

Nitrosodisulfonates and Hydroxylamine-*N,N*-disulfonates. VI. A Neutron Diffraction Study of the 'Symmetry-Free' Very Short Hydrogen Bonds in $K_5[H\{ON(SO_3)_2\}_2].H_2O$

BY BEVERLY E. ROBERTSON*

Department of Physics and Astronomy, University of Regina, Regina, Saskatchewan S4S 0A2, Canada

ELMER O. SCHLEMPER, FRED K. ROSS AND C. K. FAIR†

Department of Chemistry, University of Missouri, Columbia, Missouri 65201, USA

AND JOHN S. RUTHERFORD

Department of Chemistry, University of Transkei, Private Bag X1001, Umtata, Transkei, South Africa

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Abstract

$K_5[H\{ON(SO_3)_2\}_2].H_2O$, $M_r = 599.47$, is triclinic, space group $P1$, with $a = 13.879$ (6), $b = 15.998$ (9), $c = 11.705$ (6) Å, $\alpha = 103.07$ (6), $\beta = 106.62$ (3), $\gamma = 86.13$ (3)°, $V = 2426$ (5) Å³, $Z = 6$, $D_x = 2.443$ g cm⁻³ at 50 K. The intensities of 4836 independent reflections were measured using monochromatic neutrons ($\lambda = 1.072$ Å), for which $\mu = 0.27$ cm⁻¹ on a crystal of dimensions $3 \times 2 \times 1.3$ mm. The final R factor for 4240 unique reflections was 0.059. The structure contains three independent anions of formula $[(SO_3)_2NO \cdots H \cdots ON(SO_3)_2]^{5-}$ in the asymmetric unit, with central O—O distances averaging 2.44 (2) Å. The bridging H atoms lie close to, but not precisely at, the centres of these bonds. However, the deviations from the symmetric position may be explained as resulting from differences in the nitrosyl O-atom environments, particularly the extent to which they act as acceptors of weak hydrogen bonds from the water molecules. This suggests that very short hydrogen bonds should, in fact, be symmetric in symmetric environments.

Introduction

In discussing the evidence for symmetrically placed H atoms in strong hydrogen bonds involving two O atoms, Catti & Ferraris (1976) pointed out that there is a shortage of precise and unequivocal neutron diffraction data on bonds of this type. The main problem is that in most cases studied the hydrogen bond is constrained in the crystal structure to lie on a symmetry element, *i.e.* it is a 'type A' (Currie & Speakman, 1970) or 'SR' (symmetry-restricted) bond (Catti & Ferraris, 1974). Olovsson, Olovsson & Lehman (1984) have compiled a list of hydrogen maleate compounds with

symmetry-free (SF) short hydrogen bonds. They find O—H bonds symmetric within the e.s.d.'s only in two compounds. A list given earlier by Joswig, Fuess & Ferraris (1982) contains three additional examples of SF short hydrogen bonds symmetric within the e.s.d.'s. However, in all cases the O—O distances are very short at *ca* 2.40 Å. Compilations such as that of Speakman (1973) appeared to progressively limit the possible range of symmetric hydrogen bonds to shorter and shorter distances, even perhaps to below 2.43 Å. It was clear to us that when the title compound was found to have three symmetry-free hydrogen bonds in the critical region around 2.45 Å (Robertson, Guttormson, Rutherford & Russell, 1988), a precise low-temperature neutron diffraction study would yield valuable additional data.

Crystallization of the alkali-metal salts of hydroxylamine-*N,N*-disulfonic acid from basic solution produces a variety of crystals with interesting structures. While the sodium salt contains the nitrosyldisulfonate ion $[ON(SO_3)_2]^{3-}$ only (Rutherford & Robertson, 1975), in the case of potassium and of rubidium this ion combines with a hydroxylamine-*N,N*-disulfonate to produce an apparently symmetric ion, $H[ON(SO_3)_2]^{5-}$.

In the rubidium salt (Guttormson, Rutherford, Robertson & Russell, 1974), there are two such crystallographically independent dimers, which have central hydrogen bonds of length 2.41 (2) and 2.43 (2) Å. However these lie on centres of symmetry and are therefore SR bonds. The three independent hydrogen bonds in the potassium salt, although longer [2.446 (7), 2.473 (7) and 2.474 (7) Å], were, however, symmetry free, and therefore appeared to warrant further study as indicated above.

Experimental

A parallelogram solid crystal ($\sim 3 \times 2 \times 1.3$ mm) was prepared by D. B. Russell, University of Saskatchewan,

* Author to whom correspondence should be addressed.

† Current address: Enraf-Nonius, 390 Central Avenue, Bohemia, New York 11716, USA.

and was mounted on an aluminium pin inside a Displex cooling unit [50 (1) K] for neutron data collection. The data collection was on the 2XE neutron diffractometer at the Missouri University Research Reactor (MURR) [$\lambda = 1.072$ (3) Å], where the figure in parentheses indicates the dispersion of the wavelength used. The e.s.d.'s in the lattice constants are less than this, indicating that the centring procedure correctly identifies values corresponding to the average wavelength given. Lattice parameters were based on 28 reflections, $25 \leq 2\theta \leq 45^\circ$.

A total of 8583 reflections with $2\theta \leq 75^\circ$ was collected in the hkl range: $h = -15$ to 15 , $k = -18$ to 17 , $l = 0$ to 12 . Of these only 4836 were accepted for detailed scanning based on a prescan criterion of 'peak > 1.5 background'. Three standard reflections measured after every 60 reflections showed 0.3% average deviation during data collection. No absorption correction was deemed necessary ($\mu = 0.27 \text{ cm}^{-1}$; estimated transmission range less than 5%). After merging ($R_{\text{int}} = 2.2\%$) there were 4240 unique reflections including 304 with $I < 2\sigma(I)$ which were included in the refinement. The non-H-atom positions from the X-ray structure were used to calculate a difference Fourier map from which the H atoms were located. The positional parameters, anisotropic temperature factors and isotropic extinction parameter [Zachariasen, 1963; $g = 2.18$ (4) $\times 10^{-4}$] were refined (767 variables), minimizing $\sum w(|F_o| - |F_c|)^2$ with $w = 4F_o^2/[\sigma^2(\text{counting}) + (0.05F_o^2)^2]$. The final agreement factors based on F were $R = 5.9$, $wR = 8.0\%$ and $S = 2.29$ with the maximum shift to e.s.d. being 0.03 in the last cycle.* All calculations were performed on a PDP 11/34 computer with Enraf-Nonius (1979) SDP programs. The values for the scattering lengths were taken from *International Tables for X-ray Crystallography* (1974).

Discussion

The final positional parameters are given in Table 1, and interatomic distances and angles, including all those involving hydrogen atoms, in Table 2. The atom numbering follows that used in the room-temperature X-ray study (Robertson *et al.*, 1988), and includes a subcell indicator, $A, B...F$, which distinguishes atoms which are equivalent in the smaller 'average unit cell' of this commensurate superstructure. In this nomenclature the three distinct anion dimers are formed from the combinations of units labelled A and F' , B and E' , and C and D' , where the primes indicate a relation through

*Lists of observed and calculated structure amplitudes and anisotropic temperature factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44701 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional parameters with e.s.d.'s in parentheses*

$$B_{\text{eq}} = \frac{4}{3} \sum_i \sum_j B_{ij} a_i \cdot a_j$$

	x	y	z	$B_{\text{eq}} (\text{\AA}^2)$
K(1A)	0.9177 (5)	0.1583 (5)	0.4053 (7)	3.2
K(1B)	0.7443 (5)	0.4854 (4)	0.2202 (6)	2.8
K(1C)	0.5749 (7)	0.8273 (5)	0.0710 (7)	5.0
K(2A)	0.0628 (4)	0.0756 (4)	0.1364 (5)	2.1
K(2B)	0.8824 (4)	0.4204 (4)	0.9689 (5)	2.1
K(2C)	0.7115 (5)	0.7553 (4)	0.8173 (6)	2.7
K(2D)	0.5376 (5)	0.0923 (4)	0.6463 (5)	2.4
K(2E)	0.3751 (5)	0.4158 (4)	0.4795 (6)	3.0
K(2F)	0.2211 (5)	0.7395 (4)	0.3039 (5)	2.4
K(3A)	0.7010 (4)	0.0626 (4)	0.9868 (6)	2.6
K(3B)	0.5289 (4)	0.3994 (4)	0.8292 (6)	2.3
K(3C)	0.3529 (5)	0.7444 (4)	0.7244 (6)	2.7
K(3D)	0.1927 (4)	0.0740 (4)	0.5682 (5)	2.0
K(3E)	0.0378 (5)	0.3966 (4)	0.4138 (7)	3.1
K(3F)	0.8713 (4)	0.7267 (4)	0.1586 (5)	2.2
S(1A)	0.4977 (5)	0.0659 (4)	0.1756 (6)	1.4
S(1B)	0.3266 (5)	0.4004 (5)	0.0086 (6)	1.7
S(1C)	0.1271 (5)	0.7354 (5)	0.8427 (6)	1.7
S(1D)	-0.0386 (5)	0.0716 (4)	0.6745 (6)	1.5
S(1E)	0.8048 (5)	0.4025 (5)	0.5028 (6)	1.7
S(1F)	0.6685 (5)	0.7311 (5)	0.3372 (6)	1.5
S(2A)	0.6386 (5)	0.0968 (4)	0.4220 (6)	1.5
S(2B)	0.4755 (5)	0.4162 (5)	0.2466 (7)	1.9
S(2C)	0.3022 (5)	0.7389 (4)	1.0465 (7)	1.7
S(2D)	0.1358 (5)	0.0768 (5)	0.8827 (6)	2.0
S(2E)	0.9600 (6)	0.4344 (5)	0.7295 (7)	2.4
S(2F)	0.7977 (5)	0.7683 (4)	0.5865 (6)	1.4
O(1A)	0.4506 (3)	0.0955 (2)	0.3724 (3)	1.75
O(1B)	0.2891 (3)	0.4271 (2)	0.2130 (3)	1.70
O(1C)	0.1246 (3)	0.7602 (2)	1.0604 (3)	1.67
O(1D)	-0.0424 (3)	0.1009 (2)	0.8954 (3)	1.74
O(1E)	0.7779 (3)	0.4342 (2)	0.7142 (3)	1.88
O(1F)	0.6107 (3)	0.7680 (2)	0.5288 (3)	1.95
O(2A)	0.4009 (3)	0.0965 (3)	0.1224 (3)	2.27
O(2B)	0.2277 (3)	0.4357 (3)	-0.0331 (4)	2.39
O(2C)	0.0272 (3)	0.7712 (3)	0.8233 (4)	2.97
O(2D)	-0.1405 (3)	0.1018 (3)	0.6552 (4)	3.3
O(2E)	0.6997 (3)	0.4150 (4)	0.4681 (5)	3.8
O(2F)	0.5714 (3)	0.7614 (3)	0.2770 (4)	2.69
O(3A)	0.5749 (3)	0.0938 (3)	0.1338 (3)	2.71
O(3B)	0.3992 (3)	0.4299 (3)	-0.0366 (4)	3.2
O(3C)	0.1840 (3)	0.7685 (4)	0.7794 (4)	4.4
O(3D)	0.0149 (3)	0.1049 (4)	0.6093 (4)	3.7
O(3E)	0.8568 (4)	0.4487 (3)	0.4475 (4)	3.3
O(3F)	0.7472 (3)	0.7600 (3)	0.2997 (4)	3.01
O(4A)	0.4986 (3)	-0.0267 (2)	0.1678 (3)	1.93
O(4B)	0.3225 (3)	0.3091 (2)	-0.0050 (4)	2.38
O(4C)	0.1242 (4)	0.6447 (3)	0.8217 (4)	3.6
O(4D)	-0.0349 (4)	-0.0209 (3)	0.6567 (4)	3.8
O(4E)	0.8314 (4)	0.3142 (3)	0.4926 (4)	3.7
O(4F)	0.6699 (3)	0.6411 (2)	0.3335 (3)	2.28
O(5A)	0.6374 (3)	0.1616 (3)	0.5276 (4)	2.77
O(5B)	0.4837 (3)	0.4757 (3)	0.3586 (4)	3.4
O(5C)	0.3326 (3)	0.7875 (4)	1.1682 (4)	3.9
O(5D)	0.1669 (4)	0.1321 (4)	0.9969 (4)	4.2
O(5E)	0.9734 (3)	0.5012 (3)	0.8405 (4)	3.4
O(5F)	0.7946 (3)	0.8367 (3)	0.6891 (3)	2.42
O(6A)	0.7138 (3)	0.1070 (3)	0.3652 (4)	2.53
O(6B)	0.5471 (3)	0.4287 (3)	0.1874 (4)	2.90
O(6C)	0.3595 (3)	0.7609 (3)	0.9723 (4)	2.77
O(6D)	0.1911 (3)	0.0863 (3)	0.8013 (4)	3.5
O(6E)	1.0236 (3)	0.4447 (3)	0.659 (3)	2.56
O(6F)	0.8779 (3)	0.7782 (3)	0.5361 (4)	2.41
O(7A)	0.6334 (3)	0.0108 (3)	0.4418 (4)	2.66
O(7B)	0.4676 (3)	0.3288 (3)	0.2535 (5)	3.8
O(7C)	0.2954 (3)	0.6493 (3)	1.0377 (5)	4.0
O(7D)	0.1227 (3)	-0.0099 (3)	0.8906 (5)	4.7
O(7E)	0.9629 (3)	0.3506 (3)	0.7547 (4)	3.14
O(7F)	0.7926 (3)	0.6857 (2)	0.6112 (3)	2.18
O(8A)	0.7326 (3)	0.0174 (3)	0.7681 (4)	3.4
O(8B)	0.0933 (4)	0.3206 (3)	0.0651 (5)	4.0
O(8C)	0.4266 (4)	0.6585 (3)	0.3890 (5)	3.9
N(1A)	0.5249 (2)	0.1164 (1)	0.3239 (2)	1.47
N(1B)	0.3618 (2)	0.4454 (1)	0.1606 (2)	1.45
N(1C)	0.1845 (2)	0.7778 (1)	0.9907 (2)	1.49
N(1D)	0.0174 (2)	0.1146 (1)	0.8226 (2)	1.39
N(1E)	0.8420 (2)	0.4549 (1)	0.6526 (2)	1.56
N(1F)	0.6884 (2)	0.7866 (1)	0.4837 (2)	1.53
H(CD)	0.0821 (5)	0.8298 (5)	0.0825 (6)	2.4
H(BE)	0.2576 (4)	0.4943 (4)	0.2486 (5)	2.6
H(AF)	0.4185 (5)	0.1631 (5)	0.4200 (7)	2.9
H(108A)	0.2262 (6)	0.9554 (6)	0.2672 (8)	5.0

Table 1 (cont.)

	x	y	z	$B_{eq}(\text{\AA}^2)$
H(208B)	0.0501 (7)	0.2936 (7)	0.089 (1)	6.2
H(208C)	0.3899 (8)	0.6307 (6)	0.418 (1)	6.1
H(208A)	0.288 (1)	0.0365 (6)	0.279 (1)	6.6
H(108B)	0.110 (1)	0.3730 (6)	0.1170 (9)	7.0
H(108C)	0.449 (1)	0.7088 (6)	0.439 (1)	8.5

Table 2. Bond distances (\AA) and bond angles ($^\circ$) with *e.s.d.*'s in parentheses

S(1A)—O(2A)	1.416 (7)	S(2C)—O(7C)	1.422 (8)
S(1A)—O(3A)	1.431 (7)	S(2C)—N(1C)	1.709 (6)
S(1A)—O(4A)	1.462 (8)	S(2D)—O(5D)	1.394 (7)
S(1A)—N(1A)	1.686 (6)	S(2D)—O(6D)	1.422 (7)
S(1B)—O(2B)	1.441 (7)	S(2D)—O(7D)	1.437 (7)
S(1B)—O(3B)	1.415 (7)	S(2D)—N(1D)	1.720 (6)
S(1B)—O(4B)	1.436 (8)	S(2E)—O(5E)	1.458 (5)
S(1B)—N(1B)	1.701 (6)	S(2E)—O(6E)	1.409 (5)
S(1C)—O(2C)	1.440 (7)	S(2E)—O(7E)	1.431 (6)
S(1C)—O(3C)	1.422 (7)	S(2E)—N(1E)	1.678 (6)
S(1C)—O(4C)	1.418 (7)	S(2F)—O(5F)	1.439 (5)
S(1C)—N(1C)	1.687 (6)	S(2F)—O(6F)	1.433 (5)
S(1D)—O(2D)	1.434 (6)	S(2F)—O(7F)	1.425 (7)
S(1D)—O(3D)	1.407 (7)	S(2F)—N(1F)	1.700 (6)
S(1D)—O(4D)	1.445 (7)	O(1A)—N(1A)	1.402 (4)
S(1D)—N(1D)	1.687 (6)	O(1B)—N(1B)	1.400 (4)
S(1E)—O(2E)	1.412 (7)	O(1C)—N(1C)	1.400 (4)
S(1E)—O(3E)	1.430 (7)	O(1D)—N(1D)	1.405 (5)
S(1E)—O(4E)	1.422 (7)	O(1E)—N(1E)	1.391 (7)
S(1E)—N(1E)	1.709 (9)	O(1F)—N(1F)	1.404 (6)
S(1F)—O(2F)	1.439 (7)	O(1A)—H(AF)	1.22 (1)
S(1F)—O(3F)	1.426 (7)	O(1B)—H(BF)	1.166 (8)
S(1F)—O(4F)	1.429 (8)	O(1C)—H(CD)	1.235 (7)
S(1F)—N(1F)	1.696 (8)	O(1D)—H(CD)	1.211 (7)
S(2A)—O(5A)	1.425 (8)	O(1E)—H(BE)	1.249 (8)
S(2A)—O(6A)	1.424 (7)	O(1F)—H(AF)	1.23 (1)
S(2A)—O(7A)	1.455 (7)	O(8A)—H(108A)	0.97 (1)
S(2A)—N(1A)	1.722 (6)	O(8A)—H(208A)	0.93 (1)
S(2B)—O(5B)	1.415 (8)	O(8B)—H(208B)	0.90 (1)
S(2B)—O(6B)	1.410 (8)	O(8B)—H(108B)	0.92 (1)
S(2B)—O(7B)	1.433 (8)	O(8C)—H(208C)	0.88 (1)
S(2B)—N(1B)	1.710 (6)	O(8C)—H(108C)	0.90 (1)
S(2C)—O(5C)	1.418 (8)	H(108A)—H(208A)	1.56 (1)
S(2C)—O(6C)	1.443 (8)	H(208B)—H(108B)	1.49 (1)
S(2C)—O(7C)	1.422 (8)	H(208C)—H(108C)	1.47 (1)

O(2A)—S(1A)—O(3A)	113.3 (5)	O(6B)—S(2B)—O(7B)	113.7 (5)
O(2A)—S(1A)—O(4A)	112.2 (5)	O(6B)—S(2B)—N(1B)	106.2 (4)
O(2A)—S(1A)—N(1A)	104.5 (4)	O(7B)—S(2B)—N(1B)	107.5 (4)
O(3A)—S(1A)—O(4A)	113.5 (5)	O(5C)—S(2C)—O(6C)	111.7 (5)
O(3A)—S(1A)—N(1A)	103.9 (4)	O(5C)—S(2C)—O(7C)	113.9 (5)
O(4A)—S(1A)—N(1A)	108.7 (4)	O(5C)—S(2C)—N(1C)	103.0 (4)
O(2B)—S(1B)—O(3B)	113.5 (5)	O(6C)—S(2C)—O(7C)	114.2 (5)
O(2B)—S(1B)—O(4B)	111.1 (5)	O(6C)—S(2C)—N(1C)	104.1 (4)
O(2B)—S(1B)—N(1B)	103.2 (4)	O(7C)—S(2C)—N(1C)	108.7 (4)
O(3B)—S(1B)—O(4B)	115.8 (5)	O(5D)—S(2D)—O(6D)	113.4 (4)
O(3B)—S(1B)—N(1B)	104.1 (4)	O(5D)—S(2D)—O(7D)	112.8 (4)
O(4B)—S(1B)—N(1B)	107.9 (4)	O(5D)—S(2D)—N(1D)	102.6 (4)

Table 2 (cont.)

O(2C)—S(1C)—O(3C)	111.8 (5)	O(6D)—S(2D)—O(7D)	115.7 (4)
O(2C)—S(1C)—O(4C)	110.9 (5)	O(6D)—S(2D)—N(1D)	104.8 (4)
O(2C)—S(1C)—N(1C)	104.2 (4)	O(7D)—S(2D)—N(1D)	106.1 (4)
O(3C)—S(1C)—O(4C)	115.4 (5)	O(5E)—S(2E)—O(6E)	112.9 (3)
O(3C)—S(1C)—N(1C)	103.3 (4)	O(5E)—S(2E)—O(7E)	111.5 (3)
O(4C)—S(1C)—N(1C)	110.6 (4)	O(5E)—S(2E)—N(1E)	100.9 (3)
O(2D)—S(1D)—O(3D)	113.2 (4)	O(6E)—S(2E)—O(7E)	114.4 (3)
O(2D)—S(1D)—O(4D)	110.8 (4)	O(6E)—S(2E)—N(1E)	107.6 (3)
O(2D)—S(1D)—N(1D)	104.5 (3)	O(7E)—S(2E)—N(1E)	108.7 (3)
O(3D)—S(1D)—O(4D)	114.3 (4)	O(5F)—S(2F)—O(6F)	112.5 (3)
O(3D)—S(1D)—N(1D)	104.8 (4)	O(5F)—S(2F)—O(7F)	112.5 (3)
O(4D)—S(1D)—N(1D)	108.7 (4)	O(5F)—S(2F)—N(1F)	100.6 (3)
O(2E)—S(1E)—O(3E)	113.2 (4)	O(6F)—S(2F)—O(7F)	114.6 (3)
O(2E)—S(1E)—O(4E)	112.2 (5)	O(6F)—S(2F)—N(1F)	107.1 (3)
O(2E)—S(1E)—N(1E)	104.1 (4)	O(7F)—S(2F)—N(1F)	108.5 (3)
O(3E)—S(1E)—O(4E)	114.6 (4)	S(1A)—N(1A)—S(2A)	119.2 (3)
O(3E)—S(1E)—N(1E)	102.1 (5)	S(1A)—N(1A)—O(1A)	108.2 (3)
O(4E)—S(1E)—N(1E)	109.6 (4)	S(2A)—N(1A)—O(1A)	106.3 (3)
O(2F)—S(1F)—O(3F)	112.1 (5)	S(1B)—N(1B)—S(2B)	118.1 (3)
O(2F)—S(1F)—O(4F)	112.8 (5)	S(1B)—N(1B)—O(1B)	109.0 (3)
O(2F)—S(1F)—N(1F)	103.0 (4)	S(2B)—N(1B)—O(1B)	106.8 (3)
O(3F)—S(1F)—O(4F)	114.7 (5)	S(1C)—N(1C)—S(2C)	115.4 (3)
O(3F)—S(1F)—N(1F)	103.4 (4)	S(1C)—N(1C)—O(1C)	107.7 (3)
O(4F)—S(1F)—N(1F)	109.7 (5)	S(2C)—N(1C)—O(1C)	107.4 (3)
O(5A)—S(2A)—O(6A)	115.1 (5)	S(1D)—N(1D)—S(2D)	116.2 (3)
O(5A)—S(2A)—O(7A)	112.2 (5)	S(1D)—N(1D)—O(1D)	109.9 (3)
O(5A)—S(2A)—N(1A)	100.4 (4)	S(2D)—N(1D)—O(1D)	106.9 (3)
O(6A)—S(2A)—O(7A)	114.3 (5)	S(1E)—N(1E)—S(2E)	115.5 (4)
O(6A)—S(2A)—N(1A)	106.5 (4)	S(1E)—N(1E)—O(1E)	109.7 (5)
O(7A)—S(2A)—N(1A)	107.0 (4)	S(2E)—N(1E)—O(1E)	107.6 (4)
O(5B)—S(2B)—O(6B)	113.7 (5)	S(1F)—N(1F)—S(2F)	117.7 (4)
O(5B)—S(2B)—O(7B)	113.8 (5)	S(1F)—N(1F)—O(1F)	108.9 (4)
O(5B)—S(2B)—N(1B)	100.7 (4)	S(2F)—N(1F)—O(1F)	106.1 (3)
N(1A)—O(1A)—H(AF)	106.6 (6)	O(1C)—H(CD)—O(1D)	178.6 (7)
N(1B)—O(1B)—H(BE)	103.9 (5)	O(1B)—H(BE)—O(1E)	178.8 (9)
N(1C)—O(1C)—H(CD)	101.5 (4)	O(1A)—H(AF)—O(1F)	177.7 (9)
N(1D)—O(1D)—H(CD)	102.8 (4)	H(108A)—O(8A)—H(208A)	111.1 (1)
N(1E)—O(1E)—H(BE)	102.5 (5)	H(208B)—O(8B)—H(108B)	110.2 (7)
N(1F)—O(1F)—H(AF)	107.1 (6)	H(208C)—O(8C)—H(108C)	112.5 (6)

a centre of symmetry. Fig. 1 illustrates this in a general view of the structure.

The structural parameters are not significantly different from those determined from the room-temperature X-ray study, except that temperature factors are smaller here, as expected. Fig. 2 shows the details of the geometry of the dimers with the atoms represented by thermal ellipsoids. As expected, the short axes of the ellipsoids of the six O atoms involved in the short hydrogen bonds are approximately along the bonds. The thermal ellipsoids of the H atoms are longer than those of the O atoms, with r.m.s. displacement axial lengths 0.16 (1), 0.18 (1) and

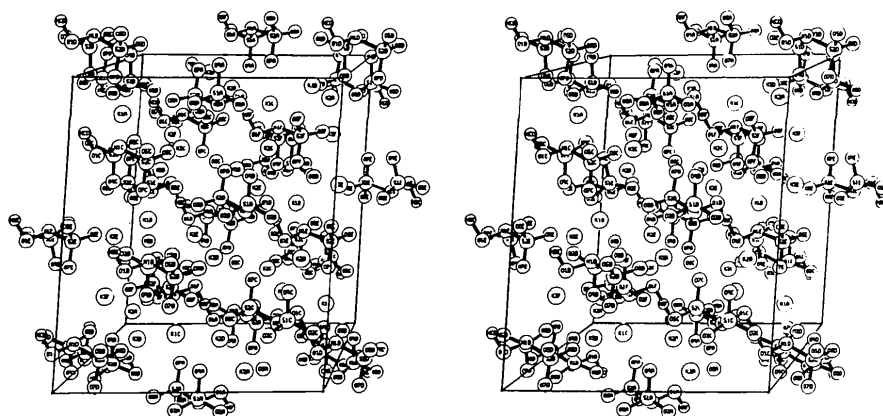


Fig. 1. General stereoscopic view of the structure and atomic labelling. The *a* axis is to the right, the *b* axis up, and the *c* axis is out of the plane of the page.

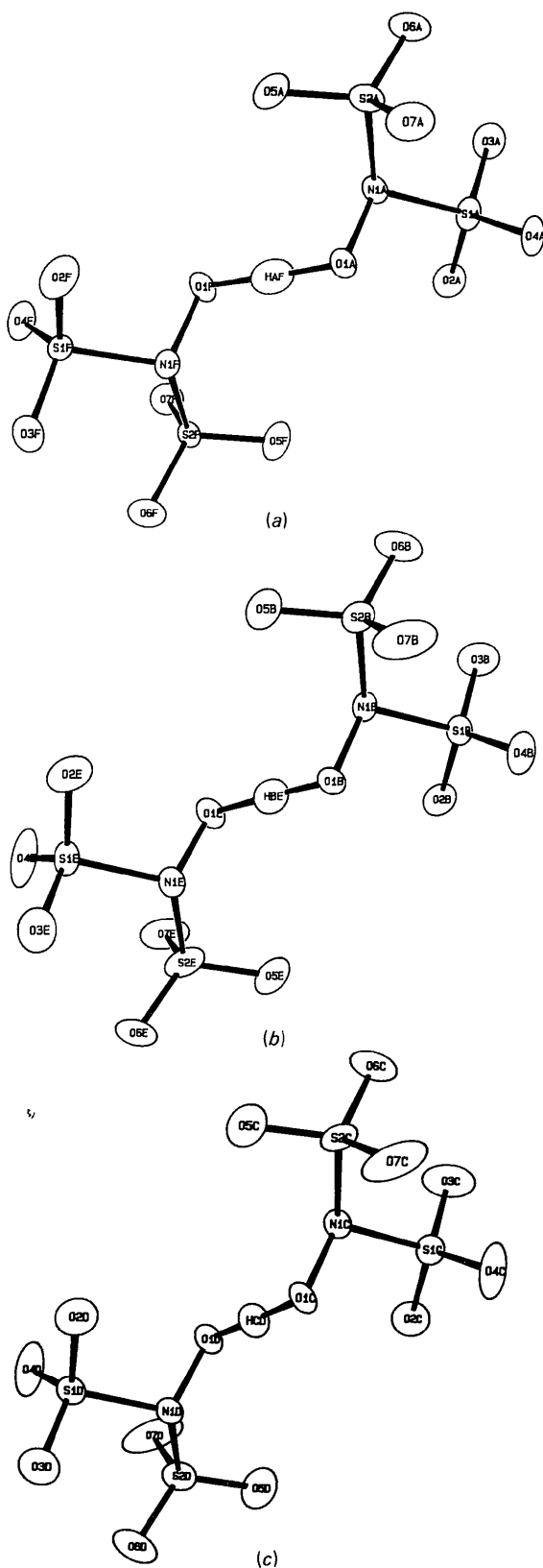


Fig. 2. Details of the geometry of the dimers (a) *AF*, (b) *BE*, (c) *CD* with thermal ellipsoids.

0.22 (1) Å for H(*AF*), 0.17 (1), 0.17 (1) and 0.21 (1) Å for H(*BE*), and 0.15 (1), 0.18 (1) and 0.19 (1) Å for H(*CD*). It has been proposed by several authors (Speakman, 1973; de la Vega, 1982) that the potential function for the proton in short hydrogen bonds is either double wellled or flat and broad, primarily along the direction of the bond.* The relatively large r.m.s. displacements of the H atoms observed here are consistent with the assumption of a flat potential function, but the direction of the axes of the longest r.m.s. displacements with respect to the O—O vector seems to be random; *i.e.*, close to parallel for H(*AF*) and close to perpendicular for H(*CD*).

Fig. 3 shows the details of the individual dimers together with the water molecules associated with them by hydrogen bonding. The central O...O distance in the dimers averages 2.44 (2) Å. The bond in the *BE* case is significantly shorter than the other two at 2.415 (5) Å. The central hydrogen bonds are linear, and have very similar O—H distances [1.22 (3) Å], and again only in the *BE* case is the bonding significantly asymmetric.

However, there are considerable variations in the hydrogen bonding of the water molecules. Each water H atom is associated with one nitrosyl O atom, but also with one or two sulfonate O atoms in a bifurcated or trifurcated arrangement, and the strength of the interaction with the nitrosyl group also varies markedly. In order to examine the possibility that the positions of the central H atoms were determined by these variations in their environment, bond-valence sums were calculated. The low-temperature neutron diffraction bond lengths were found unsuitable for bond-valence sums. This is to be expected because the parameters provided by Brown (1981) relate to structures deter-

* We thank a referee for bringing this subject matter to our attention.

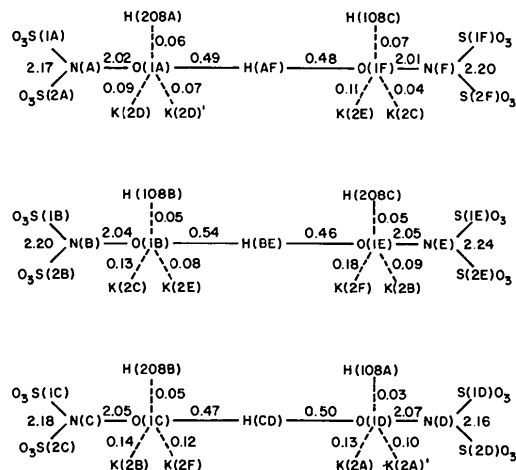


Fig. 3. The crystal environment of the three dimers with valence sums to the NO group and the N—O bond-valence-sum contribution.

Table 3. Selected bond-valence sums

	O(1A)	O(1F)		O(1B)	O(1E)		O(1C)	O(1D)		O(8A)	O(8B)	O(8C)	SO ₃	Totals (H)
	(a)	(b)	(a)-(b)	(c)	(d)	(c)-(d)	(e)	(f)	(e)-(f)					
Central H	(g)	0.49	0.48	0.01	0.54	0.46	0.08	0.47	0.50	-0.03				
Water H	(h)	0.06	0.07		0.05	0.05		0.05	0.03	1.74	1.74	1.69	0.52	0.97, 1.00, 0.97
O-N bond	(i)	2.02	2.01		2.04	2.05		2.05	2.07					1.00 × 6
N-S bonds	(j)	2.17	2.20		2.20	2.24		2.18	2.16					
K(2)	(k)	0.09	0.04		0.13	0.09		0.14	0.13	0.09	0.05	0.07		
K(2')	(l)	0.07	0.11		0.08	0.18		0.12	0.10	0.06	0.09	0.08		
K(3)	(m)									0.17	0.15	0.14		
Total	(h)-(m)	4.41	4.43	-0.02	4.50	4.61	-0.11	4.54	4.49	0.05				
Total	(g)-(m)	4.90	4.91		5.04	5.07		5.01	4.99		2.06	2.03	1.98	

mined at room temperatures, and the shorter interatomic distances at low temperatures produce atomic valences which are considerably too large. Therefore the X-ray room-temperature distances were used for the non-H atoms, the neutron bond lengths for the bridging H atoms, and the neutron positions of the water H atoms were adjusted by slight extension along the O-H vector, so that their hydrogen valences summed to one. Brown's parameters of the form $S = \exp[(R - R_p)/0.39]$ were used, except that best agreement for the NO group, treated as a combined atom, was achieved by using a term $2(R/1.43)^{-4}$ to include the electrons of the NO bond.

The results relevant to the hydrogen-bonding scheme are collected in Table 3. Each water molecule forms a weak bridge O(1)···H-O(8)-H···O(1) linking neighbouring dimers, and contributing to the valence sum at the highly basic O(1) atom. However, in this structure the water H atoms still have a residual Lewis acidity of about 0.07 bond-valence units, and the hydrogen-bond bifurcation or trifurcation is a result of this. By comparison, the water O atoms each form three bonds to K, with an average bond valence of 0.10 bond-valence units.

When we consider the NO···H···ON groups, the sums at H are in each case close to one, although the asymmetry of the hydrogen bond varies from dimer to dimer. It is instructive to compare the two halves of each dimer; for O(1) there will be environmental effects which comprise the asymmetry of the central hydrogen bond, differences in direct-bond valences to K and water H, and differences in the hydrogen bonding and coordination of the sulfonate O atoms, reflected in changes to the N-S and N-O bond distances. Table 3 is drawn up so as to show that the asymmetry of the central hydrogen bond clearly parallels, and comes near to compensating for, the other effects listed, even in the two cases where the deviations from the central position are not themselves significant. That is, although each dimer itself is very close to being centrosymmetric about the H position, it is long-range environmental effects which control the precise degree of asymmetry of the bond. A similar conclusion was reached by Kvik, Koetzle, Thomas & Takusagawa (1974) and by Vanhouteghem, Lenstra & Schweiss (1987).

The latter authors recently reported the neutron diffraction structure of magnesium bis(hydrogen malate) hexahydrate. They find a slightly asymmetric intramolecular SF short hydrogen bond with O-H distances 1.228 (7) and 1.186 (7) Å. The O atom involved in the larger O-H distances is also the receptor of a hydrogen bond, $[H \cdots O] = 1.865$ (7) Å. They also calculated the bond lengths using geometry-relaxed 4-21G *ab initio* methods and concluded that to explain their experimental results they would need to include crystal-field effects from surrounding water molecules.

Therefore we must conclude from this study that hydrogen bonds between O atoms which are in the region of 2.45 Å apart are not inherently symmetric or asymmetric, but may show significant asymmetry provided the environmentally determined Lewis basicities of the two O atoms are sufficiently different. At these O-O distances this appears to be the major effect inducing asymmetry in the hydrogen bond, although the alternative explanation of an improved valence sum at H obviously comes into play at greater O-O distances. If this is indeed the case, asymmetry at these distances is only to be expected in certain SF bonds. SR bonds, where the environment itself is symmetric, should not show asymmetry.

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Evidence for a New Structural Modification in KSn_2F_5

BY S. VILMINOT* AND H. SCHULZ

Max-Planck Institut für Festkörperforschung, Heisenbergstrasse 1, Stuttgart 80, Federal Republic of Germany

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Abstract

Potassium pentafluorodistannate(II), $M_r = 371.5$, trigonal, $P\bar{3}$, $a = 7.330$ (1), $c = 9.900$ (2) Å, $V = 460.7$ Å³, $Z = 3$, $D_m = 4.01$, $D_x = 4.017$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 91.1$ cm⁻¹, $F(000) = 492$, $T = 408$ K, $R = 0.026$, $wR = 0.023$ for 907 unique reflections. A phase transition between room temperature and 408 K was revealed by structure refinement and was confirmed by specific heat measurements, which showed an anomaly at 378 K. The structure consists of a succession of layers in the c -axis direction. Evolution of the fluorine distribution between room temperature and 408 K is discussed. The conduction mechanism was determined from calculations of probability density functions.

Introduction

Structural determinations on superionic conductors have led to the conclusion that the mobile ion is displaced from its ideal position. Another approach is to consider that the mobile ion vibrates anharmonically around its rest position. Using relations determined from statistical thermodynamics (Willis, 1969), Zucker & Schulz (1982*a*) have shown that of the different formalisms proposed, the best results are obtained using the Gram–Charlier expansion to analyse the anharmonic thermal motions. Study of Li_3N (Zucker & Schulz, 1982*b*), whose deviations from harmonicity could not be interpreted by interstitial sites or split positions, illustrated the use of anharmonic temperature factors up to the sixth order and allowed the diffusion process to be explained. This interpretation used calculations of the probability density function

(PDF), Fourier transform of the temperature factor, and of the effective atomic potential. All calculations were performed with the program system *PROMETHEUS* (Zucker, Perenthaler, Kuhs, Bachmann & Schulz, 1983).

Conduction paths of the mobile ions have been studied in the case of cationic conductors: Ag^+ in AgI , Ag_3SI and Ag_2S (Schulz & Zucker, 1981); Na^+ in *Nasicon* (Kohler, Schulz & Melnikov, 1983); Cu^+ in CuTeBr (Bachmann, Kreuer, Rabenau & Schulz, 1982); and anionic conductors: F^- in PbF_2 (Bachmann & Schulz, 1983). KSn_2F_5 belongs to the $M\text{Sn}_2\text{F}_5$ family ($M = \text{Na}, \text{K}, \text{Rb}, \text{Cs}, \text{Tl}$ and NH_4) which exhibits fluorine ionic conductivity (Al Uraibi, 1981). Above 428 K, it presents a superionic modification as revealed by conductivity measurements. A structure determination at room temperature (Vilminot, Bachmann & Schulz, 1983) revealed that KSn_2F_5 has an original structure, not deduced from fluorite for example. According to these results, the structure is strongly anisotropic and KSn_2F_5 can be considered as a two-dimensional ionic conductor. In order to obtain more information concerning the conduction process, we have undertaken structural determinations at higher temperatures. In this first part, we present the structure obtained at 408 K, that is below the superionic transition, and compare the results with those at room temperature.

Experimental

KSn_2F_5 prepared according to Vilminot *et al.* (1983). Crystal: irregular hexagonal plate $0.30 \times 0.22 \times 0.06$ mm in glass capillary. D_m by pycnometry. Temperature achieved by blowing heated air. Philips PW 1100 diffractometer. Intensity measurements by $\omega/2\theta$ scans. Unit-cell dimensions from least-squares refinement on 25 reflections ($\theta > 15^\circ$). Corrections for

* Alexander von Humboldt Fellow. Present address: Département Science des Matériaux EHICS, 1 rue B. Pascal, 67008 Strasbourg CEDEX, France.