodicity in the Patterson projection.

This structural model was completed by placing two sodium atoms in fourfold positions in the tunnels formed by the junctions of the groups, giving the formula $\text{Na}_2\text{Ti}_7\text{O}_{15}$. Three-dimensional electron density sections confirmed this general arrangement, but sev-

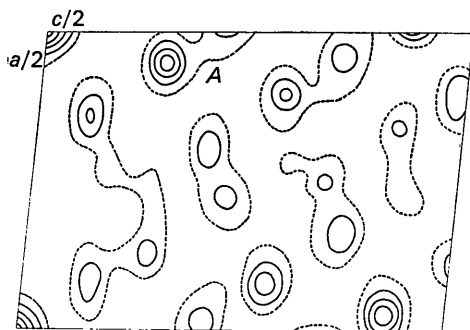


Fig. 1. Projection of the Patterson function, $P(u, w)$. The strong vector *A* was the origin selected for image-seeking by superposition.

eral additional subsidiary maxima appeared for which there was no meaningful explanation. These were subsequently eliminated by refinement procedures, and evidently resulted from series termination. A number of iterative three-dimensional difference syntheses were computed, and least-squares refinement was used at the same time to evaluate standard deviations as well as individual isotropic temperature factors. A persistent small peak at the origin of the difference syntheses was identified as a sodium atom in the point position 2(*a*) of $C2/m$, and because of this the remaining six sodium atoms in the unit cell were distributed over the two fourfold sites originally chosen. Refinement would not go beyond an *R* index of 12.2%. Final atomic parameters are listed in Table 2, where the standard deviations and temperature factors are averaged out for atoms of the same kind. A comparison of observed and calculated structure factors is given in Table 3. The calculated *F* values for all reflexions observed zero were all very small and are omitted. The structure is illustrated in Fig. 2 as a ball-and-spoke drawing and as an idealized octahedral model by Fig. 3(*b*).

Table 2. Fractional atomic parameters for $\text{Na}_2\text{Ti}_7\text{O}_{15}$

Space group $C2/m$. E.s.d.'s in parentheses.					
Point position	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>	
Na(1)	2(<i>a</i>)	0	0	0	2.4 Å ²
$\frac{2}{3}\text{Na}(2)$	4(<i>i</i>)	0.962 (6)	0	0.395 (4)	2.4
$\frac{2}{3}\text{Na}(3)$	4(<i>i</i>)	0.069 (6)	0	0.183 (4)	2.4
Ti(1)	4(<i>i</i>)	0.6965 (27)	0	0.0430 (18)	1.1
Ti(2)	4(<i>i</i>)	0.7477 (27)	0	0.1863 (18)	1.1
Ti(3)	4(<i>i</i>)	0.6237 (27)	0	0.3279 (18)	1.1
Ti(4)	4(<i>i</i>)	0.6718 (27)	0	0.4717 (18)	1.1
Ti(5)	4(<i>i</i>)	0.3520 (27)	0	0.0996 (18)	1.1
Ti(6)	4(<i>i</i>)	0.4007 (27)	0	0.2439 (18)	1.1
Ti(7)	4(<i>i</i>)	0.2775 (27)	0	0.3852 (18)	1.1
O(1)	4(<i>i</i>)	0.646 (7)	0	0.119 (5)	1.5
O(2)	4(<i>i</i>)	0.686 (7)	0	0.250 (5)	1.5
O(3)	4(<i>i</i>)	0.517 (7)	0	0.280 (5)	1.5
O(4)	4(<i>i</i>)	0.576 (7)	0	0.412 (5)	1.5
O(5)	4(<i>i</i>)	0.185 (7)	0	0.472 (5)	1.5
O(6)	4(<i>i</i>)	0.137 (7)	0	0.328 (5)	1.5
O(7)	4(<i>i</i>)	0.380 (7)	0	0.449 (5)	1.5
O(8)	4(<i>i</i>)	0.332 (7)	0	0.313 (5)	1.5
O(9)	4(<i>i</i>)	0.454 (7)	0	0.155 (5)	1.5
O(10)	4(<i>i</i>)	0.402 (7)	0	0.018 (5)	1.5
O(11)	4(<i>i</i>)	0.831 (7)	0	0.100 (5)	1.5
O(12)	4(<i>i</i>)	0.892 (7)	0	0.244 (5)	1.5
O(13)	4(<i>i</i>)	0.752 (7)	0	0.386 (5)	1.5
O(14)	4(<i>i</i>)	0.216 (7)	0	0.042 (5)	1.5
O(15)	4(<i>i</i>)	0.266 (7)	0	0.186 (5)	1.5

Despite high standard deviations, the interatomic distances for the titanium–oxygen octahedra listed in Table 4 show the spread of values normal for low symmetry titanate structures. The environment of sodium is of two kinds. Na(2) has two bonds each of 2.56, 2.52, 3.22 and 3.07 Å while Na(3) has two each of 2.64, 2.56, 2.93 and 2.82 Å (all ± 0.13 Å). Both atoms are displaced from the centres of distorted cubes of oxygen atoms (Fig. 2) in exactly the same way as in the hexatitanates $\text{Na}_2\text{Ti}_6\text{O}_{13}$ (Andersson & Wadsley, 1962*a*) and $\text{K}_2\text{Ti}_6\text{O}_{13}$ (Cid-Dresdner & Buerger, 1962).

Na(1) occupying the twofold position at the origin, on the other hand, is at the centre of a square of oxygens [the atoms O(4)], with four equal bonds $2.43 \pm 0.2 \text{ \AA}$, which is much the same as Na in the bronze Na_xTi₄O₈ (Andersson & Wadsley, 1962*b*).

Discussion

Problems of the present kind pose a number of difficulties centring around the small percentage of reflexions of measurable intensity which are recorded, despite the large number of atoms in the asymmetric unit. This scarcity of data is caused by the quasi-orthogonal sub-structure dominating the reciprocal lattice. The 'superlattice' reflexions appear sporadically instead of falling close to a sub-structure spot, and the correct assignment of indices, particularly at high angles, is a matter of considerable initial uncertainty. Light atoms in special positions such as Na(1), contributing equally to all reflexions, may go unnoticed in an electron density map containing only a small fraction of the data. Even a heavy atom under similar circumstances appears deceptively small (Roth & Wadsley, 1965). Difference syntheses are perhaps the best way of attacking these problems, particularly if appraised in conjunction with temperature factors, which are sensitive to incorrectly weighted scattering curves.

Even so, the distribution of sodium in Na₂Ti₇O₁₅ must be considered indecisive, as any number of combinations of occupancy and thermal motion are possible. The alkali metals in tunnel compounds behave erratically, and for two members of the class, NaTi₂Al₅O₁₂ (Mumme & Wadsley, 1967) and Na_{0.9}Fe_{0.9}Ti_{1.1}O₄ (Mumme & Reid, 1968), where in both cases the diffraction data were more complete, the temperature factors in the tunnel directions were very large. This can be attributed to the freedom of these atoms to vibrate relatively unhindered in this particular direction. Nevertheless, in the present case it is conceivable that all of the sodium positions might be completely occupied if aluminum substitutes isomorphously for titanium, when the formula is Na_{2.5}(Ti_{6.5}Al_{0.5})O₁₇.

The structural implications of this compound are more significant than its exact stoichiometry. Fig. 3(a)

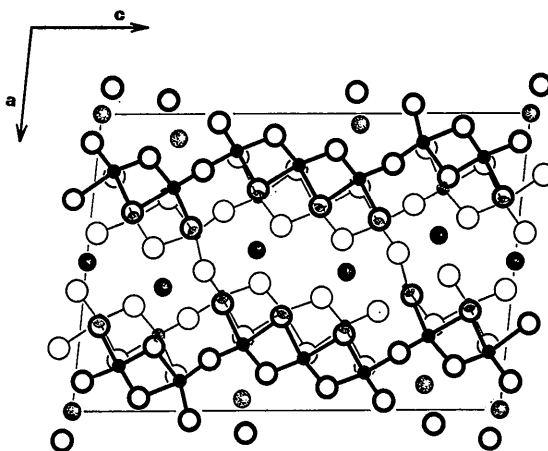


Fig. 2. Structure of Na₂Ti₇O₁₅. Smallest circles Ti, largest O, intermediate (stippled) Na.

Table 3. Observed and calculated structure factors

H	K	L	F _o	F _c	H	K	L	F _o	F _c	H	K	L	F _o	F _c	
0	0	0	1205	975	14	0	4	-3912	-3573	15	1	3	-1481	-1612	
0	0	5	-1798	-1377	14	0	-8	2048	2331	15	1	13	1531	1391	
0	0	14	-7017	-7471	16	0	-16	-3420	-3196	15	1	-13	2814	2769	
0	0	21	3247	4261	16	0	25	2431	3198	17	1	1	-4913	-3224	
2	2	0	-5859	-5892	16	0	-13	-1957	-1865	17	1	-6	-4913	-3224	
2	2	0	-2592	-2616	18	0	1	-2635	-2724	0	2	7	710	769	
2	2	0	3175	4265	1	1	1	-3875	-4086	0	2	14	-1432	-1077	
2	2	0	1584	726	1	1	2	1189	134	0	2	14	-6446	-5753	
2	2	0	-1683	-182	1	1	5	3129	2675	0	2	21	3465	3456	
2	2	0	1167	1662	1	1	11	1265	1826	0	2	28	-5953	-3371	
2	2	0	9129	9157	1	1	21	-2225	-1974	0	2	35	-2423	-2244	
2	2	0	-421	-4521	1	1	31	1115	1321	0	2	42	3288	3261	
2	2	0	-2829	-2342	1	1	41	-2245	-3015	0	2	49	6128	5933	
2	2	0	-2975	-1529	1	1	51	4183	4133	0	2	56	-1461	-2585	
4	4	0	11777	10227	3	3	7	7935	5218	0	2	63	1088	1088	
4	4	0	3339	2819	3	3	17	-1265	-132	0	2	70	1101	1195	
4	4	0	2115	2241	3	3	27	-1847	-2575	0	2	77	-1117	-1079	
4	4	0	-1647	-1702	3	3	37	1647	2265	0	2	84	7329	6929	
4	4	0	-1927	-201	3	3	47	-1429	-1899	0	2	91	1825	1674	
4	4	0	1923	1386	3	3	57	-1581	-2396	0	2	98	-3322	-3819	
4	4	0	1127	588	3	3	67	-1742	-2273	0	2	105	-1377	-1226	
4	4	0	-1661	-2524	3	3	77	-3176	-3638	0	2	112	751	6999	
4	4	0	-11877	-11735	3	3	87	1273	2252	0	2	119	2192	2253	
4	4	0	2357	2376	3	3	97	-2673	-2470	0	2	126	-2495	-2611	
4	4	0	2929	3191	3	3	107	-4262	-4331	0	2	133	-1629	-2226	
6	6	0	-12153	-11469	5	5	1	1283	670	0	2	140	-1435	-648	
6	6	0	1778	-2842	5	5	11	4241	3764	0	2	147	1435	-977	
6	6	0	3119	3159	5	5	21	1826	2217	0	2	154	-3225	-3179	
6	6	0	7173	6883	5	5	31	-5388	-5995	0	2	161	-9234	-8215	
6	6	0	4047	4147	5	5	41	-3377	-3426	0	2	168	2289	2282	
6	6	0	-2391	-2943	5	5	51	2859	2195	0	2	175	-1372	-1538	
6	6	0	1172	1276	5	5	61	7616	6929	0	2	182	-7147	-6728	
6	6	0	3375	2858	5	5	71	1313	1665	0	2	189	-1763	-2252	
6	6	0	1817	1820	5	5	81	-1623	-1421	0	2	196	3421	3421	
6	6	0	12	2127	2691	7	7	-11	-1461	-1810	0	2	203	7284	5176
6	6	0	-2659	-2228	7	7	11	1647	1669	0	2	210	3827	3222	
6	6	0	3227	2523	7	7	21	-2673	-2784	0	2	217	-4325	-4375	
6	6	0	-1862	-1923	7	7	31	-3259	-2734	0	2	224	1072	1338	
6	6	0	-2223	-2223	7	7	41	-2112	-2210	0	2	231	1928	2287	
6	6	0	4963	4767	7	7	51	2562	2322	0	2	238	1468	1652	
6	6	0	1817	2271	7	7	61	2794	2379	0	2	245	-1752	-1823	
6	6	0	-2767	-3251	7	7	71	-3443	-2461	0	2	252	3827	3222	
6	6	0	-2437	-2180	7	7	81	3177	2333	0	2	259	-4325	-4375	
6	6	0	1888	1825	7	7	91	-1647	-2434	0	2	266	-1426	-1426	
6	6	0	1798	2024	7	7	101	-3177	-3227	0	2	273	3324	3324	
6	6	0	-2177	-2524	7	7	111	2572	2697	0	2	280	1517	1928	
6	6	0	3693	3794	7	7	121	-2176	-1992	0	2	287	1977	2174	
6	6	0	-2571	-1929	7	7	131	-2729	-2501	0	2	294	2577	3123	
6	6	0	1729	1241	7	7	141	-3245	-2212	0	2	301	-3305	-3393	
6	6	0	-2829	-3782	7	7	151	3228	2775	0	2	308	4273	4289	
6	6	0	-3275	-4227	7	7	161	2268	2111	0	2	315	-2019	-2033	
6	6	0	3321	3277	7	7	171	-3275	-1062	0	2	322	-2365	-3226	
6	6	0	2797	1929	7	7	181	2679	2918	0	2	329	1828	1313	
6	6	0	-2767	4252	7	7	191	-2259	-2252	0	2	336	2661	2726	
6	6	0	-1119	-3701	7	7	201	-2247	-2291	0	2	343	-2481	-2595	
6	6	0	2392	2294	7	7	211	1	1	0	2	350	-2553	-2666	

Table 4. Interatomic distances for Ti octahedra in Na₂Ti₇O₁₅

Metal	Bonded oxygen atoms*	Distances (Å)			O-O distances (Å)		
		(same order as in column 2)	Average	Max.	Min.	Average	
Ti(1)	14 (2); 1, 11, 10', 14'	1.89 (2); 1.83, 2.21, 1.83, 2.32	1.99	2.97	2.73	2.80	
Ti(2)	15 (2); 1, 2, 12, 11	1.89 (2); 1.95, 1.70, 2.34, 2.30	2.01	3.09	2.66	2.83	
Ti(3)	6 (2); 2, 3, 4, 13	1.88 (2); 1.96, 1.78, 1.97, 2.15	1.93	2.90	2.64	2.73	
Ti(4)	5 (2); 4, 7', 5', 13	1.88 (2); 1.79, 1.91, 2.28, 2.26	2.00	3.00	2.69	2.81	
Ti(5)	11 (2); 9, 10, 14, 15	1.90 (2); 1.80, 1.94, 2.24, 2.33	2.01	3.02	2.73	2.83	
Ti(6)	12 (2); 8, 3', 9, 15	1.87 (2); 1.86, 1.81, 2.10, 2.22	1.95	2.95	2.58	2.76	
Ti(7)	13 (2); 5, 7, 8, 6	1.91 (2); 2.40, 1.91, 1.79, 2.29	2.03	3.01	2.73	2.85	

* Given by numbers only. The first, followed by (2) and a semicolon, are the two atoms lying over and under the metal. E.s.d.'s of Ti-O distances are $\pm 0.10 \text{ \AA}$; for oxygen-oxygen, $\pm 0.14 \text{ \AA}$.

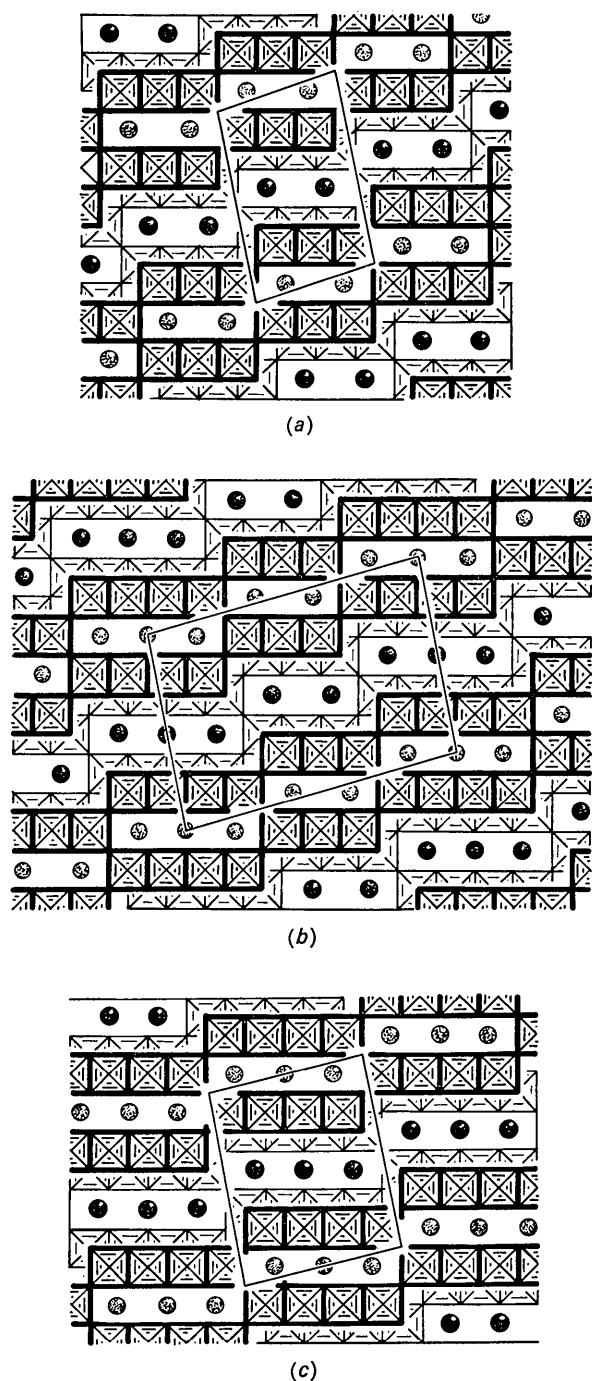
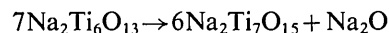


Fig. 3. Idealized structures of monoclinic sodium titanates in projection on to (010). The squares are Ti-O octahedra; the heavy and light outlines represent the two levels in the unit cells, which are outlined. Na atoms are stippled circles. (a) $\text{Na}_2\text{Ti}_6\text{O}_{13}$ (Andersson & Wadsley, 1962a). The octahedra join, by sharing edges, into groups of three. (b) $\text{Na}_2\text{Ti}_7\text{O}_{15}$, with alternating groups of three and four octahedra sharing edges. The sodium positions not at the origin and side centre are incompletely filled. (c) Hypothetical $\text{Na}_2\text{Ti}_8\text{O}_{17}$, with groups of four octahedra. The distribution of Na is unknown. (b) is a hybrid or intergrowth of (a) and (c).

and (b) show its relationship to sodium hexatitanate $\text{Na}_2\text{Ti}_6\text{O}_{13}$ (Andersson & Wadsley, 1962a), which is built up from zigzag units of octahedra, three wide, and joined in an identical manner to form a three-dimensional framework structure. We can also visualize the octatitanate $\text{Na}_2\text{Ti}_8\text{O}_{17}$ [or perhaps $\text{Na}_3(\text{AlTi}_7)\text{O}_{17}$] in Fig. 3(c), identical with $\text{Na}_2\text{Ti}_6\text{O}_{13}$ except for the size of the octahedral groups which are *four* wide instead of three. $\text{Na}_2\text{Ti}_7\text{O}_{15}$ containing both groups, three and four wide alternating regularly, is thus a hybrid, or an ordered *intergrowth* at the unit-cell level of these two structures. A number of examples of this particular phenomenon have been reported; for example, the pseudobinary mixed oxide $\text{W}_4\text{Nb}_{26}\text{O}_{77}$ contains alternating segments of the two phases $\text{WNb}_{12}\text{O}_{33}$ and $\text{W}_3\text{Nb}_{14}\text{O}_{44}$ (Andersson, Mumme & Wadsley, 1966).

Up to the present, however, the octatitanate has not been prepared. We have no doubt that a compound with its predicted structure can be made, but these titanates $\text{Na}_2\text{Ti}_7\text{O}_{15}$ and $\text{Na}_2\text{Ti}_8\text{O}_{17}$ do not form by the simple expedient of heating the weighed and mixed oxides in a sealed system. The readily made sodium hexatitanate could be expected to decompose in the solid state according to the equation



provided it can be heated to a sufficiently high temperature without fusing. The decomposition of one phase to another one of like structure and composition occurs by the cooperative diffusion of non-metals as well as metal ions within the solid (Andersson & Wadsley, 1966). The formation of $\text{Na}_2\text{Ti}_7\text{O}_{15}$ from the composition $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{TiO}_2$ (*i.e.* 'NaAlTiO₄') may simply be due to Al_2O_3 altering the phase diagram so as to permit such a diffusion reaction to take place.

The structures of the tri-, hexa- and heptatitanates afford additional examples of two working rules found to be useful in crystal chemical studies of lattice compounds of the transition metals, notably the oxides of Ti, V, Nb, Mo, Ta and W (Wadsley, 1967). The three- and four-member octahedral groups illustrate the first, that *an octahedron, centred around a transition metal ion in its maximum valency state, is attracted towards similar octahedra and unites with them so as to have the maximum edge (or face) sharing compatible with the stoichiometry of the phase in which it occurs.* The second states that *these groups replace the single octahedron as the basic unit of structure, and can join by peripheral corner- or edge-sharing with the same or with different groups to form three-dimensional networks, which may include another kind of metal ion at suitable interstices.*

Finally, these titanates may be regarded as derivatives of a parent structure characterized by the ideal stoichiometry $\text{M}^+\text{A}^{3+}\text{TiO}_4$, M^+ being an alkali metal K, Rb or Cs. The relationships with the alkali titanates will be discussed in a forthcoming publication (Mumme, Reid & Wadsley, 1968).

References

- ANDERSSON, S., MUMME, W. G. & WADSLEY, A. D. (1966). *Acta Cryst.* **21**, 802.
- ANDERSSON, S. & WADSLEY, A. D. (1961). *Acta Cryst.* **14**, 1245.
- ANDERSSON, S. & WADSLEY, A. D. (1962*a*). *Acta Cryst.* **15**, 194.
- ANDERSSON, S. & WADSLEY, A. D. (1962*b*). *Acta Cryst.* **15**, 201.
- ANDERSSON, S. & WADSLEY, A. D. (1966). *Nature, Lond.* **211**, 581.
- BAYER, G. & HOFFMANN, W. (1965). *Z. Kristallogr.* **121**, 9.
- CID-DRESDNER, H. & BUERGER, M. J. (1962). *Z. Kristallogr.* **117**, 411.
- DALY, J. J., STEPHENS, F. S. & WHEATLEY, P. J. (1963). Monsanto Research, S.A. Final Report no. 52.
- GATEHOUSE, B. M. & WADSLEY, A. D. (1964). *Acta Cryst.* **17**, 1545.
- International Tables for X-ray Crystallography* (1962). Vol. III, p. 202. Birmingham: Kynoch Press.
- MUMME, W. G. & REID, A. F. (1968). *Acta Cryst.* To be published.
- MUMME, W. G., REID, A. F. & WADSLEY, A. D. (1968). In preparation.
- MUMME, W. G. & WADSLEY, A. D. (1967). *Acta Cryst.* **23**, 754.
- REID, A. F., WADSLEY, A. D. & SIENKO, M. J. (1968). *Inorg. Chem.* In the press.
- ROTH, R. S. & WADSLEY, A. D. (1965). *Acta Cryst.* **19**, 38.
- SUZUKI, J. (1960). *Acta Cryst.* **13**, 279.
- WADSLEY, A. D. (1967). *Helv. Chim. Acta*. Fasc. extraord. Alfred Werner, p. 207.

Acta Cryst. (1968). **B24**, 396

The Crystal Structure of the 1:2 Copper(II) Nitrate–Methyl Cyanide Complex

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The structure of Cu(NO₃)₂·2CH₃CN has been solved by the heavy-atom method and refined to $R=0.15$ by least-squares analysis based on 292 partial three-dimensional data. The complex crystallizes in the monoclinic space group $P2_1/c$ with unit-cell dimensions $a=8.81$, $b=7.36$, $c=14.73$ Å, $\beta=94^\circ$, and $Z=4$. Each copper atom in the structure is in a (4+1) tetragonal pyramidal environment and half the nitrate groups act as bridging ligands, linking tetragonal pyramids related by the twofold screw axes, to form infinite chains parallel to the b crystallographic axis. The remaining nitrate groups are unidentate, forming only one bond to the copper atom. Methyl cyanide molecules, coordinated to copper through their nitrogen atoms, occupy *trans* positions in the copper square plane. The structure is compared with the structures of α -cupric nitrate and its complex with nitromethane.

Introduction

The crystal structure of the 1:2 complex between anhydrous cupric nitrate and methyl cyanide has been determined in order to compare the structure of α -cupric nitrate (Wallwork & Addison, 1965) with the crystal structures of its complexes with organic ligands. It would be of interest to determine any changes in metal–nitrate bonding which may occur on complex formation and to investigate the effect of the organic ligands on the copper coordination sphere.

Experimental

Anhydrous cupric nitrate, prepared by the method of Addison & Hathaway (1958), was dissolved in freshly distilled methyl cyanide at 40°C until a saturated solution was obtained. Deep blue crystals of the methyl cyanide adduct were deposited on standing and analysis

for copper content confirmed the 1:2 composition. Because of the deliquescent nature of the complex, suitable crystals were sealed in thin-walled Pyrex capillary tubes in a dry box.

Using Cu $K\alpha$ radiation, equi-inclination multiple film Weissenberg photographs were taken of the zero levels for the crystal rotating about the a and c crystallographic axes and of the zero and first levels for the b -axis rotation. The intensities were measured visually using standard calibrated scales and were converted to observed structure factor values in the usual way. No correction was made for absorption. By comparing equivalent planes observed from different rotation axes, the 292 independent reflexions were placed on a common arbitrary scale.

The crystal data are as follows:

Cu(NO₃)₂·2CH₃CN, F.W. 269.6. Monoclinic, $a=8.81$ (2), $b=7.36$ (2), $c=14.73$ (3) Å, $\beta=94$ (1)°, $U=953$ Å³, $D_m=1.825$ g.cm⁻³, $Z=4$, $D_x=1.879$ g.cm⁻³, Cu $K\alpha$ radiation ($\lambda=1.5418$ Å). Space group, $P2_1/c$ (no. 14).

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