6,25; $c = 7{,}22$ et 7,92 Å respectivement (Thummel & Hoppe, 1974; Duquenoy, 1971), qui nous incite à ne pas considérer le problème structural de K_2TeO_4 résolu, tant qu'une étude sur monocristal n'aura pas été effectuée.

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Ordered AsO_4 and SO_4 Tetrahedra in Diammonium Trihydrogenarsenate Sulfate

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

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

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Abstract. $(NH_4)_2H_3AsO_4SO_4$, $M_r = 274{\cdot}08$, monoclinic, $P2_1/c$, $a = 11{\cdot}95\,(1)$, $b = 7{\cdot}660\,(5)$, $c = 9{\cdot}658\,(6)$ Å, $\beta = 92{\cdot}40\,(1)°$, $V = 883{\cdot}1$ Å^3, $Z = 4$, $D_x = 2{\cdot}0621$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å, $\mu = 4{\cdot}306$ mm^{-1}, $F(000) = 552$, $T = 293$ K, final $R = 0{\cdot}043$ for 1324 independent reflections. $(NH_4)_2H_3AsO_4SO_4$ has a structure closely related to those of the mixed salts $M_2H_3PO_4SO_4$ (M = K, NH_4) but in the title compound order is observed between the two kinds of XO_4 groups. $[H_3AsO_4SO_4]^{2-}$ groups linked by two ammonium ions run along the [101] direction building up chains interconnected by hydrogen bonds. Mean bond lengths and angles in the tetrahedral oxo ions are: $\langle As–O\rangle = 1{\cdot}686\,(6)$ Å; $\langle O–As–O\rangle = 109{\cdot}4\,(2)°$; $\langle S–O\rangle = 1{\cdot}473\,(5)$ Å; $\langle O–S–O\rangle = 109{\cdot}5\,(3)°$.

Introduction. The present work is part of a systematic investigation on the possibility of order between two different isolated XO_4 oxo ions in various salts. A great number of compounds possess two types of tetrahedral oxo ion in their framework, but in most of them they are randomly distributed (*Dana's System of Mineralogy*, 1963; Giusepetti, Coda, Mazzi & Tadini, 1962; Sakae, Nagata & Sudo, 1978). Up to now, the only example of ordering between isolated XO_4 tetrahedra has been provided by $Ag_6SO_4SiO_4$ (Keller & Müller-Bushbaum, 1974). We start this investigation by describing the chemical preparation and the crystal structure of $(NH_4)_2H_3AsO_4SO_4$, a new example of such an order.

Experimental. Crystals of ammonium hydrogenarsenate sulfate are produced from a stoichiometric solution of ammonium sulfate and arsenic acid:

$$(NH_4)_2SO_4 + H_3AsO_4 \rightarrow (NH_4)_2H_3AsO_4SO_4.$$

Pure arsenic acid is produced by oxidation of As_2O_3 by hydrogen peroxide. The resulting solution is kept at room temperature. A few days later, thick diamond-like platelets of $(NH_4)_2H_3AsO_4SO_4$ crystallize.

Spherical crystal ($\varnothing \simeq 0{\cdot}21$ mm). Philips PW 1100 diffractometer. Systematic absences: $h0l$, $l = 2n$; $0k0$, $k = 2n$. Mo $K\alpha$ radiation, graphite monochromator, ω scan, scan width 1·60°, scan speed 0·02° s^{-1}, total background measurement time 12 s. 14 reflections used for refining lattice parameters ($14{\cdot}5 < \theta < 18°$). Lorentz and polarization but no absorption corrections ($\mu\varnothing \simeq 0{\cdot}92$). $2\theta_{\max} = 60°$. h,k,l range: ±16, 10, 13. Reference reflections (800, $\bar{8}00$) show no appreciable intensity variation. 1759 independent reflections measured; 435 reflections rejected: 4 incorrectly measured (failure of the 'automatic attenuation system'), 431 with $I < 3\sigma(I)$. Classical methods for structure determination: Patterson and successive Fourier syntheses. Attempts to localize hydrogen atoms by difference-Fourier syntheses unsuccessful. Refinement on F. Final fitness parameters: $R = 0{\cdot}043$, $wR = 0{\cdot}048$, $S = 0{\cdot}671$ ($R = 0{\cdot}076$ for the complete set of collected reflections). Unit weights. Max. $\Delta/\sigma = 0{\cdot}0$. Max. peak height in final difference-Fourier synthesis $0{\cdot}717$ e Å^{-3}. No extinction correction. Scat-

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tering factors for neutral atoms and f', f'' values from *International Tables for X-ray Crystallography* (1974). Computer program used: Enraf–Nonius (1977) *Structure Determination Package.* Computer: PDP 11·70.

Discussion. Final positional parameters and their e.s.d.'s are given in Table 1.* Unlike similar compounds (Averbuch-Pouchot & Durif, 1980; Averbuch-Pouchot, 1981), the arsenate and sulfate oxo ions here are ordered (Fig. 1): $[H_3AsO_4SO_4]^{2-}$ groups linked by ammonium ions run along the [101] direction, building up chains interconnected by hydrogen bonds.

AsO_4^{3-} and SO_4^{2-} tetrahedra

Mean X—O distances are ⟨As—O⟩ = 1·686, ⟨S—O⟩ = 1·473 Å (Table 2), which are close to the values commonly found in these oxo ions. The arsenate ion is slightly distorted, probably because acid hydrogen atoms are bonded to the oxygen atoms of the three longest As—O bonds; this would be in agreement with the relative pK's of arsenic and sulfuric acids.

Ammonium groups

The coordination polyhedron of the two ammonium ions is built up of seven oxygen atoms, of which six can be seen as the vertices of a distorted octahedron (Table 3). N—O bond lengths seem to indicate competition between three of the four hydrogen atoms (N—O > 3 Å) to fulfil H-bonding requirements, giving rise to bi- or trifurcated bonds or even making the ammonium ions free to rotate around their shortest N—O bond.

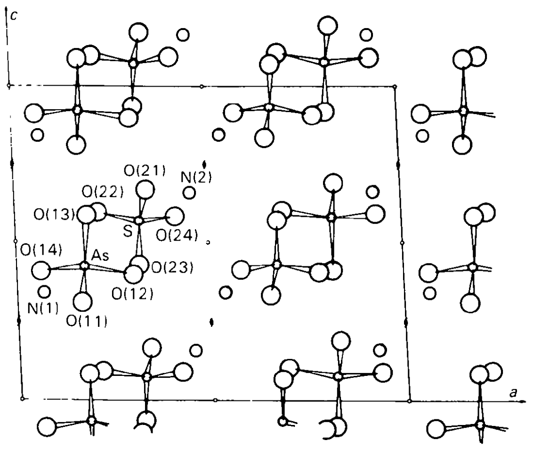

Fig. 1. Projection of the atomic arrangement of $(NH_4)_2H_3AsO_4SO_4$ along the b axis.

Table 1. *Positional parameters and their e.s.d.'s*

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

	x	y	z	B_{eq}(Å^2)
As	0·17602 (6)	0·1862 (9)	0·42489 (7)	1·88 (1)
S	0·3224 (1)	0·6841 (2)	0·5702 (2)	1·90 (3)
O(11)	0·1672 (4)	0·0160 (7)	0·3126 (5)	2·8 (1)
O(12)	0·3024 (4)	0·2821 (6)	0·4000 (5)	2·8 (1)
O(13)	0·1840 (6)	0·0992 (8)	0·5881 (5)	3·8 (2)
O(14)	0·0664 (4)	0·3131 (8)	0·4075 (5)	2·8 (1)
O(21)	0·3407 (4)	0·5400 (7)	0·6713 (5)	2·7 (1)
O(22)	0·2149 (4)	0·7686 (7)	0·5948 (6)	2·8 (1)
O(23)	0·3189 (5)	0·6122 (7)	0·4282 (5)	3·1 (2)
O(24)	0·4149 (4)	0·8092 (8)	0·5863 (5)	2·9 (1)
N(1)	0·0657 (5)	0·6667 (8)	0·3414 (6)	2·4 (2)
N(2)	0·4554 (5)	0·1848 (10)	0·6586 (6)	2·5 (2)

Table 2. *Main interatomic distances* (Å) *and bond angles* (°) *in* AsO_4 *and* SO_4 *tetrahedra and in oxygen polyhedra of the ammonium groups*

As	O(11)	O(12)	O(13)	O(14)
O(11)	1·696 (4)	2·713 (5)	2·735 (6)	2·750 (6)
O(12)	105·8 (2)	1·705 (4)	2·735 (6)	2·834 (5)
O(13)	106·8 (2)	106·4 (2)	1·710 (4)	2·738 (6)
O(14)	111·3 (2)	116·1 (2)	109·9 (2)	1·634 (4)

⟨As—O⟩ 1·686
⟨O—As—O⟩ 109·4
⟨O—O⟩ 2·751

S	O(21)	O(22)	O(23)	O(24)
O(21)	1·484 (4)	2·405 (5)	2·416 (5)	2·402 (6)
O(22)	109·2 (2)	1·467 (4)	2·395 (6)	2·415 (5)
O(23)	109·4 (3)	108·9 (3)	1·477 (4)	2·404 (6)
O(24)	109·0 (2)	110·8 (3)	109·5 (2)	1·466 (4)

⟨S—O⟩ 1·473
⟨O—S—O⟩ 109·5
⟨O—O⟩ 2·406

N(1)	O(14)	O(14)	O(14)	O(11)	O(22)	O(22)
O(14)	2·783 (7)	5·102	3·761	5·601	4·281	4·794
O(14)	122·5 (2)	3·034 (6)	4·925	3·772	5·794	3·417
O(14)	81·9 (2)	110·7 (2)	2·953 (6)	4·699	3·417	5·989
O(11)	154·9 (2)	78·1 (2)	105·4 (2)	2·956 (6)	3·348	3·099
O(22)	93·9 (2)	143·5 (2)	69·1 (1)	67·5 (1)	3·068 (6)	4·837
O(22)	109·8 (2)	68·0 (1)	167·2 (2)	61·8 (1)	103·9 (2)	3·074 (6)

N(1)···O(23) 3·133 (6)

N(2)	O(24)	O(12)	O(12)	O(21)	O(24)	O(24)
O(24)	2·995 (7)	4·822	4·596	5·732	5·316	3·968
O(12)	87·7 (2)	3·123 (6)	4·854	3·299	5·888	3·447
O(12)	99·4 (2)	104·1 (2)	3·033 (6)	3·356	3·447	5·902
O(21)	142·9 (2)	64·6 (1)	67·0 (1)	3·051 (7)	4·069	4·741
O(24)	124·6 (2)	147·5 (2)	69·6 (1)	84·4 (2)	3·010 (6)	4·914
O(24)	84·9 (2)	69·9 (1)	172·6 (2)	106·1 (2)	113·0 (2)	2·882 (6)

N(2)···O(21) 3·086 (6)

Table 3. *Comparative table of the atomic positions of the non-hydrogen atoms in the disordered and ordered structures*

	x'	y'	z'		x'	y'	z'
As	0·25	0·19	0·10	P/S	0·25	0·18	0·10
S	0·25	0·18	0·11				
O(11)	0·15	0·02	0·98	O(2)	0·16	0·03	0·99
O(21)	0·17	0·04	0·99				
O(12)	0·10	0·28	0·20	O(3)	0·11	0·27	0·19
O(22)	0·12	0·27	0·19				
O(13)	0·40	0·10	0·27	O(4)	0·39	0·10	0·25
O(23)	0·39	0·11	0·25				
O(14)	0·34	0·31	0·97	O(1)	0·33	0·31	0·99
O(24)	0·33	0·31	1·00				
N(1)	0·23	0·17	0·59	N	0·21	0·17	0·61
N(2)	0·20	0·19	0·61				

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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 42412 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Similarity with $(NH_4)_2H_3PO_4SO_4$ (*Averbuch-Pouchot*, 1981)

From the transformations

$$R=\begin{bmatrix}\frac{1}{2} & 0 & \frac{1}{2}\\ 0 & 1 & 0\\ \frac{1}{2} & 0 & \frac{1}{2}\end{bmatrix} + \tau = \begin{bmatrix}0\\ 0\\ \frac{1}{2}\end{bmatrix},$$

we derive the new fractional coordinates of the atoms and compare them with those in the P/S disordered structure (Table 3). We can see that small displacements are required to go from the disordered structure to the ordered one and that the ordering of XO_4 groups is reached by doubling the unit-cell volume. The title structure is then a superstructure of the disordered one. Baur (1981) gives for phosphate, sulfate and arsenate groups the following mean bond lengths: $\langle P—O\rangle = 1{\cdot}537$, $\langle S—O\rangle = 1{\cdot}473$, $\langle As—O\rangle = 1{\cdot}682$ Å. The differences between the mean X—O bond lengths of the two tetrahedral oxo ions $[\delta(X/Y) = |\langle X—O\rangle - \langle Y—O\rangle|]$ involved in each structure agree with the accepted ideas about possible order (disorder) in the two different tetrahedral groups: $\delta(P/S) = 0{\cdot}06$, $\delta(As/S) = 0{\cdot}21$ Å.

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Structure of Tetrapotassium Tetrametaphosphate Tetrahydrate

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

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

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Abstract. $K_4P_4O_{12}.4H_2O$, $M_r = 544{\cdot}35$, tetragonal, $I\bar{4}$, $a = 9{\cdot}061\,(3)$, $c = 10{\cdot}284\,(5)$ Å, $V = 844{\cdot}3$ Å^3, $Z = 2$, $D_x = 2{\cdot}141$ Mg m^{-3}, $\lambda(\mathrm{Ag}\ K\alpha) = 0{\cdot}5608$ Å, $\mu = 0{\cdot}76$ mm^{-1}, $F(000) = 544$, $T = 293$ K, final $R = 0{\cdot}030$ for 826 independent reflexions. P_4O_{12} ring anions are located around the $\bar{4}$ axis and form layers in planes $z = 0$ and 0·5. These layers are interconnected by K polyhedra and H bridges of the water molecules.

Introduction. The existence of two crystalline forms for potassium tetrametaphosphate tetrahydrate and of two forms for the anhydrous salt are reported in the chemical literature (Van Wazer, 1966). We recently described the chemical preparation and crystal structure of a triclinic dihydrate: $K_4P_4O_{12}.2H_2O$ (Averbuch-Pouchot & Durif, 1985). The present work deals with the crystal structure of the tetragonal tetrahydrate.

Experimental. As described in a previous paper (Averbuch-Pouchot & Durif, 1985), $K_4P_4O_{12}.2H_2O$ is easily prepared by adding freshly prepared tetrametaphosphoric acid to an iced solution of $KHCO_3$ or K_2CO_3. To the resulting solution is then added a large excess of ethyl alcohol to precipitate the tetrametaphosphate. The precipitate so obtained is very often a gel, crystallizing slowly and producing $K_4P_4O_{12}.2H_2O$ crystals. If some pellets of KOH are added to a freshly prepared gel, the speed of crystallization is increased and the resulting crystals are large pseudo-hexagonal prisms of $K_4P_4O_{12}.4H_2O$.

Crystal size: $0{\cdot}40 \times 0{\cdot}40 \times 0{\cdot}40$ mm; D_m not measured; Philips PW 1100 diffractometer; graphite monochromator; systematic absences: $h + k + l = 2n$; 15 reflexions ($10 < \theta < 13°$) for refining the unit cell; ω scan; scan speed: $0{\cdot}02°\ s^{-1}$; scan width: 1·20°; total background measuring time: 20 s; intensity and orientation reflexions: 008 and $00\bar{8}$ (no significant variation in intensity); θ range: 3–30°; 1212 reflexions measured; $H_{max} = 16$, $L_{max} = 18$; Lorentz–polarization correction; no absorption correction; classical methods for structure determination: Patterson function and successive Fourier syntheses; H atoms located from

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