produced in this way are, in fact, mixtures of two isomers, a 2-hydroxycycloheptatriene and a 2-oxo-cycloheptadiene. These isomers can be distinguished by their different melting points, infrared spectra and solubilities in organic solvents. The crystal structure of the 2-oxocycloheptadiene isomer is reported in this work.

The molecules are linked into dimers by two almost linear N–H· · ·O hydrogen bonds of length 2·889 (5) Å. The coordination at nitrogen is planar. The bond lengths within the ring are normal with the exception of the N–C(6) distance of 1·413 (6) Å which is particularly short compared with 1·474 in methylamine (Lide, 1957) or 1·498 Å in N,N-dimethyl-p-nitroaniline (Mak & Trotter, 1965). This phenomenon is indicative of a strong interaction between the nitrogen lone pair and the dienic system of the ring. The P–N bond length of 1·664 (4) Å is very similar to 1·656 (10) Å in $PO(NH_2)_3$ (Bullen, Stephens & Wade, 1969) and 1·647 (6) Å in $PO(NMe_2)_2C_4H_4$ (Born, 1969). The P=O distance of 1·476 (3) Å is identical with 1·476 (4) Å

in the former though somewhat shorter than 1·510 (3) Å in the latter.

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α Form of Sodium Metavanadate

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Abstract. α-$NaVO_3$, monoclinic, $C2/c$, $Z=4$, $a=10·552$ (3), $b=9·468$ (2), $c=5·879$ (2) Å, $\beta=108·47$ (3)°. $D_{calc}=2·91$ g cm^{-3}. Colourless, transparent crystals of α-$NaVO_3$ were synthesized from a 1:1 mixture of Na_2CO_3 and V_2O_5 by the Bridgman method. The structure is of the diopside type.

Introduction. The systematic absences were hkl for $h+k$ odd and $h0l$ for l odd. For intensity measurements, a crystal with dimensions of about 0·13 ×

0·11 × 0·11 mm was used. Intensities were collected on a Rigaku automated four-circle diffractometer with Mo $K\alpha$ radiation monochromated by a graphite plate. The $\omega-2\theta$ scan technique was employed with a scanning speed of 2° min^{-1} in ω. In all, 859 independent reflexion data, with $|F|$'s larger than $3\sigma(|F|)$, were obtained within the range $2\theta \le 65°$. Intensities were corrected for Lorentz and polarization effects. Absorption corrections were also made assuming a sphere of 0·11 mm in diameter for the crystal shape.

Table 1. *Final atomic parameters* (× 10^5) *for* α-$NaVO_3$

The thermal parameters are in the form exp $[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
V	29227 (3)	8979 (3)	26127 (5)	168 (2)	276 (3)	455 (8)	−35 (2)	50 (3)	26 (4)
Na(1)	50000	20571 (15)	75000	534 (13)	449 (14)	1432 (39)	0	−139 (18)	0
Na(2)	50000	41223 (13)	25000	292 (10)	371 (12)	1003 (31)	0	145 (14)	0
O(1)	12750 (14)	10125 (16)	16687 (25)	249 (11)	449 (16)	990 (38)	16 (11)	102 (17)	56 (20)
O(2)	35556 (17)	24768 (18)	32358 (29)	478 (15)	443 (16)	1433 (45)	−179 (13)	247 (21)	−148 (22)
O(3)	35245 (15)	741 (18)	3818 (26)	290 (12)	643 (17)	881 (38)	−5 (12)	124 (18)	−274 (21)

The structure was refined with the full-matrix least-squares program *RSFLS*-4 (Sakurai, 1967) on the assumption of the centrosymmetric space group $C2/c$. The calculation was initiated with the atomic parameters of diopside given by Warren & Bragg (1928). Two strong reflexions, which were supposed to have strong extinction effects, were excluded from the final stage of the refinement. The R value dropped to 0·024 for 857 observed reflexions. Because of the good agreement of the calculated structure amplitudes with the observed ones, the true space group of α-NaVO₃ was reasonably assumed to be $C2/c$, and refinement was not attempted with the non-centrosymmetric space group Cc. Unit weights were allotted to all reflexions. The atomic scattering factors used are those given by Fukamachi (1971) for neutral atoms. The final atomic parameters are given in Table 1.* The interatomic distances and bond angles are given in Table 2.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30406 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Interatomic distances and bond angles with their estimated standard deviations in parentheses*

Na(1)-O(1^ii)	2·410 (2) Å	(2×)	V----O(3)	1·805 (2) Å
Na(1)-O(2)	2·519 (2)	(2×)	V----O(3^iv)	1·801 (2)
Na(1)-O(3^iv)	2·611 (2)	(2×)	O(1)-O(2)	2·675 (3)
Na(2)-O(1^i)	2·381 (2)	(2×)	O(1)-O(3)	2·852 (3)
Na(2)-O(1^iii)	2·396 (2)	(2×)	O(1)-O(3^iv)	2·859 (3)
Na(2)-O(2)	2·314 (2)	(2×)	O(2)-O(3)	2·821 (3)
V----O(1)	1·653 (2)		O(2)-O(3^iv)	2·730 (3)
V----O(2)	1·631 (2)		O(3)-O(3^iv)	2·943 (3)

O(1)-V-O(2)	109·1 (1)°	O(2)-V-O(3^iv)	105·3 (1)°
O(1)-V-O(3)	111·0 (1)	O(3)-V-O(3^iv)	109·4 (1)
O(1)-V-O(3^iv)	111·7 (1)	V----O-V^iv	140·6 (1)
O(2)-V-O(3)	110·2 (1)		

Symmetry codes

	x	y	z
None			
i	$\frac{1}{2}-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$
ii	$\frac{1}{2}-x$	$\frac{1}{2}-y$	$1-z$
iii	$\frac{1}{2}-x$	$\frac{1}{2}-y$	$-z$
iv	x	$-y$	$\frac{1}{2}+z$
v	x	y	$1+z$

Discussion. Two polymorphs of NaVO₃ are known, the high-temperature α-form being more common than the low-temperature β-form. The α-form is exclusively

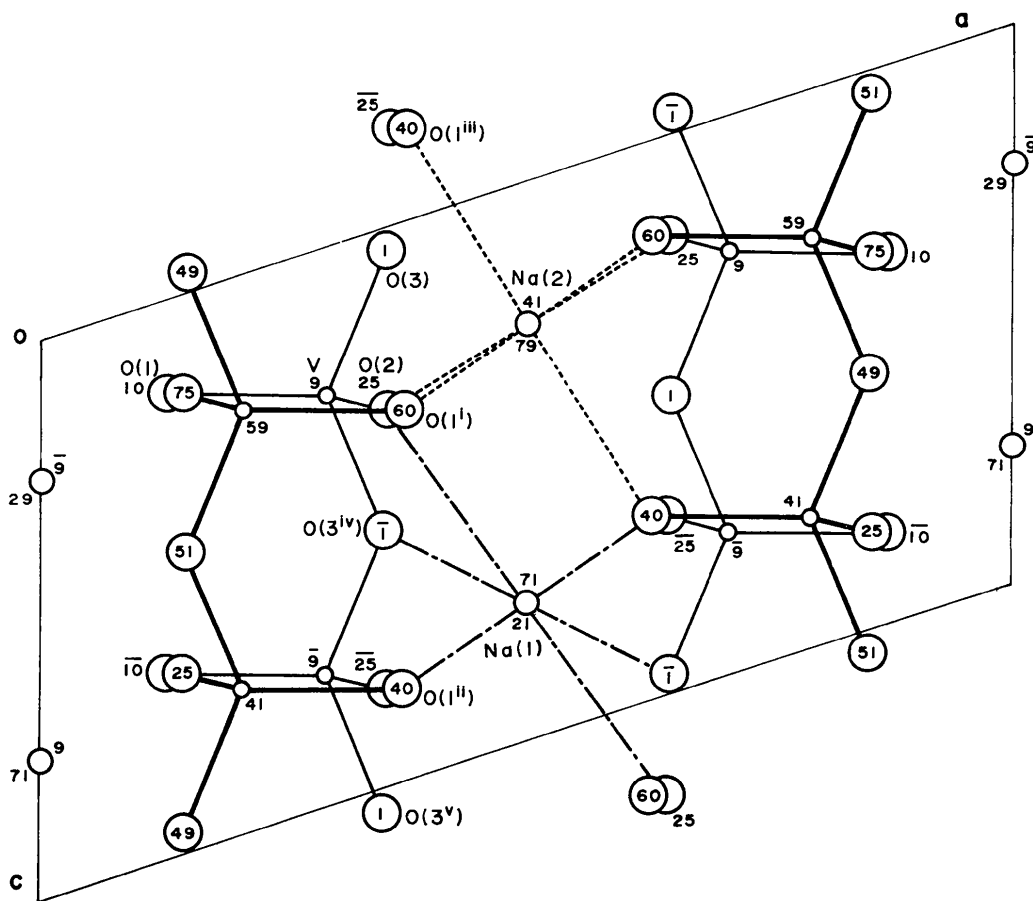Fig. 1. The crystal structure of α-NaVO₃ viewed along the b axis. Heights of atoms from the ac plane are indicated as percentages of the b length. Na(1) and Na(2) atoms fall on the same position in this projection.

obtained when the compound is synthesized by dry methods. The β-form is derived from the hydrated sodium metavanadate through dehydration, and irreversibly transforms to the α-form at $403 \sim 405\,°C$ (Lukács & Strusievici, 1962). A crystal of α-NaVO$_3$ was studied by the single-crystal X-ray method by Sørum (1943) and shown to have a diopside-type structure. Recently, Feigelson, Martin & Johnson (1972) suggested that the true space group of α-NaVO$_3$ might not be $C2/c$ but Cc. Refinement of the crystal structure was undertaken in order to settle the symmetry problem and to get exact atomic parameters.

The structure is essentially identical with that of diopside, as shown in Fig. 1. Fig. 2 is the VO$_3$ chain in α-NaVO$_3$ and the SiO$_3$ chain in diopside projected perpendicular to (100). The shapes of the chains are quite similar, as seen in the figures. There are two independent sodium atoms, Na(1) and Na(2), which are at the sites corresponding to M_I and M_{II} respectively in clinopyroxene structures. The most prominent difference from the diopside structure is that the cation at the M_I site is surrounded by only six oxygen atoms in α-NaVO$_3$, while the corresponding cation is surrounded by eight oxygen atoms in diopside. This results from the mutual shift of the two VO$_3$ chains related by a centre of symmetry along the c axis direction from the disposition of the SiO$_3$ chains in the diopside structure. The M_I–O(3^i) distance, which is longest among the eight M_I–O bonds in diopside, becomes as long as $3\cdot239$ Å in α-NaVO$_3$, and O(3^i) cannot be included among the atoms coordinated to Na(1) (Fig. 1 and Table 2). Although the coordination number of M_I is also six in clinoenstatite, the coordinating atoms are not the same as in α-NaVO$_3$.

The bond lengths between the vanadium and oxygen atoms shared by two neighbouring VO$_4$ tetrahedra are much longer than those between the vanadium and unshared oxygen atoms. This tendency is well known in silicates, but the difference is much larger in α-NaVO$_3$ than in clinopyroxenes. The ratios of the longer bond distances to the shorter ones are $1\cdot043$ in clinoenstatite, $1\cdot033$ in pigeonite, and $1\cdot032$ in diopside, compared with $1\cdot099$ in α-NaVO$_3$. The valency sums are compared in Table 3 for oxygen atoms in diopside and α-NaVO$_3$. The larger deformation of the VO$_4$ tetrahedron corresponds to the larger deviations of the valency sums from the charge of the oxygen anion in α-NaVO$_3$. There is a small but significant difference between the lengths of V–O(1) and V–O(2), as seen in Table 2. The difference is also attributable to the difference in valency sums for O(1) and O(2) atoms. Both Na(1) and Na(2) atoms are surrounded by six oxygen atoms. The coordination around Na(2) is octahedral to a good approximation, while the oxygen atoms are arranged
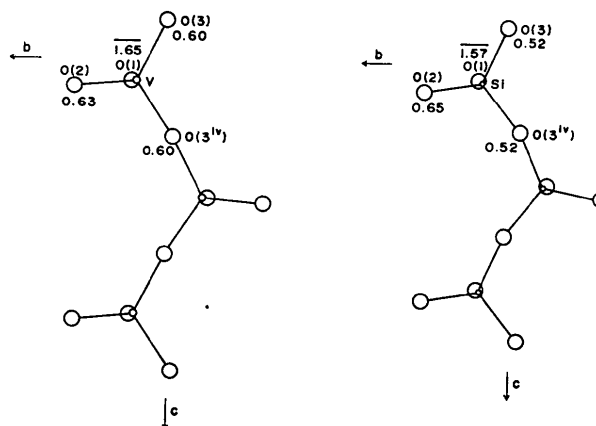

Fig. 2. A comparison of the VO$_3$ chain in α-NaVO$_3$ and the SiO$_3$ chain in diopside. The chains are projected perpendicularly to (100).

rather irregularly around Na(1). The mean Na(1)–O distance of $2\cdot51$ Å is somewhat longer than the mean Na(2)–O distance of $2\cdot36$ Å. This is in line with the fact that the larger cation, Ca^{2+}, is at the M_I site and the smaller one, Mg^{2+}, is at the M_{II} site in diopside.

Table 3. *The valency sums of oxygen atoms in* α-NaVO$_3$ *and diopside*

Oxygen atoms	α-NaVO$_3$	Diopside
O(1)	1·750	1·917
O(2)	1·583	1·583
O(3)	2·667	2·500

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