Ferraris, Fuess & Joswig, 1986; Ardon & Bino, 1987).

From X-ray investigations it is well known that among the sulfates and selenates of natrochalcite type, the hydrogen-bond lengths vary considerably: O(H)···O(H) = 2·44 to 2·61 Å, O(H)···O(2) = 2·70 to 3·11 Å (Giester & Zemann, 1987, 1988; Giester, 1989). Neutron work on further members would provide information on the influence of the chemistry and stereochemistry of the compounds on the geometry of the hydrogen-bond system: a problem of considerable interest. Such investigations have, however, to await the growth of crystals of suitable size.

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Structure of the Trivanadate TlV_3O_8

BY R. BENCHRIFA, M. LEBLANC AND R. DE PAPE

Laboratoire des fluorures, UA CNRS n° 449, Faculté des sciences, 72017 Le Mans CEDEX, France

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Abstract. Thallium trivanadate, $M_r = 485·2$, monoclinic, $P2_1/m$, $a = 7·780\,(2)$, $b = 8·423\,(3)$, $c = 4·993\,(1)$ Å, $\beta = 96·48\,(2)°$, $V = 325·2$ Å^3, $Z = 2$, $D_x = 4·957$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0·71069$ Å, $\mu = 2·90$ cm^{-1}, $F(000) = 428$, $T = 293$ K, $R = 0·049$ for 2032 unique observed reflections. Full isotypy with the known CsV_3O_8 structure is found, but e.s.d. values are about four times better. The structure is built from $V(2)O_5$ square-pyramidal units; these entities share a common edge in order to give condensed $V_2O_8^{6-}$ polyanions. Their corner sharing leads to infinite chains $(V_2O_7^{4-})_\infty$ lying along the b axis. The V(1) atoms occupy an octahedral coordination between these chains; the result is a packing of corrugated sheets $(V_3O_8^-)_\infty$ parallel to the (100) plane.

Introduction. The hydrothermal treatment of a mixture of $V_2O_5 + V_2O_3 + Tl_2CO_3 + H_2O$ (mole ratio 0·5/0·12/0·38/99) at 473 K during 24 h in a sealed glass tube leads to three phases: (*a*) microcrystalline tetragonal phase $Tl_2V^{IV}V_2^{V}O_8$ (Tudo & Jolibois, 1971; Théobald & Théobald, 1984); (*b*) colorless needles of the metavanadate $TlVO_3$ (Ganne, Piffard & Tournoux, 1974; Howard & Evans, 1960); (*c*) red-orange crystals. The crystallographic characterization of the last crystals allowed us to deduce first the composition TlV_3O_8 and second their full isotypy with the homologous K, Rb, Cs and NH_4 compounds (Kelmers, 1961; Howard, Evans & Block, 1966). This analogy was suggested on the grounds of powder data (Tudo & Jolibois, 1971); these last authors obtained TlV_2O_8 as a red-orange powder by reaction at 643 K of a mixture of Tl_2CO_3 and $3V_2O_5$ under inert atmosphere; we show that their published powder data are in accordance with the calculated intensities obtained from our single-crystal study.

Experimental. [001]-elongated prismatic crystal with ±(010), ±(410) lateral faces; 0·15 × 0·07 × 0·06 mm. Siemens AED2 four-circle diffractometer (graphite monochromator); 26 reflections used for measuring

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lattice parameters, $15 \leq \theta \leq 16°$; $\omega/2\theta$ scan, angular range $4{\cdot}8 \leq 2\theta \leq 90°$; explored reciprocal space: $0 \leq h \leq 15$; $0 \leq k \leq 16$; $-10 \leq l \leq 10$. Absorption correction by the Gaussian method: $A_{max} = 0{\cdot}264$; $A_{min} = 0{\cdot}114$; number of measured reflections: 2810; number of independent observed reflections $[\sigma(I)/I \leq 0{\cdot}33]$ used in the refinements: 2032. Three standard reflections (104, 142, $\bar{1}21$), no intensity variation. Atomic scattering factors f, f', f'' from *International Tables for X-ray Crystallography* (1974) for Tl^+, V^{5+}, O^{2-}. Refinements with *SHELX*76 (Sheldrick, 1976). Starting set of coordinates from CsV_3O_8 (Howard *et al.*, 1966). The residuals drop to $R = 0{\cdot}049$ and $wR = 0{\cdot}057$ with anisotropic thermal parameters for all the atoms.* Weights are calculated from $w = K/[\sigma^2(F) + |G|F^2]$, with $|G| = 0{\cdot}00181$ and the scale factor $K = 1{\cdot}755$; $\sum w(F_o - F_c)^2$ minimized, max. Δ/σ 0·03; secondary-extinction factor $x = 4{\cdot}9 \times 10^{-7}$, max. and min. heights in the final difference Fourier map: $+5{\cdot}3$ and $-3{\cdot}9$ e Å^{-3}, the maximum being at 0·68 Å from the Tl^+ ion.

Discussion. Table 1 presents the final atomic parameters and Fig. 1 shows a perspective view of the structure. It is built from corrugated sheets packed along the *a* axis with Tl^+ ions possessing an irregular 12-fold coordination between the sheets. The coordination of the V(1) atom is a strongly distorted octahedron [distances 1·601 (5) to 2·287 (4) Å], but the V(2) environment is better described as a square-pyramidal coordination [five O atoms between 1·605 (3) and 2·005 (3) Å; O(1) at 2·915 Å]. Table 2 presents selected bond lengths in TlV_3O_8.

An important feature of the structure is the very short distance between the next nearest neighbor O(3) atoms, 2·362 (4) Å, nearly as low as the corresponding value encountered in the CsV_3O_8 structure: 2·30 (2) Å (Howard *et al.*, 1966); we note that each of the O(3) atoms has three vanadium neighbors [V(1) at 1·837 (3) Å; V(2) at 2·005 (3) Å; and V(2) at 1·955 (3) Å], so the O(3^{ii})—O(3) pair is subjected to a strong positive electrostatic potential from four V^{5+} ions, allowing an uncommon shortening of the O(3^{ii})—O(3) distance (Fig. 1).

The actual atomic positions are found to conform very well to the valence bond theory; by using the parameters from Brown & Shannon (1973), the calculated ionic valences are very close to the formal charges: V(1): 5·05; V(2): 4·95; O(1): 1·91; O(2): 2·18; O(3): 2·08; O(4): 1·96; O(5): 1·88 v.u.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52260 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional coordinates and equivalent isotropic temperature factors* (Å^2) *in* TlV_3O_8 (*e.s.d.'s in parentheses*)

$B_{eq} = \frac{4}{3}\sum_i\sum_j b_{ij}(\mathbf{a}_i.\mathbf{a}_j)$ (Hamilton, 1959).

	Site	*x*	*y*	*z*	B_{eq}
Tl(1)	2(*e*)	0·05573 (4)	0·2500	0·94825 (7)	2·32 (1)
V(1)	2(*e*)	0·5755 (1)	0·2500	0·9174 (2)	0·65 (2)
V(2)	4(*f*)	0·6870 (1)	0·0540 (1)	0·4375 (1)	0·68 (1)
O(1)	2(*e*)	0·4305 (6)	0·2500	0·1207 (11)	1·3 (1)
O(2)	2(*e*)	0·7598 (5)	0·2500	0·5915 (10)	0·77 (9)
O(3)	4(*f*)	0·5056 (3)	0·0863 (3)	0·6874 (6)	0·85 (7)
O(4)	4(*f*)	0·1664 (5)	0·0664 (4)	0·4340 (7)	1·43 (9)
O(5)	4(*f*)	0·7377 (4)	0·0996 (3)	0·1146 (5)	0·84 (6)

Table 2. *Selected bond lengths* (Å) *in* TlV_3O_8 (*e.s.d.'s in parentheses*)

The Roman numerals as superscripts indicate that the atom is in a unit cell, the relationship of which to the primary unit cell is given by: (i) $x, \frac{1}{2}-y, z$; (ii) $-x, -y, -z$; (iii) $-x, \frac{1}{2}+y, -z$; the *a* superscript indicates the translation (0,0,1).

O(3)	O(2)	2·501 (4)	Tl(1)	O(1^{iii})	2·946 (5)
O(5^{i})	O(5)	2·529 (4)	Tl(1)	O(2^{iii})	2·748 (4)
O(3^{ii})	O(3)	2·362 (5)	Tl(1)	O(4^{iii})	2·924 (3)
O(5^{ii})	O(3)	2·729 (4)	Tl(1)	O(4^{iiia})	3·198 (3)
O(5)	O(2)	2·686 (4)	Tl(1)	O(4^{i})	3·602 (3)
O(5)	O(3)	2·638 (4)	Tl(1)	O(4^{iia})	2·924 (3)
O(4^{ii})	O(2)	2·732 (7)	Tl(1)	O(4^{ii})	3·198 (3)
O(4^{ii})	O(5)	2·685 (7)	Tl(1)	O(5^{iii})	2·980 (3)
O(1)	O(3)	2·685 (5)	Tl(1)	O(5^{i})	3·387 (3)
O(1^{i})	O(5)	2·708 (5)	Tl(1)	O(5^{ii})	2·980 (3)
O(4^{ii})	O(3)	2·980 (7)	Tl(1)	O(5)	3·387 (3)
O(4^{ii})	O(4)	2·962 (7)	Tl(1)	O(4)	3·602 (3)
O(4)	O(3)	2·800 (4)			
V(1)	O(1)	1·601 (5)	V(2)	O(2)	1·881 (2)
V(1)	O(2)	2·287 (4)	V(2)	O(3)	2·005 (3)
V(1)	O(3)	1·837 (3)	V(2)	O(5)	1·746 (3)
V(1)	O(5)	1·971 (3)	V(2)	O(4^{ii})	1·605 (3)
V(1)	O(5^{i})	1·967 (3)	V(2)	O(3^{ii})	1·955 (3)
V(1)	O(3^{i})	1·837 (3)			
V(1^{iii})	V(1)	4·474 (4)			
V(2^{iii})	V(1)	3·612 (8)			
V(2^{i})	V(1)	3·112 (10)			
V(2^{ii})	V(1)	3·612 (8)			

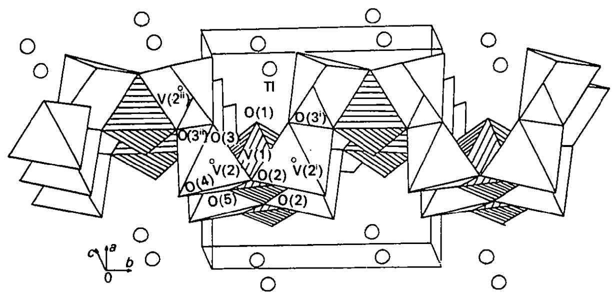

Fig. 1. Perspective view of a layer of TlV_3O_8 along the *c* axis. $V(1)O_6$ octahedra are hatched; the short distance O(3^{ii})—O(3), 2·362 Å, corresponds to a common edge shared by two $V(2)O_5$ square pyramids.

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Crystal Chemistry of *cyclo*-Hexaphosphates. VI. Structure of Ammonium *cyclo*-Hexaphosphate Tellurate Dihydrate

BY M. T. AVERBUCH-POUCHOT AND A. DURIF

Laboratoire de Cristallographie, associé à l'Université J. Fourier, CNRS, 166 X, 38042 Grenoble CEDEX, France

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Abstract. $(NH_4)_6P_6O_{18}.Te(OH)_6.2H_2O$, $M_r = 847{\cdot}73$, triclinic, $P\bar{1}$, $a = 9{\cdot}899\,(4)$, $b = 11{\cdot}042\,(7)$, $c = 7{\cdot}632\,(9)$ Å, $\alpha = 109{\cdot}53\,(6)$, $\beta = 106{\cdot}74\,(6)$, $\gamma = 100{\cdot}91\,(4)°$, $V = 714{\cdot}2$ Å^3, $Z = 1$, $D_x = 1{\cdot}971$ Mg m^{-3}, $\lambda(\text{Ag } K\bar{\alpha}) = 0{\cdot}5608$ Å, $\mu = 0{\cdot}790$ mm^{-1}, $F(000) = 426$, $T = 294$ K, final $R = 0{\cdot}018$ for 6013 observed reflections. Almost regular $Te(OH)_6$ octahedra and slightly distorted P_6O_{18} ring anions alternate in planes $z = 0$. These planes are interconnected by the ammonium groups and the water molecules through a three-dimensional network of hydrogen bonds. The water molecules are statistically located on two general positions. The hydrogen-bond scheme is described.

Introduction. Addition compounds between telluric acid and water-soluble phosphates have been extensively investigated by the authors. These adducts have been observed for almost all types of phosphates, condensed or not. A good review of the present state of this field has been recently reported by Boudjada (1985).

The title compound is the first example of a *cyclo*-hexaphosphate–tellurate.

Experimental. Crystals of the title compound can be prepared by slow evaporation at room temperature of an aqueous solution of telluric acid and ammonium *cyclo*-hexaphosphate with a stoichiometric ratio P/Te = 6. Crystals of $(NH_4)_6P_6O_{18}.Te(OH)_6.2H_2O$ appear as elongated monoclinic prisms.

Crystal size: 0·24 × 0·24 × 0·24 mm. Density not measured. Nonius CAD-4 diffractometer, graphite monochromator. 24 reflections ($11{\cdot}0 < \theta < 15{\cdot}0°$) for refining unit-cell dimensions. ω scan, scan width: 1·20°, scan speed variable between 0·02 and 0·06° s^{-1}, total background measuring time: between 30 and 10 s. 9148 reflections collected, $3 < \theta < 35°$, $\pm h$, $\pm k$, l, $h_{max} = 16$, $k_{max} = 20$, $l_{max} = 13$. Two orientation ($63\bar{2}$ and $3\bar{7}\bar{1}$) and two intensity (361 and 633) control reflections without any significant variation. 8551 reflections obtained after averaging Friedel pairs ($R_{int} = 0{\cdot}01$). Lorentz and polarization corrections, no absorption correction. Structure solved by direct methods (*MULTAN77*, Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1977). H atoms located by difference-Fourier syntheses. Anisotropic full-matrix least-squares refinements (on F), isotropic for H atoms. Unit weights. Final refinement cycles with 6013 reflections ($I > 9\sigma_I$). Final $R = 0{\cdot}018$ ($wR = 0{\cdot}023$), $S = 0{\cdot}498$, max. $\Delta/\sigma = 0{\cdot}05$. Max. peak height in the final difference-Fourier synthesis: 0·684 e Å^{-3}. No extinction correction. For the total set of 8551 reflections the R value is 0·031. Scattering factors for neutral atoms and f', f'' from *International Tables for X-ray Crystallography* (1974). Enraf–Nonius (1977) *SDP* used for all calculations. Computer used: MicroVAXII.

Discussion. Table 1 reports the final atomic coordinates.* The $Te(OH)_6$ group is located around the inversion center at 0,0,0. As usually observed in this kind of compound it corresponds to an almost regular octahedron with O—Te—O angles ranging from 87·88 to 89·80° and Te—O distances varying from 1·877 to 1·931 Å.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52257 (50 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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