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Tripotassium Hydroxylaminetrisulfonate Sesquihydrate, Neutron Data*

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Abstract. $K_3[SO_3ON(SO_3)_2].\frac{3}{2}H_2O$, monoclinic, $I2/c$ (distinguished from Ic by intensity statistics), a = 25·5873 (40), b = 6·7771 (4), c = 13·9694 (12) Å, β = 92·08 (1)° [λ(Mo $K\alpha$) = 0·71069 Å, 23·5 ± 1·0°C], Z = 8, ρ_c = 2·275 g cm^{-3}. Angle data: S–N–S, 118·9 (1); S–N–O, 105·4 (1) and 106·3 (1); N–O–S, 113·8 (1); H–O–H, 106·9 (3) and 107·2 (6)°. Bond lengths: N–S, 1·745 (2) and 1·755 (2); N–O, 1·434 (1); S–O (O on N), 1·664 (2); S–O (SO_3 groups), 1·432 (2) to 1·444 (2), mean 1·437 (r.m.s.d. = 0·004) Å. There is only one hydrogen bond of significant strength, with distances O···O and H···O of 2·935 (2) and 2·022 (3) Å and angle O–H···O = 161·6 (3)°.

Introduction. The cell parameters were derived by the least-squares method from angle data for 12 Mo $K\alpha$ reflections in the 2θ range 36 to 47°. The choice of the space group $I2/c$ rather than Ic,‡ the solution by Long's (1965) direct method, and preliminary refinement were all based on a set of 2872 reflection intensities [Mo $K\alpha$ radiation, $(\sin\theta)/\lambda \le 0.650$ Å^{-1}], corrected for absorption. The space-group specification was made by an analysis of intensity statistics with the program *ORESTES* written by W. E. Thiessen & H. A. Levy (*World List of Crystallographic Computer Programs*, 1973). The H atoms were located in a difference map. The refinement with X-ray data converged at $R(F)$ = 0·048 and σ_1 = 1·297 (standard deviation of an observation of unit weight§).

Final refinement was based on a set of 3065 nonequivalent neutron intensity data [$(\sin\theta)/\lambda \le 0.675$ Å^{-1}, λ = 1·249 Å] recorded with the instrument and procedures used by Lisensky, Johnson & Levy (1976) from a colorless, transparent specimen about 1·3 × 2·8 × 3·4 mm. The preliminary data-processing steps were generally the same as described by Lisensky *et al.* (1976). The same correction was applied to the statistical variances of the F_o^2 data. The absorption correction factors applied to the F_o^2 data ranged from 1·08 to 1·21 (μ = 0·615 cm^{-1}).

The coherent nuclear scattering amplitudes were from a compilation by Shull (1972): $b_{\rm H}$ = −0·3740, $b_{\rm N}$ = 0·940, $b_{\rm O}$ = 0·5803, $b_{\rm S}$ = 0·2847, $b_{\rm K}$ = 0·370, all in units of 10^{-12} cm. In the final least-squares cycles 'type 1' anisotropic extinction corrections (Coppens & Hamilton, 1970) were calculated and applied to the F_o^2 values, the largest correction factor being 2·73. At convergence the usual measures of goodness of fit for the 3065 reflections were: $R(F)$ = 0·066, $R(F^2)$ = 0·053, $R_w(F^2)$ = 0·072, σ_2 = 1·011. The corresponding values calculated for the 2546 reflections with $F_o^2 > \sigma(F_o^2)$ were 0·047, 0·048, 0·066, and 1·028. The final atomic coordinates are presented in Table 1.‡

Table 1. *Fractional coordinates* (×10^5)

	x	*y*	*z*
K(1)	8099 (7)	63807 (28)	−1248 (13)
K(2)	7142 (7)	85213 (27)	30878 (13)
K(3)	23345 (7)	−3017 (28)	−15190 (12)
N	11906 (2)	19120 (8)	12231 (4)
S(1)	12627 (7)	34510 (28)	22206 (12)
S(2)	5580 (7)	13100 (29)	7912 (12)
S(3)	19539 (7)	−4789 (30)	8723 (13)
O(1)	18155 (4)	33612 (18)	24458 (8)
O(2)	10815 (5)	53203 (16)	18493 (8)
O(3)	9493 (5)	26297 (18)	29615 (7)
O(4)	6710 (5)	3212 (21)	−869 (8)
O(5)	3262 (4)	385 (21)	14773 (8)
O(6)	3138 (4)	32006 (18)	6693 (10)
O(7)	21687 (4)	13592 (19)	5447 (9)
O(8)	22682 (5)	−14665 (21)	15976 (9)
O(9)	17615 (5)	−17099 (23)	1047 (9)
O(10)	14351 (4)	865 (14)	15021 (6)
O(*W*1)	0	57316 (33)	25000
O(*W*2)	15487 (5)	34402 (24)	−9479 (11)
H(*W*1)	2082 (14)	49083 (54)	21282 (36)
H1(*W*2)	16972 (11)	29025 (41)	−3754 (19)
H2(*W*2)	18139 (12)	41606 (50)	−12382 (24)

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‡ We use the nonstandard space groups Ic and $I2/c$ so as to have β near 90°. If the corresponding standard space groups Cc and $C2/c$ (*International Tables for X-ray Crystallography*, 1952) are used, the unit cell has a = 28·7033 (28) Å and β = 117·02 (1)°, with b and c the same as for the body-centered cell.

§ The measures of goodness of fit used in this paper are defined explicitly by Hall & Brown (1971) and in other places.

‡ Lists of neutron structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32406 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Discussion. Originally the crystal structure analysis reported here was undertaken in the hope that detailed knowledge of the crystal structure would aid in identifying a number of free radicals containing nitrogen whose spectra were observed in an ESR study of the subject crystal (Holmberg & Wilson, 1972). The packing of the anions with the K^+ ions and the water molecules is shown in the stereoscopic drawing of Fig. 1. The most interesting feature is the incomplete utilization of the water OH groups in hydrogen bonding. The contacts of the H atoms with O atoms of the $[SO_3ON(SO_3)_2]^{3-}$ ion are indicated in Fig. 1, and details are given in Table 2, along with details of the geometry of the water molecules. There is only one normal hydrogen bond, $O(W2)-H1(W2)\cdots O(7)$, of length 2·935 Å. Each of the other two H atoms is in contact with two sulfonyl O atoms, but the $H\cdots O$ separations (2·30 Å or longer) do not suggest significant hydrogen bonding.

Each water molecule has two K^+ ion near neighbors, which with the two H atoms are in an irregular tetrahedral arrangement about the O atom. In each tetrahedron the H–O–H angle is about 107° and the K–O–K angle is about 92°. In addition to the two

Table 2. *Geometry of the water molecules and their contacts with sulfonyl oxygen atoms*

Water molecule	Angle (°) H–O–H	Hydrogen bonds†	O–H	Distances (Å) O···O	H···O	Angle (°) O–H···O
*W*1*	107·2 (6)	$O(W1)-H(W1)\cdots O(2^{i})$	0·941 (4)	2·957 (1)	2·299 (4)	126·5 (3)
		$O(W1)-H(W1)\cdots O(6^{ii})$		3·206 (2)	2·368 (5)	148·2 (4)
*W*2	106·9 (3)	$O(W2)-H1(W2)\cdots O(7^{iii})$	0·946 (3)	2·935 (2)	2·022 (3)	161·6 (3)
		$O(W2)-H2(W2)\cdots O(1^{iv})$	0·940 (4)	3·211 (2)	2·490 (3)	133·6 (3)
		$O(W2)-H2(W2)\cdots O(8^{iii})$		3·193 (2)	2·457 (4)	135·2 (3)

* Molecule on twofold axis.

† Superscripts to atom numbers define symmetry transformations: (i) $\frac{1}{2}-x, \frac{1}{2}-y, \frac{1}{2}-z$; (ii) $x, -y, \frac{1}{2}+z$; (iii) $x, 1+y, z$; (iv) $\frac{1}{2}-x, 1\frac{1}{2}+y, -z$.

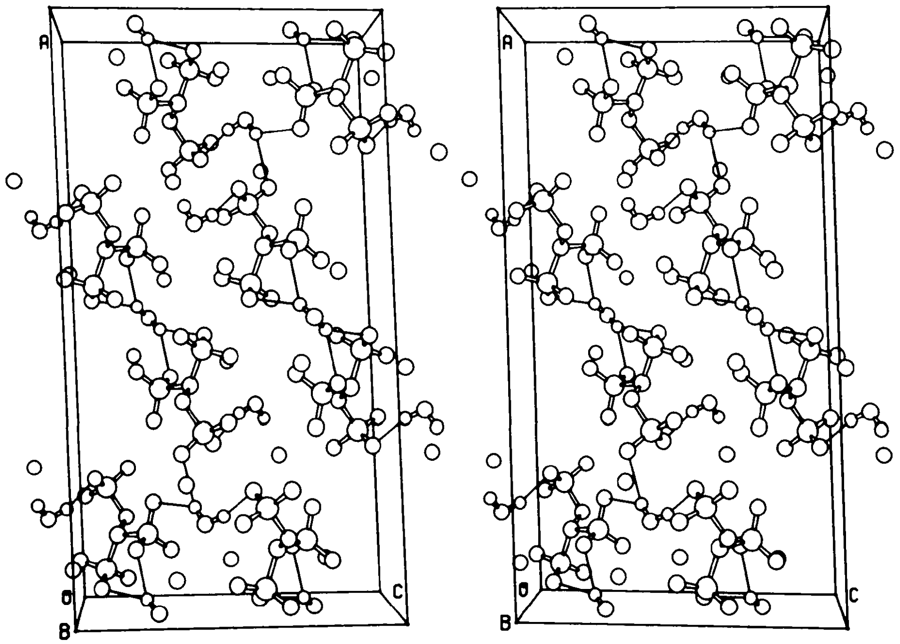

Fig. 1. Stereoscopic view of the crystal structure of $K_3[SO_3ON(SO_3)_2].\frac{3}{2}H_2O$. The circles not connected to other circles represent potassium ions. The contacts tabulated in Table 2 are indicated by thin lines connecting the hydrogen atoms to oxygen atoms of the sulfonyl groups.

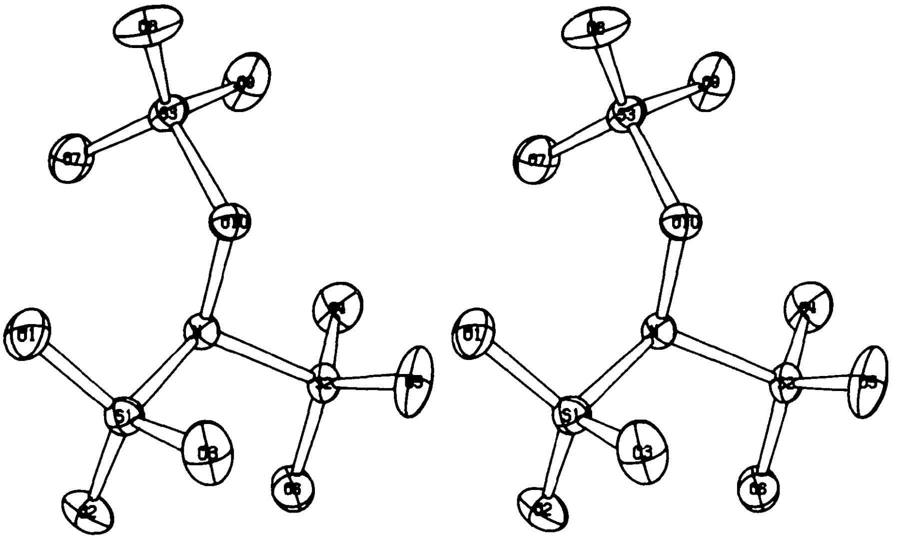

Fig. 2. Stereoscopic view of the hydroxylaminetrisulfonate ion, showing the thermal ellipsoids of 50% probability (Johnson, 1976).

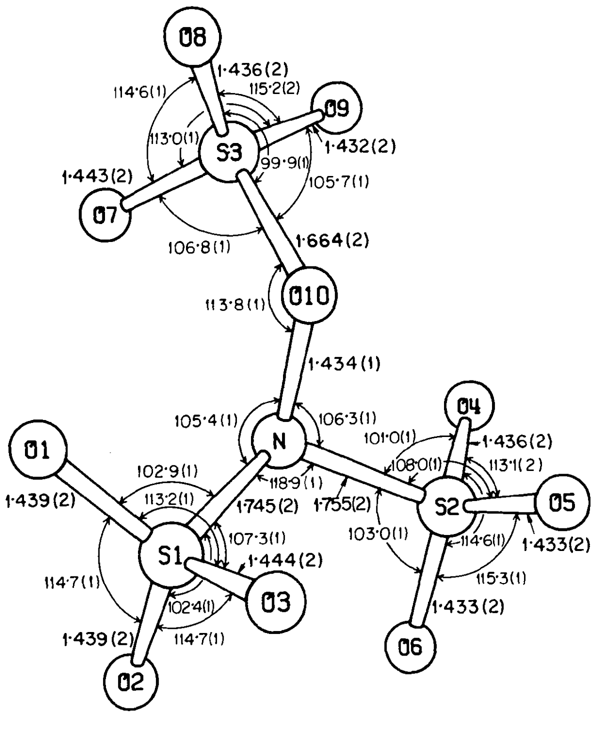

Fig. 3. Bond lengths (Å) and valence angles (°) in the hydroxylaminetrisulfonate ion.

closest K^+ ions at 2·816 (2) and 3·004 (3) Å, O(*W*2) has a third K^+ neighbor at 3·351 (3) Å. Except for its two closest K^+ neighbors at 2·735 (2) Å, O(*W*1) has no K^+ closer than 4·105 (2) Å.

The geometry of the anion $[SO_3ON(SO_3)_2]^{3-}$ is shown more clearly in the stereoscopic view of Fig. 2. The thermal ellipsoids representing the atoms in this figure appear generally sensible. Bond lengths and valence angles in the anion are shown in Fig. 3. Corresponding portions of this anion and those in $Rb_5\{[ON(SO_3)_2H\}.3H_2O$ (Guttormson, Rutherford, Robertson & Russell, 1974) and $Na_3[ON(SO_3)_2].3H_2O$ (Rutherford & Robertson, 1975) are quite similar in geometry. The average N—S bond length, 1·750 Å, is significantly longer than the N—S length 1·67 (2) Å reported in potassium hydroxylamine-*N*-sulfonate (Belt & Baenziger, 1957).

The SO_3 groups show significant distortions from trigonal symmetry about the bonds linking them to the remainder of the ion, especially in the ranges of the O—S—N and O—S—O(10) angles. Similar distortions appear in the structures reported by Guttormson *et al.* (1974) and Rutherford & Robertson (1975).

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Ammonium Hydrogen Phthalate Hemihydrate(?)*

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Abstract. $NH_4(C_8H_5O_4).\frac{1}{2}H_2O$(?), monoclinic, $C2/c$, $Z = 8$, $a = 13{\cdot}564$ (8), $b = 21{\cdot}173$ (11), $c = 6{\cdot}840$ (5) Å, $\beta = 112{\cdot}8$ (8)°, $\rho_o = \rho_c = 1{\cdot}41$g cm^{-3}. The structure was solved by direct methods and refined by full-matrix least squares to $R = 7{\cdot}3$% for 518 counter reflexions. The planes of the carboxyl groups are inclined to that of the aromatic ring at 7 and 85°. A random disorder of N and O atoms at the general position is assumed.

Introduction. The original purpose of this series was described in part I (Smith, 1975*a*). The title compound was an additional product of the synthesis of anhydrous ammonium hydrogen phthalate (Smith, 1975*b*). The crystal structure determination was undertaken to obtain more data on the possible shapes that the phthalate ion may adopt.

The crystals are tiny prismatic needles. Careful examination under a microscope was necessary to distinguish them from the anhydrous salt, and this made chemical analysis difficult. The density, determined by flotation, is the same as that of the anhydrous salt, thus precluding separation by that means. The observed density indicates $\frac{1}{2}$ a molecule of water of crystallization per asymmetric unit. A small batch was separated under a microscope and used for chemical analysis which indicated ~ 6% nitrogen; but the possibility that the sample contained some of the anhydrous salt cannot be excluded; the small sample size also lowers the reliability of the analysis. The title compound contains 7·2% N.

A well formed crystal, 0·02 × 0·02 × 0·09 mm, was found and used for diffraction study (repeated attempts to obtain larger ones having failed). Preliminary photographic data yielded rough cell constants and the other unit-cell data. No evidence for a supercell was found in these photographs. Accurate cell dimensions were obtained from several intense high-angle reflexions (Cu $K\alpha_1$ radiation, no monochromator) on a Picker FACS1 diffractometer. A unique set of data in the range $0 \le 2\theta \le 110°$ (Cu $K\alpha$ radiation, graphite monochromator) was collected in the coupled $\omega/2\theta$ scan mode with 3 min scans through 2° in 2θ; background was measured for 40 s on either side of the peak. The data were reduced to $|F|$ and σF with $p = 0{\cdot}06$ (Doedens & Ibers, 1967). Of the 1127 reflexions not affected by systematic absence, only 518 had $I \ge 3\sigma I$ and were used in subsequent calculations. No absorption corrections were applied [μ(Cu $K\alpha$) = 9 cm^{-1}].

The structure was solved by *MULTAN* (Germain, Main & Woolfson, 1971); *E* statistics strongly favoured space group $C2/c$. At the initial stages of refinement the $\frac{1}{2}$ water molecule of crystallization was assumed to occupy the special position 0,0·55,0·25, and was thus required to possess a twofold axis. With Cromer & Mann's (1968) scattering factors the heavy atoms were refined with isotropic temperature factors for the C atoms and anisotropic ones for N and O to $R = 7{\cdot}7$%. The inclusion of the four H atoms attached to the aromatic ring in the calculated positions reduced R to 7·5%. At this stage it was noted that the atom at the special position had a large thermal vibration and was tetrahedrally surrounded by two independent O atoms, both at 2·88 (1) Å. Neither of these O atoms was expected to have its own H attached to it in view of the shape of the carboxylic acid groups of which they were part; both were 0·075 ± 0·010 Å closer to the C atoms than were the other pair. An electron density map was calculated and showed two independent peaks ~ 0·75 Å from the special position and disposed along the same vectors as the O atoms; only one independent peak is expected for a water molecule. The situation at the general position was the reverse of this with short contacts to O(4), O(2) and O(1) of 2·61 (1), 2·76 (1) and

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* The Crystal Structures of a Series of Salts of Phthalic Acid. V.