The Crystal Structure of Potassium N,N-Dimethylnitrogentrioxosulphate·0.66-Hydrate, $K(CH_3)_2N(SO_3)\cdot 0.66H_2O$

ALAN J. MORRIS, COLIN H. L. KENNARD*, JOHN R. HALL

Department of Chemistry, University of Queensland, Brisbane, Qld. 4067, Australia

GRAHAM SMITH

Department of Chemistry, Queensland Institute of Technology, Brisbane, Qld. 4000, Australia

and ALLAN H. WHITE

Department of Physical and Inorganic Chemistry, University of Western Australia, Nedlands, W.A. 6009, Australia

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Introduction

A series of methyl substituted nitrogen trioxosulphates have been studied [1] in order to find the effect of the methyl group on nitrogen stereochemistry. This compound completes the series.

Experimental

Preparation

$K(CH_3)_2N(SO_3)$ was prepared by adding stoichiometric equivalents of potassium carbonate to an aqueous solution of N,N-dimethylsulphamic acid $[H(CH_3)_2N^+(SO_3)^-]$ to give, on concentration, a solid product which was recrystallized from aqueous ethanol. The compound was characterised by infrared, Raman and proton magnetic resonance spectroscopy. *Anal.* Found: C, 14.8; H, 3.6; N, 8.5%. Calcd. for $C_2H_{6.66}KO_{3.66}NS$: C, 14.7. H, 3.7, N, 8.6%.

Crystal Data

$C_2H_6KNO_3S(0.66H_2O)$, M = 175.1, trigonal, a = 10.96(2), c = 11.88(3) Å, U = 1235.9 Å. D_c = 1.41 g cm^{-3}, Z = 6, $F(000)$ = 498.0 space group $P\bar{3}$ (C_{3i}^1, No. 147), Mo $K\alpha$ radiation (graphite monochromator), λ = 0.7107 Å, μ(Mo $K\alpha$) = 3.8 cm^{-1}.

Structure Determination and Refinement

A single crystal (0.25 × 0.15 × 0.10 mm) of $K(CH_3)_2N(SO_3)\cdot 0.66H_2O$ epoxy coated to exclude moisture, was used for data collection on a computer controlled Syntex $P2_1$ four-circle diffractometer. 1110 out of 1419 unique reflections with $I > 2.5\sigma(I)$ were considered observed ($\theta < 25°$). Data were corrected for Lorentz-polarization effects but not for absorption. The structure was solved using the SHELX centrosymmetric direct methods approach [2] and refined by full matrix least squares with anisotropic thermal parameters for atoms except the disordered water and the potassium atoms at special positions. No hydrogen atoms were located. The conventional R was reduced from an initial 0.49 to 0.149 and Rw = 0.164. The high residual R was probably due to disorder. A weighting scheme with $w = 1.0/(\sigma^2 F_o + 8 \times 10^{-3} F_o^2)$ was applied. A final difference-Fourier showed no features larger

TABLE I. Atomic Coordinates of Non-hydrogen Atoms (×10^4) with Estimated Standard Deviations in Parentheses.

Atom	*x/a*	*y/b*	*z/c*	Wyckoff Notation
K(1)*	−2426(4)	7351(4)	3844(3)	g
K(2)	3333	6667	4778(3)	d
K(3)	0	0	5000	b
N	−29(13)	6331(14)	2014(11)	g
C(1)	1358(22)	7073(19)	1463(15)	g
C(2)	−1008(23)	4968(23)	1423(16)	g
S	40(3)	6028(3)	3396(3)	g
O(1)	977(15)	7371(11)	3865(10)	g
O(2)	634(17)	5096(16)	3497(11)	g
O(3)	−1382(12)	5329(16)	3789(11)	g
O(4)	0	0	0	a
O(5)*	−1731(21)	7642(20)	1598(15)	g

*Site occupancy = 0.5.

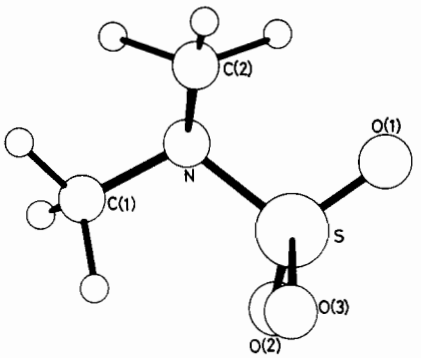

Fig. 1. Molecular configuration and atom naming scheme for $(CH_3)_2N(SO_3)^-$ viewed perpendicular to a CNS plane. Hydrogen atoms are shown in calculated positions.

*Author to whom correspondence should be addressed.

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TABLE II. Interatomic Bond Distances (Å) and Angles (°) with Estimated Standard Deviations in Parentheses.

N–S	1.684(7)	S–O(1)	1.403(5)		
N–C(1)	1.471(11)	S–O(2)	1.465(6)		
N–C(2)	1.508(11)	S–O(3)	1.428(6)		
C(1)–N–S	114.0(6)	N–S–O(1)	104.5(4)	O(1)–S–O(2)	114.4(5)
C(2)–N–S	109.8(6)	N–S–O(2)	107.3(4)	O(1)–S–O(3)	113.5(4)
C(1)–N–C(2)	111.5(7)	N–S–O(3)	106.3(4)	O(2)–S–O(3)	110.2(5)

TABLE III. Comparison with Similar Compounds.

	Ref.	d(N–S) Å	Σ (N) deg	d(S–O) Å	O–S–O (deg)	Torsion	Angles X–N–S–O	(deg)
$K_3N(SO_3)_3 \cdot 2H_2O$	6	1.710(2)	360	1.43(2)	114(1)	+180	−62	+62
$K_2NH(SO_3)_2$	4	1.674(5)	348	1.44(1)	113(1)	+173	−66	+54
$KNH_2(SO_3)$	5	1.666(6)	330	1.45(1)	113(1)	+179	−61	+61
$K_2N(CH_3)(SO_3)_2$	1	1.750(3)	356	1.43(2)	114(2)	−150	+74	−42
						−170	+91	−30
$KN(CH_3)_2(SO_3) \cdot 0.66H_2O$	This paper	1.684(7)	335	1.43(1)	113(1)	+179	−63	+59
						−175	+62	−55
$KNH(CH_3)(SO_3)$	1	1.637(4)	330	1.45(1)	113(1)	+179	−61	+59
$NH_3(SO_3)$	7	1.76(2)		1.44(2)	115(1)			
$NH(CH_3)_2(SO_3)$	1	1.790(6)		1.41(1)	116(1)			
$N(CH_3)_3(SO_3)$	8	1.844(2)		1.41(2)	116(1)			
$K_2CH_2(SO_3)_2$	9	1.770(7)		1.46(1)	114(1)			
$K_3CH(SO_3)_3 \cdot H_2O$	10	1.810(1)		1.46(1)	113(I)			

Fig. 2. Stereoscopic view of the packing in the unit cell for $K(CH_3)_2N(SO_3) \cdot 0.66H_2O$ viewed down the *c* axis.

than 0.30 $eÅ^{-3}$. Neutral atom scattering factors [3] were used for all atoms. Atomic parameters and bond distances/angles are listed in Tables I and II respectively.

Results and Discussion

Figure 1 illustrates the molecular configuration for $K(CH_3)_2N(SO_3) \cdot 0.66H_2O$. The sum of the angles about the central atom is 335(1)°, with N 0.45(1) Å above the CCS plane, indicating a distorted tetrahedral coordination for nitrogen. The N–S bond distance, 1.684(7) Å, is comparable with that found in $K_2NH(SO_3)_2$, [1.674(5) Å], and KNH_2SO_3, [1.666(6) Å] [5].

A stereoview of the packing is shown in Fig. 2. The $[(CH_3)_2N(SO_3)]^-$ anions are in layers and arranged in a head-to-head, tail-to-tail configuration in the *ab* plane. The water molecules are in the same plane and along with some potassium atoms, lie in the spaces between layers. The potassiums form layers in the *ac* plane, being situated irregularly between the oxygens of staggered trioxosulphate groups.

A comparison with similar compounds is in Table III.

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