

Table 2 and both the X-ray and valence occupation numbers are compared in Table 1.

As a check we used the occupation numbers determined from the bond valences as fixed parameters in *SHELX76* and refined all positional and anisotropic atomic displacement parameters obtaining $wR = 0.063$, $R = 0.071$ and $S = 1.56$. Maximum final shift/e.s.d. 0.07, mean 0.02, maximum density in the final difference Fourier map $3.4 \text{ e } \text{Å}^{-3}$, minimum $-3.3 \text{ e } \text{Å}^{-3}$. because these occupation numbers correspond to an electrically neutral crystal we consider them as more reliable although, as expected, the agreement indices are slightly larger. This refinement was used to generate the final atomic coordinates listed in Table 3. Interatomic distances are given in Table 4.*

Discussion. The structure of Pb₂Sb₂S₅ proposed by Smith & Hyde (1983) has been confirmed. It consists of ribbons composed of square-pyramidal (Pb,Sb)S₅ groups. The ribbons extend indefinitely in the *c* direction, are one pyramid thick and have a width that equals four times the basal distance of the (Pb,Sb)S₅ pyramid (Figs. 1 and 2). The ribbons occurring in Pb₂Sb₂S₅ can be formed from the unit ribbon, Sb₄S₆, in stibnite (Bayliss & Nowacki, 1972) by splitting it and introducing four PbS₅ pyramids in the middle or, as in the alternative description of Smith & Hyde (1983), by introducing layers of the thallium iodide type structure (*B33*) into the stibnite

* Observed and calculated structure factors and anisotropic atomic displacement parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52413 (20 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of Na_{0.56}V₂O₅

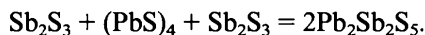
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Abstract. $M_r = 194.75$, monoclinic, $C2/m$, $a = 11.663$ (9), $b = 3.6532$ (7), $c = 8.92$ (1) Å, $\beta = 90.91$ (4)°, $V = 379.9$ (7) Å³, $Z = 4$, $D_x = 3.405 \text{ Mg m}^{-3}$, $\text{Mo } K\alpha$, $\lambda = 0.71073$ Å, $\mu = 4.774 \text{ mm}^{-1}$, $F(000) = 368.64$, room temperature, final $R = 0.056$ for 1234 unique observed reflections. Distorted octahedra of VO₆ are linked together to

structure. The stoichiometry is determined by the total number of PbS units that have been incorporated as:



However, the lead is not found in the middle of the ribbons. The ribbons are arranged facing each other but translated parallel to their width so that only half of each ribbon overlaps with the next. The cation sites in these parts of the ribbon are five-coordinated and are occupied mostly by antimony. The other cation sites, in places where the ribbons join with the edges of the glide-related ribbons, are seven-coordinated and are occupied mostly by lead. The cation distribution proposed by Smith & Hyde (1983) for the structure is simpler but similar to ours.

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form V₂O₅ layers parallel to (001). Na ions are situated between the layers and surrounded by seven O atoms. The structure is closely related to that of $\delta\text{-Ag}_{1-x}\text{V}_2\text{O}_5$.

Introduction. In the course of a phase equilibrium study on the NaV₂O₅–V₂O₃–V₂O₅ system (Kanke,

Takayama-Muromachi & Kato, 1990) we found a new phase, $\text{Na}_{0.56}\text{V}_2\text{O}_5$, between β ($\text{Na}_{0.22-0.40}\text{V}_2\text{O}_5$) and α' ($\text{Na}_{0.70-1.00}\text{V}_2\text{O}_5$) phases (Pouchard, Casalot, Galy & Hagenmuller, 1968).

As we could successfully prepare single-crystal samples of this new phase, we have determined the crystal structure.

Experimental. $\text{Na}_{0.56}\text{V}_2\text{O}_5$ was synthesized from NaVO_3 , V_2O_4 and V_2O_5 at 923 K. Single crystals were prepared by chemical-transport method using HCl gas as transport medium. To minimize the decomposition of the hygroscopic compound during the intensity collection, the crystal was sealed in a thin-walled (0.01 mm) glass capillary. Lath-like crystal elongated in [010] and flat in (001), size $0.26 \times 0.08 \times 0.02$ mm. Enraf-Nonius CAD-4 diffractometer, graphite-monochromated $\text{Mo K}\alpha$, lattice parameters from 22 reflections ($45 < 2\theta < 51^\circ$), intensity collection by ω - θ scan with $\Delta\omega = (1.5 + 0.35\tan\theta)^\circ$, $(\sin\theta/\lambda) < 1.0778 \text{ \AA}^{-1}$, $0 \leq h \leq 25$, $0 \leq k \leq 7$, $-19 \leq l \leq 19$, 2237 reflections measured, 807 unobserved, 1234 unique observed reflections with $I > 3\sigma(I)$. Three standard reflections measured every two hours, decrease of intensity 10.3% during the total exposure of 56.7 hours, non-linear decomposition correction applied. Computed absorption correction, correction factor for F from 1.049 to 1.223. Structure solved by Patterson method, refined by least-squares method based on F , anisotropic temperature factors,* atomic scattering factors for neutral atoms from *International Tables for X-ray Crystallography* (1974), $R = 0.056$, $wR = 0.061$, $w = 1/\sigma^2(F)$, $\Delta/\sigma < 0.005$ in final refinement cycle, $\Delta\rho = -2.6\text{--}4.2 \text{ e \AA}^{-3}$. Computer programs in *SDP* (B. A. Frenz & Associates Inc., 1985), separate version of *ORTEPII* (Johnson, 1976).

Discussion. Prior to the structure determination, it was found from a literature survey that the present compound crystallizes in the same space group and has almost the same lattice parameters as $\delta\text{-Ag}_{0.68}\text{V}_2\text{O}_5$. In view of the probable isotypism of their structures, we adopted the structure of $\delta\text{-Ag}_{0.68}\text{V}_2\text{O}_5$ (Andersson, 1965) as a starting model for our structure refinement. As the R value, however, never sank below 0.40 even after several cycles of least-squares refinement, we determined our structure *ab initio* by means of the Patterson function. The result revealed that both compounds are in fact isostructural and that the a and the b axes of

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52425 (7 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic fractional coordinates and equivalent isotropic thermal parameters (\AA^2)

	x	y	z	$B(\text{\AA}^2)^*$
V(1)	0.93676 (6)	0	0.16574 (8)	0.690 (8)
V(2)	0.23279 (6)	0	0.16614 (8)	0.714 (8)
O(1)	0.4015 (3)	0	0.1367 (4)	0.97 (4)
O(2)	0.0812 (3)	0	0.0998 (4)	0.94 (4)
O(3)	0.7614 (3)	0	0.1188 (4)	1.03 (4)
O(4)	0.9541 (3)	0	0.3457 (4)	1.44 (5)
O(5)	0.2185 (3)	0	0.3451 (4)	1.70 (6)
Na	0.5993 (8)	0	0.4803 (6)	4.4 (2)

$$*B = (8/3)\pi^2(U_{11} + U_{22} + U_{33}).$$

Table 2. Interatomic distances (\AA)

V(1)—O(4)	1.615 (3)	V(2)—O(5)	1.607 (3)
V(1)—O(2)	1.792 (3)	V(2)—O(2)	1.856 (3)
V(1)—O(1 ^{iii,v})	1.8892 (8)	V(2)—O(3 ^{iii,vii})	1.906 (1)
V(1)—O(3)	2.081 (3)	V(2)—O(1)	1.989 (3)
V(1)—O(2 ⁱⁱ)	2.374 (3)	V(2)—O(3 ⁱⁱ)	2.543 (4)
Na—O(4 ^{iii,ix})	2.482 (5)	Na—O(5 ^{iii,v})	2.604 (6)
Na—O(5 ⁱⁱⁱ)	2.614 (8)	Na—O(4 ^{iii,vii})	2.753 (6)
Na—Na ⁱⁱⁱ	2.35 (1)		

Symmetry code: (i) $1 + x, y, z$; (ii) $1 - x, y, -z$; (iii) $1 - x, y, 1 - z$; (iv) $\frac{1}{2} + x, \frac{1}{2} + y, z$; (v) $\frac{1}{2} + x, -\frac{1}{2} + y, z$; (vi) $-\frac{1}{2} + x, \frac{1}{2} + y, z$; (vii) $-\frac{1}{2} + x, -\frac{1}{2} + y, z$; (viii) $\frac{1}{2} - x, \frac{1}{2} + y, 1 - z$; (ix) $\frac{1}{2} - x, -\frac{1}{2} + y, 1 - z$.

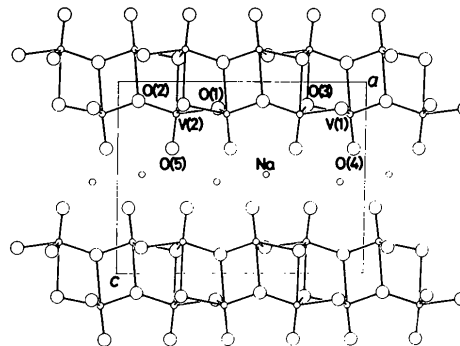


Fig. 1. Projection of the $\text{Na}_{0.56}\text{V}_2\text{O}_5$ structure onto (010).

$\text{Na}_{0.56}\text{V}_2\text{O}_5$ correspond to the $-a$ and $-b$ of $\delta\text{-Ag}_{0.68}\text{V}_2\text{O}_5$. To the β angle of the latter, corresponds the $180^\circ - \beta$ of the former.

The atomic fractional coordinates and the equivalent isotropic thermal parameters are listed in Table 1. Important interatomic distances are shown in Table 2. Fig. 1 shows the structure viewed along [010]. Distorted VO_6 octahedra are linked together by sharing edges and corners, and form a V_2O_7 column parallel to [010]. The columns are connected to each other by edge sharing to form a V_2O_5 slab parallel to (001). Na ions are accommodated in seven-coordinated sites between the slabs and bind them together. The coordination polyhedra of V(1), V(2) and Na have a plane of symmetry parallel to (010) in which the metal ions are located.

The coordination polyhedra (mono-capped trigonal prisms) of two neighboring Na sites have a prism

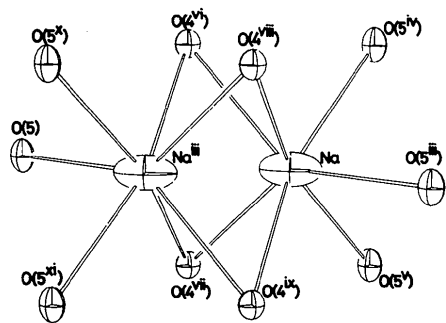


Fig. 2. Coordination of Na sites. Symmetry codes are shown in Table 2, (x) $\frac{1}{2} - x, \frac{1}{2} + y, 1 - z$; (xi) $\frac{1}{2} - x, -\frac{1}{2} + y, 1 - z$.

face in common, and the distance between the Na sites is extremely short (Table 2). It is noticeable that, in spite of these facts, 12% of the neighboring Na sites are really occupied simultaneously. If their simultaneous occupations were forbidden, the Na content of the compound could not exceed

Na_{0.50}V₂O₅. The Na ion exhibits a large, anisotropic apparent thermal motion toward the neighboring Na site (Fig. 2), which suggests that the distance between the neighboring Na sites is longer than 2.35 Å when both of them are occupied, and that it is shorter than 2.35 Å when only one is occupied.

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Structure of Calcium Manganese(II) Tetrabromide Octahydrate

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Abstract. CaMnBr₄.8H₂O, *M_r* = 558.75, monoclinic, *C2/m*, *a* = 9.062 (1), *b* = 9.582 (1), *c* = 9.405 (1) Å, β = 112.96 (1)°, *V* = 752.0 (2) Å³, *Z* = 2, *D_x* = 2.47 Mg m⁻³, Mo *Kα* radiation, λ = 0.71069 Å, μ = 11.57 mm⁻¹, *F*(000) = 530, room temperature, *R* = 0.062 (*wR* = 0.062) for 543 unique observed [*I* > 3σ(*I*)] reflections. Mn is octahedrally coordinated by four Br atoms (⟨Mn—Br⟩ = 2.71 Å) and two O_w (Mn—O = 2.18 Å). Ca is eightfold coordinated by six O_w (⟨Ca—O⟩ = 2.43 Å) and a Br and an O_w atom from an Mn(H₂O)₂Br₄ octahedron [Ca—Br = 3.073 (5), Ca—O = 3.01 (1) Å]. The structure thus consists of (H₂O)₆Ca(H₂O)BrMnBr₃H₂O molecular groups linked by hydrogen bonds. Since the Mn atom lies at a crystallographic center of symmetry, the Ca(H₂O)₆ groups are disordered on either side of the Mn(H₂O)₂Br₄ ion. Precession photographs show evidence of a superstructure with *b*' ≈ 5*b*.

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Introduction. The compound CaMnBr₄.8H₂O was first reported by Duhlev & Balarew (1987) as the only double salt found in the equilibrium CaBr₂–MnBr₂–H₂O system at 298 K. The size and hardness of the ions were considered to be the main factors affecting the molecular structure (Balarew & Duhlev, 1984), and the structure CaMnX₄.8H₂O (*X* = Cl or Br) was predicted (Balarew & Duhlev, 1983; Duhlev, 1984) to consist of Mn(H₂O)₂Br₄ and Ca(H₂O)₇Br groups sharing ligands. The aim of the present X-ray study was to check the correctness of this prediction.

Experimental. CaMnBr₄.8H₂O crystallizes as rose-colored extremely hygroscopic crystals from a saturated aqueous solution of CaBr₂ and MnBr₂ in a molar ratio 1.6:1. An approximately cylindrical crystal with diameter 0.22 mm and length 0.27 mm was coated with liquid paraffin and sealed in a thin-walled capillary under dry nitrogen. Precession photographs showed that, in addition to the reflections used in this study, most peaks had satellite