

Fig. 1. ORTEP diagram (Johnson, 1965) of tellurium pyrosulphate projected down the approximate twofold axis showing the atom labelling and the disorder in ligand (1). Longer Te...O contacts are drawn with thin lines. Thermal ellipsoids indicate 50% probability levels.

2.73 (2) or O(18B) ($x - \frac{1}{2}, y + \frac{1}{2}, z$) 2.76 (2), O(27) ($x + \frac{1}{2}, y + \frac{1}{2}, z$) 2.74 (1), O(24) ($x, 1 - y, z - \frac{1}{2}$) 2.87 (2) and O(14) ($x, 1 - y, z + \frac{1}{2}$) 3.02 (1) Å. As can be seen in Fig. 1, these contacts are arranged in a staggered manner so as to minimize interaction with the O atoms of the coordination sphere and complete an irregular dodecahedron.

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The Structure of Calcium Orthotellurate

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Abstract. Ca_3TeO_6 , monoclinic, $P2_1/n$, $a = 5.5730$ (6), $b = 5.7964$ (2), $c = 8.0113$ (3) Å, $\beta = 90.24$ (1)°, $V = 258.8$ Å³, $Z = 2$, $D_c = 4.41$ Mg m⁻³. Final $R = 0.041$ for 583 reflections. A single-crystal study confirms that the compound is isostructural with cryolite, $\alpha\text{-Na}_3\text{AlF}_6$. The Te—O octahedron is regular, as is usual for Te^{VI} oxides.

Introduction. Ca_3TeO_6 has been known since 1956 (Merz, 1956) but so far only polycrystalline material has been available. Because of this and the fact that its monoclinic angle is close to 90°, the structure has been

The bond lengths and angles within the pyrosulphate ligands could not be determined very accurately on account of the disorder outlined above. The values are in agreement with those obtained (Lynton & Truter, 1960) for $\text{K}_2\text{S}_2\text{O}_7$ [S—O(bridging) 1.645 (5); S=O(terminal) 1.437 (7) Å; S—O—S 124.2 (5)°].

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described as isomorphous both with cryolite, Na_3AlF_6 , space group $P2_1/n$ (Naray-Szabo & Sasvári, 1938), and with Ca_3UO_6 , space group $P2_1$ (Rietveld, 1966; Loopstra & Rietveld, 1969). Baglio & Natansohn (1969) conclude from powder indexing that the space group is $P2_1$ with $a = 5.794$, $b = 5.575$, $c = 8.020$ Å, $\beta = 90.29$ °. Trömel (1972) points out that the same powder data can be described by $a = 5.575$, $b = 5.773$, $c = 8.006$ Å, $\beta = 90.23$ °.

This description is in accordance with the observation that for cryolite and related structures b is smaller than a . With these cell constants all indices

Table 1. *Final coordinates*

Ca_3TeO_6				$\alpha\text{-Na}_3\text{AlF}_6$				
	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}^* (\AA^2)		<i>x</i>	<i>y</i>	<i>z</i>
Te	0	0	0	0.4	Al	0	0	0
Ca(1)	0	0	$\frac{1}{2}$	0.6	Na(1)	0	0	$\frac{1}{2}$
Ca(2)	0.5145 (3)	-0.0536 (3)	0.2460 (2)	0.8	Na(2)	0.50	-0.05 ₅	0.24
O(1)	0.1111 (9)	0.0540 (11)	0.2239 (7)	0.8	F(1)	0.06 ₅	0.06	0.22
O(2)	-0.2807 (9)	0.1774 (10)	0.0482 (7)	0.8	F(2)	-0.29	0.16	0.03
O(3)	0.1687 (9)	0.2740 (11)	-0.0674 (7)	0.9	F(3)	0.15	0.28	-0.06

* Defined according to Willis & Pryor (1975).

Table 2. *Selected bond lengths (\AA) and angles ($^\circ$)*

Te—O(1)	1.920 (6)	O(1)—Te—O(2)	89.1 (2)
Te—O(2)	1.913 (6)	O(1)—Te—O(3)	88.4 (3)
Te—O(3)	1.924 (6)	O(2)—Te—O(3)	90.8 (3)
Ca(1)—O(1)	2.321 (6)	O(1)—Ca(1)—O(2)	84.6 (2)
Ca(1)—O(2)	2.266 (6)	O(1)—Ca(1)—O(3)	85.3 (2)
Ca(1)—O(3)	2.326 (6)	O(2)—Ca(1)—O(3)	89.9 (2)

obey the conditions of $P2_1/n$ except for a very weak 104 reflection. On the basis of this evidence Trömel (1972) suggests that the space group is most probably $P2_1$.

In powder data collected in our investigation no trace of the 104 reflection was found. From a crystal-chemical point of view it seems improbable that Ca_3TeO_6 would be isomorphous with Ca_3UO_6 , the $\text{Te}^{\text{VI}}\text{O}_6$ octahedra being invariably rather more regular than the UO_6 octahedra in Ca_3UO_6 , which have distances ranging from 1.92 to 2.26 \AA . Fluorescence data (Natansohn, 1973) indicate likewise that Ca_3UO_6 and Ca_3TeO_6 are not isostructural. Therefore, when we obtained a tiny single crystal of Ca_3TeO_6 it seemed worthwhile to undertake its structure determination.

Polycrystalline Ca_3TeO_6 is obtained by heating a mixture of TeO_2 and 3CaCO_3 in air above 1000 K. To prepare single crystals of Ca_3TeO_6 we heated CaTeO_4 (Hottentot & Loopstra, 1979) and $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (weight ratio 1:10) at 1033 K for 3 d in air in a Pt crucible. Excess CaCl_2 was removed with water. From the remaining Ca_3TeO_6 we selected a single crystal of irregular shape, with dimensions in the range 0.075–0.30 mm. Intensities were measured on a Nonius CAD-3 three-circle diffractometer with Mo $K\alpha$ radiation and a θ – 2θ scan. Coordinates of the Te and Ca atoms were found from a Patterson map; O atoms were revealed by subsequent difference maps.

A final R of 0.041 was obtained for 583 reflections with $I > 3\sigma$. Extinction was corrected for, absorption was not. Final parameters are given in Table 1*

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35633 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

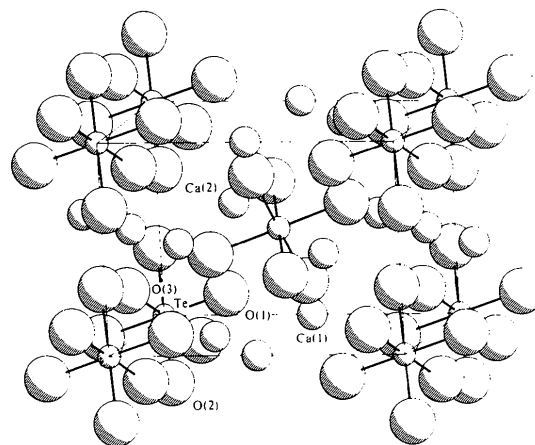


Fig. 1. A view of the cell contents; *c* is horizontal, *a* down the page.

together with those of $\alpha\text{-Na}_3\text{AlF}_6$. Table 2 gives selected bond lengths and angles. The structure is depicted in Fig. 1.

Discussion. As can be seen from Table 1, the structure is isomorphous with $\alpha\text{-Na}_3\text{AlF}_6$ and hence deviates from the ideal cubic cryolite structure (Wells, 1975). This structure has space group $Fm\bar{3}m$, with an axis of about 8 \AA . The cell of Ca_3TeO_6 is related to this cubic cell by the transformation $\frac{1}{2}, \frac{1}{2}, 0; \frac{1}{2}, -\frac{1}{2}, 0; 0, 0, 1$. The octahedra around Ca(1) and Te are almost regular, but rotated and displaced with respect to the ideal cryolite structure. The deviation from the ideal structure is conditioned by the coordination of Ca(2). Whereas in the ideal structure twelve equal $A-X$ distances are present, in this structure there are four short Ca(2)—O distances [2.339 (6) to 2.392 (6) \AA], and four longer ones [2.611 (6) to 2.948 (6) \AA] whilst the last four are so long [3.388 (6) to 3.686 (6) \AA] that no bonding interaction is assumed.

Other substances believed to be isomorphous with $\alpha\text{-Na}_3\text{AlF}_6$ are $\alpha\text{-Na}_3\text{TlF}_6$ and $\alpha\text{-Na}_3\text{InF}_6$ (Grannec, Portier & Hagenmüller, 1971), Na_3CrF_6 (de Kozak, 1971), Na_3TiOF_5 (Pausewang & Rüdorff, 1969) and probably Ca_3WO_6 (Trömel, 1972).

Table 3. *Shape of TeO₆⁶⁻ octahedra in some orthotellurates*

	Te—O (Å)	O—Te—O [maximum deviation (°) from 90°]
Ca ₃ TeO ₆	1.913 (6)–1.924 (6)	1.6 (3)
Te(OH) ₆ (monoclinic)	1.907 (1)–1.914 (1)	2.4 (1)
Te(OH) ₆ (cubic)	1.913 (6)	0.8 (3)
Cu ₃ TeO ₆	1.921 (2)	4.0 (1)
Mg ₃ TeO ₆	1.912 (3)–1.914 (3)	4.6 (1)

The shape of the TeO₆⁶⁻ octahedron is essentially the same as it is in, e.g., Te(OH)₆ (monoclinic) (Lindqvist & Lehmann, 1973), Te(OH)₆ (cubic) (Falck & Lindqvist, 1978b), Cu₃TeO₆ (Falck & Lindqvist, 1978a) and Mg₃TeO₆ (Schulz & Bayer, 1971) as can be seen in Table 3. The conclusion that the TeO₆⁶⁻ ion is rigid with bond lengths of about 1.92 Å (Falck & Lindqvist, 1978a) is confirmed by this structure determination.

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Structure of Phosphorus(III,V) Oxide P₄O₇

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Abstract. P₄O₇, monoclinic, $P2_1/n$, $a = 9.808$ (2), $b = 9.966$ (1), $c = 6.852$ (1) Å, $\beta = 96.81$ (1)°, $V = 665.0$ Å³, $Z = 4$, $D_x = 2.35$ Mg m⁻³ (the pycnometric value could not be determined), 1822 reflexions, $R = 0.08$, anisotropic temperature factors. Molecules comprising four P atoms are connected *via* six bridging O atoms to form an adamantane-like cage with one additional O atom in a terminal position at the pentavalent P. Bond lengths and angles involving trivalent phosphorus are P^{III}—O—(P^{III}) 1.64 Å, P^{III}—O—(P^V) 1.68 Å, O—P^{III}—O 99°, P^{III}—O—P^{III} 128°, P^{III}—O—P^V 124°.

Introduction. The main problem in this investigation was the difficult handling of the very hygroscopic

crystals. For X-ray investigations they were selected in a special box under a stream of nitrogen, which had been dried with liquid nitrogen, and enclosed in Mark tubes.

The symmetry of the intensities and the systematic absences were determined by film methods. The symmetry was found to be monoclinic; the systematic absences obeyed the following conditions: reflexions $h0l$ are only present when $h + l$ is even, and $0k0$ when k is even. Therefore the space group is $P2_1/n$. The cell parameters, previously calculated with film data, were refined by least-squares methods from the diffractometer settings of 14 reflexions.

A rod-shaped crystal 0.2 mm in diameter and 0.9 mm in length (direction [102]) was used for the