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$Cs_4Sr_3H_2(P_4O_{12})_3$, a New Derivative of $Al_4(P_4O_{12})_3$

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Abstract. Tetracaesium tristrontium dihydrogentris(tetrametaphosphate), $M_r = 1744·1$, cubic, $I\bar{4}3d$, $a = 15·455\ (5)$ Å, $V = 3691·5$ Å^3, $Z = 4$, $D_x = 3·138$ Mg m^{-3}, $\lambda(\text{Ag}\ K\alpha) = 0·5608$ Å, $\mu = 4·838$ mm^{-1}, $F(000) = 3216$, $T = 293$ K, final $R = 0·031$ for 286 independent reflexions. This compound is the third example of a tetrametaphosphate in which the P–O framework observed in $Al_4(P_4O_{12})_3$ remains unchanged, while associated cations have various distributions [Sr at 12(*a*), Cs at 16(*c*) ($x \sim 0·368$)].

Introduction. The crystal structure of aluminium tetrametaphosphate, $Al_4(P_4O_{12})_3$, was described as early as 1937 (Pauling & Sherman, 1937). This type of structure was later refined by Bagieu-Beucher & Guitel (1978) using the isotypic Sc salt: $Sc_4(P_4O_{12})_3$. Recently Averbuch-Pouchot & Durif (1983) described a series of tetrametaphosphates: $M^{II}_4Na_4(P_4O_{12})_3$ (M^{II} = Zn, Co, Ni, Mg) in which they observed a P–O framework identical to that of the Al salt, but with a very different distribution of the associated cations. The same observation was made by Rzaigui, Averbuch-Pouchot & Durif (1983) upon reinvestigating the crystal structure of a series of salts of general formula $LnM^IP_4O_{12}$. The title compound is the third example of a crystal structure in which the P–O framework of $Al_4(P_4O_{12})_3$ remains unchanged.

Experimental. During experiments to optimize the chemical preparations of the tetrametaphosphate–polyphosphate of Cs–Sr, $Sr_2Cs_3(P_4O_{12})(PO_3)_3$ (Averbuch-Pouchot, 1985*a*), and of the Cs–Pb polyphosphate $PbCs_2(PO_3)_4$ (Averbuch-Pouchot, 1985*b*) we frequently observed the formation of tetrahedra slightly soluble in water. This solubility proves that the compound is not a polyphosphate but probably a Cs-rich cyclophosphate. The structural analysis shows that this salt is $Cs_4Sr_3H_2(P_4O_{12})_3$.

D_m not measured. Tetrahedral crystal (edge 0·14 mm). Philips PW 1100 diffractometer. Systematic absences: *hkl*, $h + k + l = 2n$; *hhl*, $2h + l = 4n$. 16 reflexions ($8 < \theta < 12°$) for refining the unit-cell dimensions. ω scan, scan width 1·20°, scan speed 0·02° s^{-1}. Total background measuring time 20 s. 1786 reflexions measured ($3 < \theta < 25°$). $H_{max} = K_{max} = L_{max} = 24$. Intensity reference reflexions: 800 and $\bar{8}00$. 416 independent reflexions ($R_{int} = 0·017$). Lorentz and polarization correction, no absorption correction. Structure determination by analogy with the other derivative compounds. Anisotropic full-matrix least-squares refinement (on *F*). Unit weights. Final refinements with 286 reflexions corresponding to $F_o > 3\sigma_F$. Final $R = 0·031$ ($wR = 0·030$), $S = 2·415$. Max. $\Delta/\sigma = 0·04$ (scale factor).* Max. peak height in final difference Fourier 0·85 e Å^{-3}. No extinction correction. Scattering factors for neutral atoms and f' and f'' from *International Tables for X-ray Crystallography* (1974). Enraf–Nonius (1977) *SDP* used for all calculations.

Table 1. *Final atomic coordinates and B_{eq} values, with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{4}{3}\textstyle\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	B_{eq}(Å^2)
Cs	0·3678 (2)	0·3678 (2)	0·3678 (2)	5·47 (5)
Sr	0·875	0	0	3·54 (5)
P	0·2987 (1)	0·3810 (2)	0·1234 (2)	2·32 (6)
O(*L*)	0·4194 (5)	0·0352 (4)	0·3396 (4)	2·63 (20)
O(2)	0·4598 (6)	0·1730 (5)	0·2723 (5)	3·61 (25)
O(1)	0·1058 (4)	0·0863 (5)	0·4332 (5)	3·88 (25)

Table 2. *Principal interatomic distances* (Å) *and angles* (°)

The PO_4 tetrahedron

P	O(*L*)	O(*L*)	O(1)	O(2)
O(*L*)	1·615 (5)	2·512 (7)	2·553 (7)	2·536 (8)
O(*L*)	102·8 (3)	1·600 (4)	2·471 (7)	2·451 (6)
O(1)	111·8 (3)	107·1 (2)	1·468 (5)	2·563 (8)
O(2)	110·0 (3)	103·9 (3)	119·8 (3)	1·495 (6)

P—P	2·905 (2)	P—O(*L*)—P	129·3 (3)
		P—P—P	89·76 (1)

The CsO_6 polyhedron		The SrO_8 polyhedron	
Cs—O(2)	3·111 (6) (×3)	Sr—O(2)	2·644 (5) (×4)
Cs—O(1)	3·257 (5) (×3)	Sr—O(1)	2·527 (5) (×4)

Discussion. The final atomic coordinates and B_{eq} values are reported in Table 1 while the main interatomic distances and bond angles are given in Table 2.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42415 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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As suggested by the space group and the unit-cell parameter, the title compound is structurally very similar to some other types of tetrametaphosphates previously reported with various chemical formulas.

We summarize some examples: $Al_4(P_4O_{12})_3$, $I\bar{4}3d$, $\alpha = 13{\cdot}730$ Å, $Z = 4$; $Zn_4Na_4(P_4O_{12})_3$, $I\bar{4}3d$, $\alpha = 14{\cdot}57$ Å, $Z = 4$; $CeNH_4P_4O_{12}$, $I\bar{4}3d$, $a = 15{\cdot}23$ Å, $Z = 12$. In these three types of compounds one observes that the P_4O_{12} frameworks are strictly identical, but inside this framework the atomic distribution of the associated cations is very different. In the case of $Al_4(P_4O_{12})_3$ the 16 Al atoms are located in an octahedral void with ternary symmetry [16(*c*) with $x \sim 0{\cdot}104$]. For $Zn_4Na_4(P_4O_{12})_3$, the associated cations are twice as numerous. The 16 Na atoms are located at 16(*c*) with $x \sim 0{\cdot}110$ while the 16 Zn atoms occupy the same crystallographic position with $x \sim 0{\cdot}235$. For $CeNH_4P_4O_{12}$ the 12 Ce atoms are located at position 2(*b*) while an equal number of ammonium groups statistically occupy position 16(*c*) ($x \sim 0{\cdot}112$).

In the case of the title compound the twelve Sr atoms are at position 12(*a*) and the 16 Cs atoms at 16(*c*) ($x \sim 0{\cdot}368$).

The H atoms have not been located. Up to now no isotypic tetrametaphosphate is known for this compound.

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Structure de $SrTeO_4$ sur Monocristal. Organisation de Structures Comportant des Empilements de Chaînes $(TeO_4)_n$. Dimorphisme de Na_2TeO_4

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Abstract. Strontium tellurate(VI), $M_r = 279{\cdot}22$, *Pbcn*, $a = 5{\cdot}605\,(3)$, $b = 13{\cdot}181\,(4)$, $c = 5{\cdot}003\,(2)$ Å, $V = 370\,(1)$ Å^3, $Z = 4$, $D_x = 5{\cdot}07$ Mg m^{-3}, $\lambda(\text{Mo } K\bar{\alpha}) = 0{\cdot}7107$ Å, $\mu = 22{\cdot}01$ mm^{-1}, $F(000) = 488$, $T = 295$ K, final $R = 0{\cdot}037$ ($wR = 0{\cdot}033$) for 488 reflections. Hydrothermal synthesis. The structure contains TeO_6 octahedra which share edges, thus forming infinite chains parallel to the *c* axis which are held together by Sr^{2+} ions. The structure is similar to the *Pbcn* modification of Na_2TeO_4 (β form). In the monoclinic modification (α form) a relative motion of chains leads to the presence of two different types of channels and to different locations for the cations. An irreversible phase transition (953 K) changes the α form to the β.

Introduction. Ce travail s'inscrit dans le cadre général des études structurales des tellurates $ATeO_4$ (A = Mg, Ca, Sr, Ba, Cd, Pb). Il permet d'améliorer les résultats obtenus sur poudre par Hottentot & Loopstra (1979). Les structures de composés comportant des chaînes $(TeO_4)_n^{2n-}$ de même type sont ensuite comparées. Na_2TeO_4 qui existe sous deux formes cristallines est examiné en détail.

Partie expérimentale. Synthèse hydrothermale à la température la plus basse possible (640 K): $Sr(NO_3)_2 + Na_2TeO_3 \rightarrow SrTeO_4 + NaNO_2 + NaNO_3$. Recherche d'une éventuelle forme monoclinique semblable à $Na_2TeO_4\alpha$ (Daniel, Maurin, Moret & Philippot, 1977). Les courbes de calorimétrie différentielle à balayage des composés préparés à des pH différents ne permettent pas, pour le moment, d'envisager une autre variété que la forme orthorhombique de $SrTeO_4$. Monocristal de dimensions 0,11 × 0,05 × 0,085 mm; diffractomètre Nonius CAD-3; 20 réflexions ont servi à déterminer les paramètres de la maille; 1480 réflexions enregistrées en balayage θ–2θ ($\theta < 35°$); 488 réflexions conservées après moyenne des réflexions équivalentes et élimination lorsque $I < 3\sigma(I)$; une réflexion de référence collectée toutes les 60 mesures, pas de variation

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