Redetermination of the Crystal Structure of Dipotassium Imidobis(trioxosulphate) by Neutron Diffraction

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The crystal structure of the title compound has been redetermined from three-dimensional neutron diffraction data with 511 reflections. $Z = 4$ in the monoclinic space group $C2/c$, with cell dimensions $a = 1\,248.3(6)$, $b = 749.9(4)$, $c = 720.8(3)$ pm, $\beta = 91.21(2)°$. The structure was refined by full-matrix least-squares in the centric space group $C2/c$ to R 0.056. The nitrogen in the anion was found to be on a two-fold axis and surrounded tetrahedrally by two groups and two half hydrogen atoms. Refinement in the non-centric space C_c gave R 0.058, with the nitrogen trigonally surrounded by the trioxosulphates and one hydrogen atom. This model was rejected on the basis of Hamilton's significance test.

THE crystal structure of dipotassium imidobis(trioxosulphate), $HK_2NO_6S_2$, was determined by X-ray diffraction,[1] though the hydrogen atom was not located. In commenting on the stereochemistry of the $[NH(SO_3)_2]^{2-}$ ion, Jeffrey and Jones said that, ' although the space-group symmetry required a two-fold rotation axis in the molecule, this does not necessarily exclude a pyramidal distribution of nitrogen valencies, since the hydrogen atoms could be statistically distributed on either side of the diad axis.' Further refinement of the X-ray data did not solve the problem,[2] and the current investigation was designed to do so.

We have previously studied a related compound, tripotassium nitridotris(trioxosulphate) dihydrate,[3]

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[1] G. A. Jeffrey and D. W. Jones, *Acta Cryst.*, 1956, **9**, 283.

[2] D. W. J. Cruickshank and D. W. Jones, *Acta Cryst.*, 1963, **16**, 877.

[3] J. V. Tillack and C. H. L. Kennard, *J. Chem. Soc.* (*A*), 1970, 1637.

$K_3[N(SO_3)_3]\cdot 2H_2O$, in which the nitridotris(trioxosulphate) anion was on a crystallographic mirror plane and the central nitrogen atom was trigonally surrounded by the three trioxosulphate groups. The crystallographic mirror plane imposed an O_h symmetry on the NS_3. Overall, the symmetry of the anion approximated to C_{3h}. The most probable structure found for dipotassium imidobis(trioxosulphate) has the nitrogen in the anion on a two-fold axis and surrounded tetrahedrally by two trioxosulphate groups and two half hydrogen atoms. There was nothing in the structure refinement to indicate that the structure found was incorrect (Table 1). The compound has been shown to be isomorphous[4] with the methylene analogue $K_2[CH_2(SO_3)_2]$ not only by similarity of cell dimensions (a = 1 255, b = 775, c = 730 pm, β = 90.5°) and space group ($C2/c$), but also by the correspondence between low-order intensities. Consequently, since the carbon in the latter compound would be expected to be in a tetrahedral environment, so would the nitrogen in this compound. A neutron study of potassium sulphamate,[5] $K[SO_3NH_2]$, indicated that the nitrogen atom there had an sp^3 configuration, with a lone pair of electrons in the fourth tetrahedral position, and the S–N distance 166.6(6) pm. Our results are shown in Tables 1 and 2 and the Figure.

TABLE 1

Geometry of the compound

(*a*) Bond distances (pm)

S–O(1)	144.8(6)	N–S	167.4(5)
S–O(2)	143.8(6)	N–H	101.6(1)
S–O(3)	144.1(6)		

(*b*) Intermolecular distances (pm)

$K\cdots O(1^{I})$	285	$K\cdots O(2^{IV})$	307	$K\cdots O(3^{IV})$	285
$K\cdots O(1^{II})$	277	$K\cdots O(2^{V})$	303	$K\cdots O(3^{VII})$	273
$K\cdots O(1^{III})$	325	$K\cdots O(2^{VI})$	296	$K\cdots O(3^{III})$	273

(*c*) Interbond angles (°)

S–N–S	124.4(3)	N–S–O(3)	106.6(3)
S–N–H(1)	114.1(3)	O(1)–S–O(2)	114.1(4)
S–N–H(2)	109.0(3)	O(1)–S–O(3)	111.9(4)
N–S–O(1)	107.6(3)	O(2)–S–O(3)	113.2(2)
N–S–O(2)	102.6(4)		

Roman numeral superscripts denote the following equivalent positions relative to the reference molecule at x,y,z:

I	$x, 1-y, -\frac{1}{2}+z$	V	$-\frac{1}{2}+x, \frac{3}{2}-y, -\frac{1}{2}+x$
II	$-x, 1-y, 1-z$	VI	$-x, y, \frac{1}{2}-z$
III	$-x, 1+y, \frac{1}{2}-z$	VII	$-x, 1-y, -z$
IV	$-\frac{1}{2}+x, \frac{1}{2}+y, z$		

TABLE 2

Atomic co-ordinates (× 10^4), with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
N	0	4 264(4)	2 500
K	−1 523(4)	8 483(6)	1 432(6)
S	1 010(4)	3 223(8)	3 615(7)
O(1)	565(2)	2 293(5)	5 182(4)
O(2)	1 712(2)	4 672(4)	4 118(4)
O(3)	1 468(2)	2 009(4)	2 300(4)
H *	231(8)	5 330(15)	1 735(15)

Thermal parameters (Å^2) †

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
N	1.3(1)	1.2(1)	1.5(1)		0.1(1)	
K	2.6(2)	2.5(2)	1.6(2)	−0.1(1)	0.2(1)	−0.4(2)
S	1.1(2)	1.5(2)	1.6(2)	0.0(2)	0.1(2)	0.1(2)
O(1)	2.0(1)	3.5(2)	1.7(1)	−0.1(1)	0.1(1)	1.2(1)
O(2)	1.6(1)	2.5(1)	2.7(1)	−0.3(1)	−0.3(1)	−0.6(1)
O(3)	2.4(1)	1.9(1)	1.9(1)	0.8(1)	0.4(1)	−0.4(1)
H	3.8(5)	2.0(5)	3.4(5)	−0.3(4)	−0.6(4)	0.8(4)

* Half weight. † In the form: $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

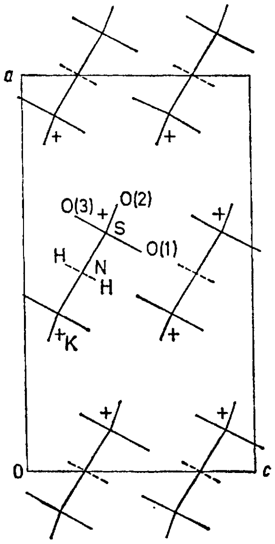

FIGURE 1 Packing diagram of dipotassium imidobis(trioxosulphate) viewed down the b (two-fold axis)

EXPERIMENTAL

Crystal Data.—$HK_2NO_6S_2$, M = 253, Monoclinic, a = 1 248.3(6), b = 749.9(4), c = 720.8(3) pm, β = 91.21(2)°, U = 0.674 nm^3, D_m = 2.49 g cm^{-3} (by flotation), Z = 4, D_c = 2.49, $F(000)$ = 504. Space group $C2/c$ (C_{2h}, No. 15) or C_c (C_s, No. 9); neutron radiation 125.3(1) pm, neutron flux 6 × 10^6 n cm^{-2} s^{-1}.

A crystal (0.25 × 0.13 × 0.072 cm) was mounted on the Australian Institute for Nuclear Science and Engineering's single-crystal computer-controlled four-circle automatic diffractometer. The installation was on the 2 Tan B beam hole of the Australian Atomic Energy Commission's reactor HIFAR at Lucas Heights, New South Wales. 459 of the 511 independent reflections, collected up to 2θ 90°, were considered observed. Data were corrected for absorption [μ 0.50(2) cm^{-1}]. An initial structure-factor calculation with the atomic parameters of Jeffrey and Jones[1] gave R 0.26, and a subsequent electron-density synthesis indicated the hydrogen atom to be statistically distributed on either side of the diad axis. Three full-matrix least-squares refinements with 60 variable parameters reduced R to 0.059, and R' to 0.056 (observed reflections only) (Table 2). Scattering lengths (fm) used were: N 9.40, O 5.75, K 3.70, S 2.847, and H −3.75. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21706 (4 pp., 1 microfiche).*

Although the structure refined with two half hydrogen about the two-fold axis, a number of calculations were carried out to check if there were other interpretations of the data. (*a*) A difference Fourier failed to reveal anything

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* See Notice to Authors No. 7, in *J.C.S. Dalton*, 1975, Index issue. Items less than 10 pp. are supplied as full-size copies.

[4] D. W. Jones, *Acta Cryst.*, 1955, **8**, 66.

[5] G. W. Cox, T. M. Sabine, V. M. Padmanabhan, N. T. Ban, M. T. Chung, and A. J. Surjadi, *Acta Cryst.*, 1967, **23**, 578.

unusual. (*b*) A least-squares refinement on all atoms except hydrogen increased R from 0.084 to 0.146, indicating that the hydrogen was there. (*c*) A least-squares refinement with the hydrogen atom on the mirror plane and 100 pm from the nitrogen reduced R from 0.187 to 0.145, but the temperature factor for this atom increased to 13.79 Å^2. Consequently, in this case a trigonal model for nitrogen was rejected. (*d*) All atoms except hydrogen were used in a non-centric C_c structure-factor calculation which gave an initial R of 0.202, with the electron-density map echoing the centric structure. However there was a negative peak along the pseudo-two-fold axis, where the hydrogen atom could have been. Five cycles of full-matrix least-squares refinement with 107 variable parameters reduced R to 0.058, and R' to 0.053, observed reflections only, with the temperature factor for K(12) becoming non-positive definite.

A hypothesis based on Hamilton's[6] significance test rejected the non-centric structure at the 0.005 significance level (R_o 1.037; $R_{60\ 404\ 0.005}$ 1.1096). Interatomic distances were: N–H 101.3, N–S 164.6 and 171.5, S–O 150.2, 144.7, 137.0, and 150.9, 144.1, and 138.0 pm.

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[6] W. C. Hamilton, *Acta Cryst.*, 1965, **18**, 502.