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Structure of Hexasodium Dihydrogendivanadodiperiodate Decahydrate

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Abstract. $\mathrm{Na_6[H_2I_2V_2O_{16}].10H_2O}$, $M_r = 931{\cdot}79$, triclinic, $P\bar{1}$, $a = 8{\cdot}927\,(2)$, $b = 11{\cdot}470\,(2)$, $c = 6{\cdot}137\,(1)$ Å, $\alpha = 95{\cdot}83\,(1)$, $\beta = 98{\cdot}00\,(2)$, $\gamma = 70{\cdot}13\,(1)°$, $U = 584{\cdot}2\,(2)$ Å^3, $Z = 1$, $D_m = 2{\cdot}65$, $D_x = 2{\cdot}647$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 3{\cdot}75$ mm^{-1}, $F(000) = 448$, $T = 293$ K, final $R = 0{\cdot}021$ for 3190 independent reflections. The $\mathrm{[H_2I_2V_2O_{16}]^{6-}}$ anion is the first example of a heteropoly compound containing $\mathrm{I^{VII}}$ and V whose structure has been revealed. It consists of two $\mathrm{IO_6}$ and two $\mathrm{VO_6}$ octahedra, and has approximate C_{2h} symmetry. I—O distances range from 1·820 to 1·961 Å and V—O distances from 1·628 to 2·544 Å. The $\mathrm{VO_6}$ octahedra are considerably distorted. One H atom is connected to one of the terminal O atoms bonded to I forming an asymmetric unit.

Introduction. Some heteropolyvanadates containing iodine(VII) have been reported by Rosenheim & Yang (1923). They claimed to have obtained compounds of ratios V:I = 2:1, 7:1 by mixing a solution of $\mathrm{H_5IO_6}$ and $\mathrm{Na_3VO_4.14H_2O}$ (or $\mathrm{NH_4VO_3}$), then adding HCl (or $\mathrm{NH_3}$ solution). From a further synthetic survey, we obtained a novel anion of V:I ratio 1:1. The anion has a structure analogous to $\mathrm{[I_2Mo_2O_{16}]^{6-}}$ (Mattes, Matz & Sicking, 1977) and $\mathrm{[I_2W_2O_{16}]^{6-}}$ (Michiue, Ichida & Sasaki, 1986).

Experimental. $\mathrm{Na_3VO_4}.x\mathrm{H_2O}$ (1·4 g) was dissolved in 20 ml of water. To this solution, $\mathrm{H_5IO_6}$ solution (1 *M*) was added dropwise to adjust the pH to 7–8 (about 6 ml needed). From the yellow solution, pale-yellow prismatic crystals were obtained after a few days at room temperature. D_m by flotation (methylene iodide/ethylene bromide); single crystal of dimensions $0{\cdot}25 \times 0{\cdot}15 \times 0{\cdot}11$ mm; Rigaku RU-1000 X-ray generator and AFC-5 goniometer at High Intensity X-ray Facilities, Engineering Research Institute, Faculty of Engineering, The University of Tokyo; graphite monochromator; cell parameters refined by least squares on the basis of 24 independent reflections, $\theta_{\max} = 29{\cdot}2°$; Mo $K\alpha$ radiation; ω–2θ scan mode; $2\theta \le 60°$ ($-12 \le h \le 12$, $-16 \le k \le 16$, $0 \le l \le 8$); scan speed 8° min^{-1} (θ); three standard reflections monitored every 100 reflections and their fluctuations found to be within ±0·01; of total 3692 reflections measured, 3190 independent reflections with $F_o > 3\sigma(F_o)$ used for the structure determination; I and V atoms located from three-dimensional Patterson maps, remaining atoms except for H by successive Fourier syntheses; structure refined by block-diagonal least squares based on F; anisotropic thermal parameters for all non-H atoms; eleven H atoms found from final difference synthesis as significant peaks higher than residuals ($-1{\cdot}1$–$0{\cdot}5$ e Å^{-3}), but not refined; atomic scattering factors from *International Tables for X-ray Crystallography* (1974), including f' and f'' for all atoms; $R = 0{\cdot}021$, $wR = 0{\cdot}029$, $S = 1{\cdot}0516$, $(\Delta/\sigma)\mathrm{max.} = 0{\cdot}25$ and $w^{-1} = \sigma^2(F_o) + (0{\cdot}01F_o)^2$; calculations carried out on a Hitac M-280 H computer at the Computer Centre of the University of Tokyo, with *UNICS*III (Sakurai & Kobayashi, 1979).

Discussion. Final atomic parameters and equivalent isotropic thermal parameters are in Table 1.* Fig. 1 shows the structure of the anion projected on the plane defined by two I and two V atoms. The anion has a centre of symmetry. I and V atoms are surrounded by six O atoms, which form octahedra. The two $\mathrm{VO_6}$ octahedra are joined by edge sharing, but two $\mathrm{IO_6}$ octahedra are separated from each other. There are four types of O atoms; terminal O atoms bonded to I, O(I); terminal O atoms bonded to V, O(V); bridging O atoms coordinated to I and V, O(I,V); and central O atoms coordinated to one I and two V atoms, O(I,V,V′) (prime indicates the symmetry operation of inversion). Interatomic distances are listed in Table 2. O atoms around I coordinate at distances of 1·820–1·961 Å. These can be classified into three types by bond distances; terminal O(I)1 (1·961 Å), terminal O atoms except for O(I)1 (1·820–1·832 Å), bridging and central O atoms (1·897–1·929 Å). I—O(I)1 is too long to be a bond distance of octahedrally coordinated iodine(VII) and terminal oxygen, while I—O(I)2 and I—O(I)3 are normal {$\mathrm{[I_2Mo_2O_{16}]^{6-}}$: I—O(I) = 1·804–1·826 Å}. This

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* Lists of structure factors, anisotropic thermal parameters, interatomic angles of the anion, positional parameters of H atoms and interatomic distances and angles of water molecules have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43340 (38 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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leads to the conclusion that I—O(I)1 is longer because of the protonation of O(I)1, as is often observed for instance in $K_4H_2I_2O_{10}.8H_2O$: I—O = 1·793–1·818, I—OH = 1·980 Å (Ferrari, Braibanti & Tiripicchio, 1965). As expected from the final difference synthesis an H atom was found at 0·87 Å from O(I)1, which makes an intramolecular hydrogen bond with O(V)2 with a distance of 1·89 Å and an angle of 152°.

Table 1. *Positional parameters* (×10⁵ *for* I *and* V, ×10⁴ *for others*) *and thermal parameters* B_{eq} (Å²)

$$B_{\rm eq} = \tfrac{8}{3}\pi^2 \textstyle\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
I	13270 (2)	−22048 (1)	−15015 (3)	0·708 (4)
V	18042 (5)	3324 (4)	−5076 (8)	0·874 (11)
O(I)1	−361 (3)	−2710 (2)	−3321 (4)	1·31 (5)
O(I)2	2306 (3)	−3734 (2)	−373 (4)	1·34 (5)
O(I)3	2417 (3)	−2555 (2)	−3913 (3)	1·24 (5)
O(V)1	2741 (3)	408 (2)	−2556 (4)	1·69 (6)
O(V)2	2819 (3)	759 (2)	1765 (4)	1·36 (5)
O(I,V)	2710 (2)	−1450 (2)	250 (3)	1·07 (5)
O(I,V′)	−9 (3)	−1820 (2)	866 (3)	1·13 (5)
O(I,V,V′)	201 (2)	−533 (2)	−2192 (3)	1·06 (5)
Na1	4775 (2)	3510 (1)	3988 (2)	1·73 (3)
Na2	9210 (2)	3439 (1)	6848 (2)	1·75 (3)
Na3	7761 (2)	804 (1)	5853 (2)	1·81 (3)
O*w*1	4156 (3)	2429 (2)	429 (4)	1·91 (6)
O*w*2	4763 (3)	1584 (3)	5385 (4)	2·12 (7)
O*w*3	1958 (3)	4485 (2)	4042 (4)	1·97 (6)
O*w*4	4988 (3)	4643 (2)	7396 (4)	2·01 (6)
O*w*5	1473 (3)	4140 (2)	8324 (5)	2·39 (7)

Table 2. *Interatomic distances* (Å) *in the* $[H_2I_2V_2O_{16}]^{6-}$ *anion*

I—I′	5·0761 (3)	I—V	3·0712 (5)
V—V′	3·6974 (10)	I—V′	3·2073 (4)
I—O(I)1	1·961 (3)	V—O(V)1	1·628 (3)
I—O(I)2	1·832 (2)	V—O(V)2	1·678 (3)
I—O(I)3	1·820 (2)	V—O(I,V)	2·004 (2)
I—O(I,V)	1·897 (2)	V—O(I′,V)	1·910 (2)
I—O(I,V′)	1·929 (2)	V—O(I,V,V′)	2·109 (2)
I—O(I,V,V′)	1·898 (2)	V—O(I′,V,V′)	2·544 (2)

For the VO_6 octahedron, bond distances vary from 1·628 to 2·544 Å. The central O atoms link loosely, especially V—O(I′,V,V′). Usually, V—O is less than 2·4 Å in octahedral coordination, for example $[V_{10}O_{28}]^{6-}$ (Evans, 1966; Durif, Averbuch-Pouchot & Guitel, 1980), while in the case of five coordination, the nearest O atom not bonded to V is at least 2·68 Å from V (Wadsley, 1955). Therefore, $[H_2I_2V_2O_{16}]^{6-}$ is a unique example which has V—O distances of 2·544 Å and significantly distorted VO_6 octahedra, which is the most remarkable feature compared with the $[I_2Mo_2O_{16}]^{6-}$ anion [Mo—O(I,Mo,Mo′) = 2·214 (4), Mo—O(I′,Mo,Mo′) = 2·274 (4) Å].

A list of selected interactions within 3·1 Å is given in Table 3. Each Na^+ ion is coordinated by six O atoms of the anions or water molecules (Fig. 2). All ten H atoms of five water molecules were found at distances of

Table 3. *Selected interactions within* 3·1 Å

Na1—O(I)3^{i}	2·375 (3)	O(I)1—O(V)2^{vi}	2·747 (3)
—O*w*1	2·489 (3)	—O*w*3^{vi}	2·826 (4)
—O*w*2	2·453 (4)	O(I)2—O*w*4^{vii}	2·905 (3)
—O*w*3	2·383 (3)	—O*w*4^{iii}	2·776 (3)
—O*w*4	2·367 (3)	—O*w*5^{vii}	2·795 (4)
—O*w*4^{ii}	2·444 (3)	O(V)1—O*w*2^{viii}	3·051 (5)
		O(V)2—O*w*1	2·813 (4)
Na2—O(I)1^{i}	2·471 (3)	—O*w*2	2·908 (4)
—O(I)2^{iii}	2·642 (3)	O(I,V)—O*w*1^{i}	2·712 (3)
—O(I)3^{i}	2·507 (3)	O*w*1—O*w*5^{viii}	2·778 (3)
—O(I,V′)^{iii}	2·297 (2)	O*w*3—O*w*5	2·810 (4)
—O*w*3^{ii}	2·340 (2)		
—O*w*5^{iv}	2·448 (3)		
Na3—O(I)3^{i}	2·386 (3)		
—O(V)1^{i}	2·414 (3)		
—O(V)2^{iii}	2·644 (3)		
—O(I,V)^{iii}	2·481 (2)		
—O(I,V,V′)^{v}	2·431 (2)		
—O*w*2	2·501 (3)		

Symmetry code: (i) $1-x, -y, -z$; (ii) $1-x, 1-y, 1-z$; (iii) $1-x, -y, 1-z$; (iv) $1+x, y, z$; (v) $1+x, y, 1+z$; (vi) $-x, -y, -z$; (vii) $x, y-1, z-1$; (viii) $x, y, z-1$.

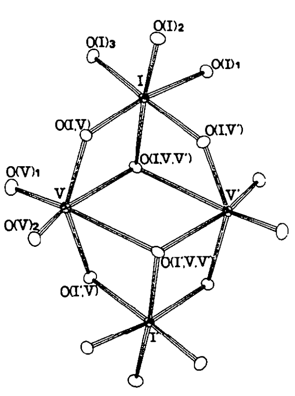

Fig. 1. An *ORTEP* view (Johnson, 1965) of the $[H_2I_2V_2O_{16}]^{6-}$ anion except for H atoms with thermal ellipsoids drawn at the 30% probability level.

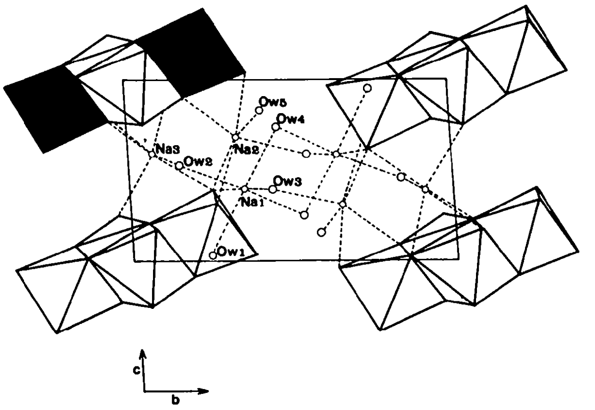

Fig. 2. The crystal packing and Na^+—O interactions projected along **a**. IO_6 octahedra are shaded.

0·81–1·01 Å (av. 0·89 Å) from O*w* atoms. Each interacts with only one O atom of an anion or another water molecule at 1·82–2·08 Å (av. 1·96 Å), except for O*w*2—H···O(V)1 = 2·37 Å. Every configuration of the O*w*—H···O hydrogen bonds is almost linear.

Note added in proof: The authors noticed lately the study of the same structure at 123 K (Mattes & Richter, 1982). Changes of the corresponding distances are found to be significant.

References

Durif, A., Averbuch-Pouchot, M. T. & Guitel, J. C. (1980). *Acta Cryst.* B**36**, 680–682.

Evans, H. T. Jr (1966). *Inorg. Chem.* **5**, 967–977.

Ferrari, A., Braibanti, A. & Tiripicchio, A. (1965). *Acta Cryst.* **19**, 629–636.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

Johnson, C. K. (1965). *ORTEP.* Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

Mattes, R., Matz, Ch. & Sicking, E. (1977). *Z. Anorg. Allg. Chem.* **435**, 207–213.

Mattes, R. & Richter, K.-L. (1982). *Z. Naturforsch. Teil B*, **37**, 1241–1244.

Michiue, Y., Ichida, H. & Sasaki, Y. (1986). In preparation.

Rosenheim, A. & Yang, K. H. (1923). *Z. Anorg. Allg. Chem.* **129**, 181–195.

Sakurai, T. & Kobayashi, K. (1979). *Rikagaku Kenkyusho Hokoku* (*Rep. Inst. Phys. Chem. Res.*), **55**, 69–77.

Wadsley, A. D. (1955). *Acta Cryst.* **8**, 695–701.

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Structure du Tétratriacontasulfure d'Octadécaindium et d'Heptaétain

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Abstract. $\mathrm{In_{18}Sn_7S_{34}}$, $M_r = 3987{\cdot}6$, orthorhombic, *Pbam*, $a = 15{\cdot}122\,(6)$, $b = 22{\cdot}70\,(1)$, $c = 3{\cdot}833\,(2)$ Å, $V = 1316\,(2)$ Å^3, $Z = 1$, $D_m = 5{\cdot}05$, $D_x = 5{\cdot}03\,(2)$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 12{\cdot}22$ mm^{-1}, $F(000) = 1776$, $T = 293$ K, final $R = 0{\cdot}082$ ($wR = 0{\cdot}055$) for 1015 independent reflections. $\mathrm{In^{3+}}$ have octahedral environments and $\mathrm{Sn^{2+}}$ lie inside dicapped trigonal prisms of S atoms. One of two Sn sites is incompletely occupied. In—S distances are 2·48–2·93 Å.

Introduction. L'étude du système ternaire In–Sn–S nous a précédemment conduits à mettre en évidence une solution solide particulière, formée à partir de $\mathrm{In_6S_7}$, de formule $\mathrm{In_{6-x}Sn_{0,5x}S_7}$ $(0 \le x \le 1)$, et dont nous avons décrit la structure cristalline pour la composition limite $x = 1$ (Likforman, Guittard & Jaulmes, 1984). Rappelons que dans cette structure, l'atome d'étain divalent occupe un demi site de coordinence 7 (prisme triangulaire monocapé de soufre) et que les atomes d'indium ont deux types d'environnement: octaèdres $\mathrm{InS_6}$, paires In–In dans lesquelles chaque indium est à l'intérieur d'un tétraèdre formé de trois atomes de soufre et par l'autre atome d'indium de la paire.

Poursuivant notre étude, nous avons mis en évidence dans le sytème quasi-binaire $\mathrm{In_2S_3}$–SnS plusieurs phases dont les structures paraissent étroitement apparentées et dont nous décrivons ici un premier exemple, de composition $\mathrm{In_{18}Sn_7S_{34}}$ (soit $\mathrm{9In_2S_3,7SnS}$).

Partie expérimentale. Monocristaux extraits d'une masse polycristalline d'un échantillon de composition $\mathrm{In_2SnS_4}$ préparé à partir d'un mélange de $\mathrm{In_2S_3}$ et SnS en ampoule scellée sous vide. Température portée en 24h à 1170K et maintenue 24h. Chauffage suivi d'un refroidissement régulier en 48 h jusqu'à la température ambiante. Après la détermination structurale, nous avons préparé suivant le même protocole un mélange de composition $\mathrm{9In_2S_3,7SnS}$, qui permet d'obtenir le composé en phase pure.

Cristal utilisé: aiguille noire, brillante, 20 × 15 × 100 µm. Pas de correction d'absorption. Masse volumique D_m mesurée par flottation. Huit réflexions indépendantes utilisées pour affiner les paramètres de la maille $(6 < \theta < 10°)$. 1985 réflexions indépendantes enregistrées à 293 K à l'aide d'un diffractomètre à quatre cercles Syntex; $\sin\theta/\lambda = 0{,}68$ Å^{-1}; $0 \le h \le 20$, $0 \le k \le 30$, $0 \le l \le 5$. Balayage ω–2θ, 2θ variant de $2\theta_1 - 0{,}7°$ à $2\theta_2 + 0{,}7°$; θ_1 et θ_2; angles de diffraction correspondant aux longueurs d'onde $K\alpha_1$ et $K\alpha_2$ du molybdène. Réflexions de contrôle (115, $0\bar{4}3$) vérifiées toutes les 50 mesures, valeur de l'ecart-type relatif sur

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