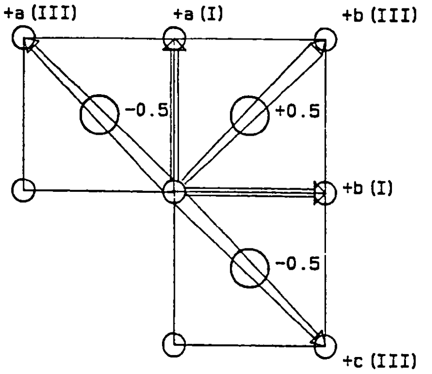

Fig. 3. A view of the unit-cell contents, with the c_I axis into the page, illustrating the transformation between the phase I structure and the phase III structure. The O atoms (I—O bonds orientated approximately along the negative direction of the phase I axes) are not shown. The I atoms are in the plane of the paper, while the atomic coordinates of the K atoms along the c_I axis are as shown. The atoms are represented by circles of decreasing size: K, I.

The triclinic symmetry of the phase III structure does not constrain the conformation of the IO_3 groups as all atoms are in general positions and some distortions of the individual groups are apparent, although the I—O bond lengths and O—I—O angles *averaged over all groups* are 1·81 (7) Å, 100·2 (3·6)° at 10 K; 1·81 (6) Å, 100·3 (3·2)° at 100 K; 1·81 (7) Å, 100·1 (3·9)° at 300 K. On transition to the rhombohedral-symmetry structure of phase I, the atoms are displaced from their phase III positions by approximately 0·1 Å for K and I atoms, approximately 0·2 Å for O atoms.* The IO_3 groups are now positioned about threefold symmetry axes, which constrain them to have the regular undistorted conformations indicated in Table 2.

The possible existence of ferroelectric-type behaviour in phase I of KIO_3 has been the subject of several investigations. Herlach (1961) reported phase I to be paraelectric, on the basis of nuclear quadrupole resonance measurements; Crane (1972) found the existence of pyroelectricity in this phase. As the present study suggests a structure with non-centrosymmetric space group *R*3, the latter observation is supported and calculation based on the proposed structure indicates an approximate spontaneous polarization of 0·16 C m^{-2}. This is comparable in magnitude to the 0·12 C m^{-2} calculated for γ-KNO_3 by Nimmo & Lucas (1976).

The previous uncertainties of the phase I KIO_3 structure, the phase-transition behaviour, and some aspects of its ferroelectric/pyroelectric properties have now been resolved.

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* See deposition footnote.

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Structure of Dithionitryl Hexafluoroarsenate(V)

By James P. Johnson, Jack Passmore and Peter S. White

Department of Chemistry, University of New Brunswick, Fredericton, New Brunswick, Canada E3B 6E2

and Arthur J. Banister and A. G. Kendrick

Department of Chemistry, University of Durham, Science Laboratories, Durham DH1 3LE, England

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Abstract. $NS_2^+.AsF_6^-$, $M_r = 267{\cdot}04$, monoclinic, $C2/m$, $a = 9{\cdot}5542\ (13)$, $b = 6{\cdot}5968\ (14)$, $c = 5{\cdot}3017\ (11)$ Å, $\beta = 91{\cdot}15\ (2)°$, $V = 334{\cdot}1\ (2)$ Å^3, $D_x = 2{\cdot}66$ Mg m^{-3} for $Z = 2$, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71073$ Å, $\mu(\text{Mo } K\alpha) = 5{\cdot}72$ mm^{-1}, $F(000) = 252$, $T = 293$ K. The structure was refined by full-matrix least squares to $R = 0{\cdot}041$,

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$wR = 0·041$ for 238 unique reflections. The structure consists of discrete linear S_2N^+ cations [S—N = 1·480 (3) Å] and approximately octahedral AsF_6^- anions [As—F = 1·696 (6), 1·705 (5) Å] of C_{2h} symmetry, with weak cation–anion interactions.

Introduction. In the course of our studies of the interactions of S_2N^+ with a variety of reagents we have obtained suitable crystals of $S_2N^+.AsF_6^-$ for X-ray analysis. Red-coated yellow crystals of $S_2N^+.AsF_6^-$ were isolated from the reaction mixture of $SN^+.AsF_6^-$ and $S_2N^+.AsF_6^-$ in SO_2 and sealed in dry quartz capillaries by previously described methods (Apblett, Grein, Johnson, Passmore & White, 1986). Single crystals from the established preparation of $S_2N^+.AsF_6^-$ (Banister, Hey, MacLean & Passmore, 1982) had the same cell dimensions as the crystal selected for intensity data collection but were of lower quality.

Experimental. Initial cell parameters were determined from precession photographs on a crystal with dimensions 0·61 × 0·33 × 0·08 mm. Lattice parameters from the settings of 25 well-centered reflections with $21 \leq 2\theta \leq 36°$. Systematic absences indicated one of the space groups *C*2, *Cm* or *C*2/*m*. Mutual exclusion of bands in the infrared and Raman solid-state vibration spectra of $S_2N^+.AsF_6^-$ indicated that both anion and cation lie on inversion centers. Only *C*2/*m* satisfies these requirements and the structure was successfully refined in *C*2/*m*. Intensities of 1239 reflections in the hemisphere $h, \pm k, \pm l$ with $2\theta_{\max} = 50°$ were measured using an Enraf–Nonius CAD-4 diffractometer in the ω–2θ mode. Three standard reflections, measured every hour, showed a long-term decay of 13%. Equivalent reflections were averaged to give 322 unique reflections and 238 observed reflections $[I \geq 3\sigma(I)]$ with $R_{\rm int} = 0·124$. The As position was deduced to lie on the origin from the Patterson function and the remaining atoms were located by a subsequent difference synthesis. A *DIFABS* empirical absorption correction (Walker & Stuart, 1983) was applied to the data set with maximum and minimum relative absorption corrections of 1·578 and 0·641 ($R_{\rm int} = 0·024$ for the corrected data). The structure was refined by full-matrix least squares using *SHELX*76 (Sheldrick, 1976) with use of anisotropic thermal parameters for all the atoms. The function minimized was $\sum w(\Delta F)^2$ with $w = 4·127[\sigma(F)^2 + 0·0003F_o]^{-1}$ where $\sigma(F)$ is directly derived from $\sigma(I)$. The final refinement converged at $R = 0·041$ and $wR = 0·041$ (0·074 and 0·055, including unobserved reflections) for 30 parameters. The maximum shift-to-e.s.d. ratio was less than 0·001 in the final cycle of refinement. No extinction correction was made. Final difference synthesis showed a maximum of 0·8 e Å^{-3} at 1 Å from the As atom with the remaining electron density ±0·5 e Å^{-3} randomly distributed throughout the cell. Atomic scattering factors corrected for anomalous dispersion were taken from *International Tables for X-ray Crystallography* (1974). The final coordinates are given in Table 1,* and interatomic distances and angles in Table 2.

Discussion. The packing within the crystal is illustrated in Fig. 1; all fluorine anion–cation contacts less than the sum of the van der Waals radii (Bondi, 1964) are

Table 1. *Fractional atomic coordinates with e.s.d.'s in parentheses*

	x	*y*	*z*	$B_{\rm eq}$(Å^2)*
S	0·6420 (3)	0	0·6169 (6)	4·93
N	½	0	½	3·60
As	0	0	0	3·18
F(1)	0·1064 (7)	0	−0·2523 (13)	5·69
F(2)	0·1021 (5)	0·1837 (9)	0·1352 (8)	5·54

* $B_{\rm eq}$ is the mean of the principal axes of the thermal ellipsoid.

Table 2. *Interatomic distances* (Å) *and angles* (°)

S—N	1·480 (3)	F(1)—As—F(2)	89·1 (2)
As—F(1)	1·696 (6)	F(2)—As—F(2)	89·4 (2)
As—F(2)	1·705 (5)		
S···F(1′)	3·115 (7)	F(1)···S—N	116·9 (2)
S···F(2′)	3·007 (5)	F(2)···S—N	156·0 (1)
		As—F(1)···S	166·3 (4)
		As—F(2)···S	110·5 (2)
		F(1)···S···F(2)	68·9 (2)
		F(2)···S···F(2)	47·5 (2)

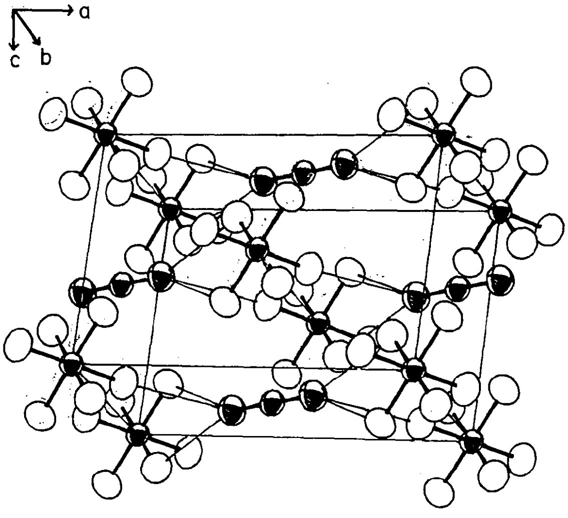

Fig. 1. Packing diagram of S_2NAsF_6 indicating anion–cation contacts.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43946 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

indicated. The hexafluoroarsenate ions occupy the corners of the cell and centers of the *ab* faces. The S_2N^+ cations occupy the remaining four faces of the cell.

The S_2N^+ cation is linear and has six weak F—S contacts (see Table 2), at approximately 90% of the sum of the van der Waals radii. The S—N bond distance in the S_2N^+ cation of $S_2N^+.AsF_6^-$ [1·480(3) Å] is longer than or equal to the corresponding bond distances in $S_2N^+.SbCl_6^-$ [1·463(4) Å] (Faggiani, Gillespie, Lock & Tyrer, 1978) or $S_2N^+.AlCl_4^-$ [1·464 (5), 1·472 (5) Å] (Thewalt, Berhalter & Müller, 1982).

The strengths of the cation–anion contacts generally increase with the Lewis basicity of the anions ($AsF_6^- < SbCl_6^- < AlCl_4^-$), and therefore it was anticipated that the S—N distance in the AsF_6^- salt might be shorter than the others. On the other hand, the averages of the symmetric and asymmetric S—N stretching frequencies in the AsF_6^- and $SbCl_6^-$ salts are almost the same, 1095 and 1093 cm^{-1}, respectively (Banister, Hey, MacLean & Passmore, 1982). Consistently, stretching frequencies and force contacts for the AsF_6^-, SbF_6^-, SO_3F^- and NO_3^- salts of the related NO_2^+ are also very similar (Qureshi, Carter & Aubke, 1971). On this basis, the S—N distances in the $SbCl_6^-$ and AsF_6^- salts would be expected to be about the same. A correction for thermal effects using the 'riding model' (Busing & Levy, 1963) gives S—N distances of 1·490 [SbF_6^-], 1·510 [AsF_6^-], 1·494 and 1·517 Å for the two S—N distances in the $AlCl_4^-$ salt (Thewalt, Berhalter & Müller, 1982). No noticeable trend is observable in these bond distances and they are not significantly different from one another.

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Crystal Structure of a New Adduct Between Telluric Acid and Alkali *cyclo*-Triphosphates: $Te(OH)_6.Na_3P_3O_9.K_3P_3O_9$

By M. T. Averbuch-Pouchot and A. Durif

Laboratoire de Cristallographie, Centre National de la Recherche Scientifique, Laboratoire associé à USTMG, 166 X, 38042 Grenoble CEDEX, France

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Abstract. $M_r = 889·74$, monoclinic, $C2/c$, $a = 18·42$ (1), $b = 10·644$ (5), $c = 12·348$ (8) Å, $\beta = 119·76$ (5)°, $V = 2102$ (2) Å^3, $Z = 4$, $D_x = 2·811$ Mg m^{-3}, $\lambda(\text{Ag } K\bar{\alpha}) = 0·5608$ Å, $\mu = 1·38$ mm^{-1}, $F(000) = 1720$, $T = 298$ K, $R = 0·017$ for 2553 independent reflexions. The crystal structure is built up of planes ($z \simeq 0·0$ and 0·5) of a hexagonal network of P_3O_9 groups centred by $Te(OH)_6$ groups, alternating with planes ($z \simeq 0·25$ and 0·75) of the associated cations.

Introduction. Addition compounds between telluric acid and alkali *cyclo*-triphosphates have been widely investigated. Structural investigations have been reported for $Te(OH)_6.2Na_3P_3O_9.6H_2O$ (Boudjada, Averbuch-Pouchot & Durif, 1981*a*; Boudjada, Lambert-Andron & Boucherle, 1985; Boudjada, 1981), $Te(OH)_6.K_3P_3O_9.2H_2O$ (Boudjada, 1981; Boudjada, Averbuch-Pouchot & Durif, 1981*b*), $Te(OH)_6.Rb_3P_3O_9.H_2O$ (Boudjada & Durif, 1982), and $Te(OH)_6.2(NH_4)_3P_3O_9$ (Boudjada, Boudjada & Guitel, 1983). Up to now, only one adduct between a mixed-alkali *cyclo*-triphosphate and telluric acid has been reported: $Te(OH)_6.Cs_2NaP_3O_9$ (Boudjada, 1985). As in all the adducts between telluric acid and various kinds of inorganic phosphates, condensed or not, one observes in their atomic frameworks the coexistence of independent $Te(OH)_6$ and phosphoric anionic groups. In the present work we

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