Crystal Structure and the Infrared and Raman Spectra of Potassium Nitridosulphonate Hydrate,† $K_3[N(SO_3)_2]\cdot H_2O$

By **John R. Hall,*** **Robert A. Johnson,** and **Colin H. L. Kennard,** Department of Chemistry, University of Queensland, Brisbane, Australia 4067
Graham Smith, Department of Chemistry, Queensland Institute of Technology, Brisbane, Australia 4000
Brian W. Skelton and **Allan H. White,** Department of Physical and Inorganic Chemistry, University of Western Australia, Nedlands, Western Australia 6009

The crystal structure of the title compound has been determined using three-dimensional *X*-ray diffraction data with 1 386 ' observed ' reflections. Crystals are triclinic, space group $P\bar{1}$ with $Z = 2$ in a cell of dimensions $a = 7.972(2)$, $b = 6.758(2)$, $c = 8.125(2)$ Å, $\alpha = 91.02(2)$, $\beta = 97.85(2)$, and $\gamma = 103.33(2)°$. The structure has been solved using direct methods and refined by full-matrix least squares to *R* 0.042. The N–S bond length [1.609(2) Å] is markedly smaller than those for $K[NH_2SO_3]$ [1.666(6)], $K_2[NH(SO_3)_2]$ [1.674(5)], $K_3[N(SO_3)_3]\cdot 2H_2O$ [1.71(2)], and $NH_3{}^+SO_3{}^-$ [1.76(2) Å]. This contraction is attributed to the participation of the two lone pairs of electrons on nitrogen in π bonding. The i.r. (50—4 000 cm^{-1}) and Raman spectra of $K_3[N(SO_3)_2]\cdot H_2O$ and its ^{15}N and ^2H derivatives at 77 K are reported and interpreted according to the crystal structure. To assist with the assignment, spectra of the anhydrous salt $K_3[N(SO_3)_2]$ and of an aqueous solution of the soluble sodium salt have also been recorded. ν_{sym}(N–S) and ν_{asym}(N–S) have been assigned wavenumbers of 794 and 1 046 cm^{-1} respectively, $\delta(NS_2)$ at 190 cm^{-1}. The SO_3 groups show their characteristic group frequencies. Infrared spectra of partially deuteriated samples confirm the presence of two types of hydrogen bond per water molecule.

THE i.r. and Raman spectra of polycrystalline potassium nitridosulphonate hydrate, $K_3[N(SO_3)_2]\cdot H_2O$, and its ^{15}N and ^2H derivatives have been recorded at liquid-nitrogen temperatures as part of an investigation into the vibrational properties of the sulphonate derivatives of ammonia, methane, and hydroxylamine. Siebert [1] recorded the Raman spectrum of an aqueous solution of this salt and the i.r. spectrum above 600 cm^{-1} of polycrystalline $Na_3[N(SO_3)_2]\cdot 12H_2O$, but proposed few assignments. In order to provide an adequate prediction of the spectra, the crystal structure of $K_3[N(SO_3)_2]\cdot H_2O$ has been determined by *X*-ray analysis. ‡ To assist with the assignment of the internal modes for $N(SO_3)_2{}^{3-}$, the aqueous solution spectrum, including qualitative Raman polarization data, of the more soluble sodium salt have been obtained. Also, spectra of the anhydrous salt, $K_3[N(SO_3)_2]$, and of partially deuteriated $K_3[N(SO_3)_2]\cdot H_2O$ samples have been recorded to assist with the lattice-water assignment.

EXPERIMENTAL

Preparations.—The hydrate $K_3[N(SO_3)_2]\cdot H_2O$ was prepared by the method described by Sisler and Audrieth [2] for $[NH_4]_3[N(SO_3)_2]\cdot H_2O$, with the modification that the imidic proton of ammonium imidosulphonate, $[NH_4]_2[NH(SO_3)_2]$, was removed in boiling 1 mol dm^{-3} K[OH] solution [equation (1)] (Found: N, 4.6; S, 20.3; H_2O, 5.9. Calc. for $H_2K_3NO_7S_2$: N, 4.5; S, 20.7; H_2O, 5.8%).

$$[NH_4]_2[NH(SO_3)_2] + 3K[OH] \longrightarrow K_3[N(SO_3)_2]\cdot H_2O + 2NH_3 + 2H_2O \quad (1)$$

The ^{15}N derivative was prepared by a similar procedure, starting with $K_2[^{15}NH(SO_3)_2]$.§ The sodium salt was obtained by using 1 mol dm^{-3} Na[OH] solution in the deprotonation step [equation (1)]. Samples of the sodium salt for spectroscopic measurements were dissolved in 1 mol dm^{-3} Na[OH] solution to prevent conversion into $NH(SO_3)_2{}^{2-}$.[5]

Anhydrous $K_3[N(SO_3)_2]$ was obtained by heating $K_3[N(SO_3)_2]\cdot H_2O$ at 400 K and 1 atm ¶ for 30 min (Found: N, 4.7; S, 21.6. Calc. for $K_3NO_6S_2$: N, 4.8; S, 22.0%). The deuteriate $K_3[N(SO_3)_2]\cdot D_2O$ was prepared by several recrystallizations of $K_3[N(SO_3)_2]\cdot H_2O$ from 0.5 mol dm^{-3} KOD–D_2O solution. Exchange of the hydrogen atoms was estimated from i.r. spectra to be *ca.* 80% complete (Found: N, 4.5; S, 20.3; D_2O, 6.5. Calc. for $D_2K_3NO_7S_2$: N, 4.5; S, 20.6; D_2O, 6.4%).

Partially deuteriated samples were prepared by the procedure previously described,[6] starting with anhydrous $K_3[N(SO_3)_2]$ and recrystallizing from H_2O–D_2O mixtures which were *ca.* 0.5 mol dm^{-3} with respect to K[OD]. The approximate concentrations of H_2O, HDO, and D_2O in the deuteriated samples were calculated by the method described by Seidl and Knop.[7]

Crystal Data.—$H_2K_3NO_7S_2$, $M = 309.45$, Triclinic, $a = 7.972(2)$, $b = 6.758(2)$, $c = 8.125(2)$ Å, $\alpha = 91.02(2)$, $\beta = 97.85(2)$, $\gamma = 103.33(2)°$, $U = 421.4$ Å^3, $D_m = 2.42$ (by flotation), $Z = 2$, $D_c = 2.45$ g cm^{-3}, $F(000) = 308$, space group $P\bar{1}$ (C_i^1, no. 2), Mo-K_α radiation (crystal monochromator), $\lambda = 0.710\ 7$ Å, μ(Mo-K_α) = 21.09 cm^{-1}.

A single crystal 0.50 × 0.48 × 0.25 mm, coated with epoxy-resin to exclude moisture, was used. Unit-cell dimensions were obtained by least-squares fit of the angular parameters of 15 reflections with 2θ *ca.* 25° and the crystal centred in the counter aperture of a Syntex $P\bar{1}$ four-circle diffractometer at the University of Western Australia. 1 386 Reflections with $I > 3\sigma(I)$ were considered observed out of 1 485 collected up to 2θ 50° and were used in the structure solution and refinement. During data collection, however, a check on the cell parameters after a realignment of the crystal indicated that one cell parameter (*c*) had changed by *ca.* 1% (8.072 to 8.125 Å) while the others remained constant. Although this phenomenon is unexplained, the new parameter was used in the rapid collection of a new data set; no significant change was ob-

---

† A more systematic name is potassium iminodisulphonate(3—) monohydrate.

‡ *Note added at proof:* P. Barbier, Y. Parent, and G. Mairisse, *Acta Cryst.*, 1979, **B35**, 1308, reported the structure for $K_3[N(SO_3)_2]\cdot H_2O$. Cell dimensions, $a_0 = 8.126(4)$, $b = 7.978(3)$, $c = 6.762(4)$ Å, $\alpha = 103.36(3)$, $\beta = 90.98(3)$, and $\gamma = 97.86(3)°$. Mean N–S 1.606(2), S–O 1.468(2) Å; S–N–S 120.83(11), N–S–O 108.70(9)°.

§ This compound was prepared by the hydrolytic decomposition [3] of $K_3[^{15}N(SO_3)_3]\cdot 2H_2O$. The latter was prepared from $Na[NO_2]$ (99.8% ^{15}N-enriched; British Oxygen Company Ltd.) and $K[HSO_3]$ by the method previously described.[4]

¶ Throughout this paper: 1 atm = 101 325 Pa.

served in the intensities of three standard reflections monitored throughout data collection. X-Ray powder patterns of the compound failed to reveal any change after exposure to Cu-K_α radiation for a total of 40 h. No corrections were made for absorption.

The structure was solved by direct methods and refined by full-matrix least squares with anisotropic thermal parameters for the non-hydrogen atoms, and U(isotropic) for the hydrogen atoms invariant at 0.05 Å^2. The data were seriously affected by extinction and the Larsen extinction parameter was refined also. Final residuals (R, R' S) are 0.042, 0.056, and 2.2, reflection weights being set at $[\sigma^2(F_o) + 0.000\,5(F_o)^2]^{-1}$. Neutral-atom scattering factors were used (except K$^+$),[8] those for the non-hydrogen atoms being corrected for anomalous dispersion ($\Delta f'$, $\Delta f''$).[9] All computations were completed on a CYBER 73 computer at the University of Western Australia, using the X-Ray system. Final atomic co-ordinates are listed in Table 1. Structure-factor tables and anisotropic thermal parameters have been deposited as Supplementary Publication No. SUP 22727 (9 pp.).*

TABLE 1

Atomic co-ordinates for $K_3[N(SO_3)_2]\cdot H_2O$ ($\times 10^5$ for K, S; $\times 10^4$ for N, O, H) with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
K(1)	82 649(9)	33 231(11)	57 658(9)
K(2)	55 580(9)	68 718(11)	75 916(9)
K(3)	15 554(9)	80 161(10)	93 595(9)
S(1)	43 811(9)	15 125(11)	72 276(9)
S(2)	19 350(9)	31 984(11)	85 438(9)
N	3 731(3)	2 493(4)	8 771(3)
O(11)	4 576(3)	2 945(4)	5 894(3)
O(12)	6 060(3)	1 132(4)	7 899(3)
O(13)	3 143(3)	−400(4)	6 618(3)
O(21)	1 938(3)	4 784(3)	7 327(3)
O(22)	1 830(3)	4 010(3)	10 206(3)
O(23)	435(3)	1 468(3)	8 020(3)
O(H)	990(4)	2 275(4)	3 911(3)
H(OH1)	370(60)	1 025(77)	3 656(61)
H(OH2)	1 701(61)	2 088(75)	4 372(63)

Spectroscopy.—Infrared spectra were recorded using Perkin-Elmer model 225 and Beckman-RIIC IR-720 spectrophotometers with low-temperature facilities and general conditions as described previously.[10] Raman spectra were recorded on a Cary model 82 laser spectrometer using 514.5 nm exciting radiation and a power of *ca.* 400 mW at the sample. Experimental conditions were as previously described.[10] Infrared and Raman spectra of both hydrated and anhydrous $K_3[N(SO_3)_2]$ recorded at ambient temperature showed little change from the spectra at 77 K. Observed bands are considered accurate to ±2 cm^{-1} below 2 000 cm^{-1} and ±4 cm^{-1} above 2 000 cm^{-1}.

RESULTS AND DISCUSSION

Crystal Structure.—The molecular conformation and atomic numbering scheme used for $K_3[N(SO_3)_2]\cdot H_2O$ is shown in Figure 1. The anionic species $N(SO_3)_2{}^{3-}$ possesses approximate C_{2v} point symmetry. The atoms O(12), S(1), N, S(2), and O(22) deviate by —0.07, 0.22, —0.32, 0.23, and —0.06 Å respectively from the least-squares plane drawn through these atoms. Interatomic distances and angles are listed in Table 2.

The N–S bond length [1.604 (3) Å] is markedly smaller than the N–S single-bond length (1.74 Å) given by the Schomaker–Stevenson rules.[11,12] This contraction is attributed to π bonding involving the lone-pair orbitals of nitrogen and the unfilled 3d orbitals of sulphur. In potassium sulphamate, $K[NH_2SO_3]$,[13,14] potassium imidosulphonate $K_2[NH(SO_3)_2]$,[15,16] and potassium nitrilosulphonate dihydrate, $K_3[N(SO_3)_3]\cdot 2H_2O$,[17] there is only one lone pair of electrons available for π bonding and consequently the N–S bond lengths are larger, 1.666(6), 1.674(5), and 1.71(2) Å respectively. In sulphamic acid, $NH_3{}^+SO_3{}^-$,[18] where there are no electrons available for π bonding, the N–S bond length is 1.76(2) Å. In spite of

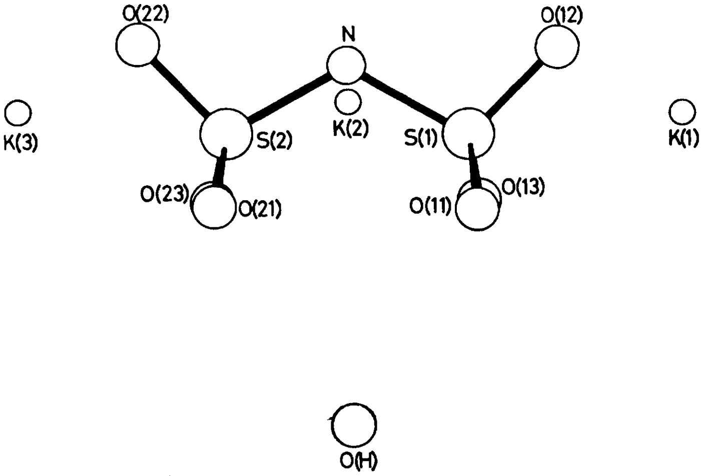


FIGURE 1 Molecular configuration and numbering scheme used for the $K_3[N(SO_3)_2]\cdot H_2O$ unit shown in perspective perpendicular to the S–N–S plane

TABLE 2

Interatomic distances (Å) and angles (°) with estimated standard deviations in parentheses

(*a*) Intramolecular distances

N–S(1)	1.609(3)	S(2)–O(21)	1.471(2)
N–S(2)	1.599(3)	S(2)–O(22)	1.469(2)
S(1)–O(11)	1.466(3)	S(2)–O(23)	1.475(2)
S(1)–O(12)	1.456(3)	O(H)–H(OH1)	0.88(5)
S(1)–O(13)	1.465(2)	O(H)–H(OH2)	0.67(5)

(*b*) Intramolecular angles

S(1)–N–S(2)	121.0(1)	O(11)–S(1)–O(12)	110.6(1)
N–S(1)–O(11)	110.3(1)	O(11)–S(1)–O(13)	110.5(1)
N–S(1)–O(12)	105.0(1)	O(12)–S(1)–O(13)	110.4(1)
N–S(1)–O(13)	109.9(1)	O(21)–S(2)–O(22)	110.5(1)
N–S(2)–O(21)	111.5(1)	O(21)–S(2)–O(23)	109.2(1)
N–S(2)–O(22)	104.2(1)	O(22)–S(2)–O(23)	109.9(1)
N–S(2)–O(23)	111.5(1)		

(*c*) Interatomic K–O distances less than 3.11 Å. Intramolecular contacts are indicated by an asterisk

	O(11)	O(12)	O(13)	O(21)
K(1)	2.909 *	2.830	2.676	2.961, 2.841
K(2)	2.859,* 2.825	2.816	3.001	2.882
K(3)		2.683	2.818	2.812 *

	O(22)	O(23)	O(H)	Mean
K(1)		2.852	3.009, 2.896	2.872
K(2)	2.736		3.100	2.888
K(3)	2.855, 2.803	2.865, 2.885	3.089	2.851

---

* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

the shorter N–S bonds in $K_3[N(SO_3)_2]\cdot H_2O$, the S–N–S angle [121.0(1)°] is smaller than that in $K_2[NH(SO_3)_2]$ [124.4(3)°]. This may be attributed to the repulsive effect of the additional lone pair of electrons in the former case.

Distortion in the O–S–O angle is common to all members of the series and is considered to be due to electrostatic repulsion between charged oxygen atoms around sulphur.[19] The mean O–S–O angle [110.2(1)°] and the O–S–N angle [108.7(1)°] represent the smallest observed deviations from the expected tetrahedral value.

The packing of the anionic and cationic species and the water molecules in the unit cell is very symmetrical (Figure 2). The plane containing N, K(2), and O(H) [plane (1)] lies at 89.9° to the plane of S(1), N, and S(2) [plane (2)] while the plane containing K(1), K(2), and K(3) [plane (3)] lies at 88.8° to plane (1), and 76.0° to plane (2). There are hydrogen-bonding associations between the hydrogen atoms of the water molecule and oxygen atoms of both sulphonate groups within the same asymmetric unit. The O(H) · · · O distances are 3.02 and 3.13 Å [O(11), O(21)] and 3.41, and 3.46 Å [O(13), O(23)]. Short inter-unit O(H) · · · O contacts are also found with O(13) (3.21 Å) and O(23) (2.86 Å), while the shortest intramolecular distances associated with the oxygen atoms lying in the molecular plane are 3.35 Å [O(22)] and 4.03 Å [O(12)]. The potassium atoms are surrounded by a sphere of seven [K(2)] or eight [K(1), K(3)] oxygen atoms from the sulphonates or water molecules with K–O distances ranging from 2.68 to 3.10 Å (mean 2.87 Å). A complete listing is given in Table 2(*c*). These values compare with those found for other members of the sulphonate series which include $K_2[CH_2(SO_3)_2]$ (2.71—3.22 Å, mean 2.89 Å), $K_2[NH(SO_3)_2]$ (2.71—3.23 Å, mean 2.89 Å), $K_2[S_2O_7]$ (2.70—3.35 Å, mean 2.96 Å),[19] and $K_3[CH(SO_3)_3]\cdot H_2O$ (2.66—3.07 Å, mean 2.83 Å).[10]

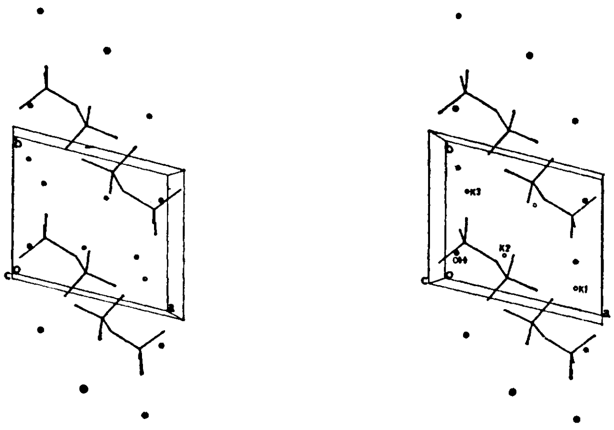


FIGURE 2 Stereoscopic view of the packing in the cell viewed down the *c* axis

Vibrational Investigation.—For an isolated $N(SO_3)_2^{3-}$ ion of C_{2v} symmetry the 21 normal modes of vibration are described by the symmetry species * $7A_1 + 4A_2 + 4B_1 + 6B_2$. The A_1, B_1, and B_2 modes are i.r. and Raman active whereas the A_2 modes are Raman active only. Approximate descriptions of these modes in terms of internal-co-ordinate contributions are given in Table 3. Considerable mixing of these motions is expected in the actual normal modes. In the crystal, all atoms of the $K_3[N(SO_3)_2]\cdot H_2O$ unit occupy general positions and hence factor-group analysis yields the vibrational representation shown in Table 4 (acoustic modes omitted). The A_g modes are Raman active only whereas A_u modes are i.r. active only. The correlation between point, site, and unit-cell symmetry species is given in Table 5. The i.r. and Raman spectra of $K_3[N(SO_3)_2]\cdot H_2O$ at 77 K are shown in Figure 3. The observed frequencies (including those for the ^{15}N and ^{2}H derivatives and the aqueous solution of the sodium salt) and their assignments are given in Table 6.

TABLE 3

Approximate internal-co-ordinate contributions to the vibrational modes of $N(SO_3)_2^{3-}(C_{2v})$

N–S stretches	$A_1 + B_2$
NS_2 deformation	A_1
S–O stretches	$2A_1 + A_2 + B_1 + 2B_2$
SO_3 deformations	$2A_1 + A_2 + B_1 + 2B_2$
SO_3 rocks	$A_1 + A_2 + B_1 + B_2$
SO_3 torsions	$A_2 + B_1$

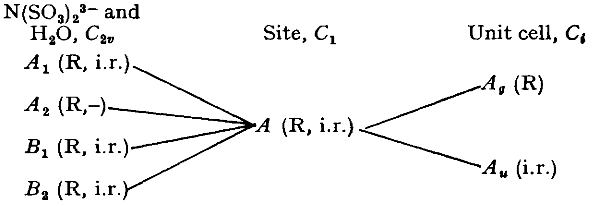
TABLE 4

Vibrational representation for $K_3[N(SO_3)_2]\cdot H_2O$

Γ[internal $N(SO_3)_2^{3-}$ modes]	$21(A_g + A_u)$
Γ(internal H_2O modes)	$3(A_g + A_u)$
Γ(rotatory modes)	$6(A_g + A_u)$
Γ(translatory modes)	$15A_g + 12A_u$

TABLE 5

Correlation scheme for $K_3[N(SO_3)_2]\cdot H_2O$



In the S–O stretching region, two polarized bands (986 and 1 074 cm^{-1}) are observed and assigned to the A_1 modes. The broad depolarized band at 1 158 cm^{-1} is split into four components in the solid-state spectrum, each with a counterpart in the infrared. These correspond to the antisymmetric S–O stretches ($A_2 + B_1 + 2B_2$). The mode having least intensity in the i.r. (1 126 cm^{-1}) is assigned to the A_2 species, which gains i.r. activity through solid-state effects only. Of the remaining bands in this region, that at 1 156 cm^{-1} is tentatively assigned to the B_1 mode and hence those at 1 162 and 1 193 cm^{-1} are assigned to the B_2 modes.

The assignment of the strong polarized band at 794 cm^{-1} to the symmetric N–S stretch (A_1) is made on the basis of the isotopic (^{15}N) frequency shifts (9—10 cm^{-1}) of the corresponding i.r. and Raman bands of the solid.

---

* The *x* axis of the isolated $N(SO_3)_2^{3-}$ ion is taken to be perpendicular to the NS_2 plane, and the *z* and *y* axes to be along and perpendicular to the NS_2 bisector respectively.

TABLE 6

Observed frequencies and assignments for the $N(SO_3)_2^{3-}$ ion, and $K_3[N(SO_3)_2]\cdot H_2O$ and its ^{15}N and ^2H derivatives

	$K_3[N(SO_3)_2]\cdot H_2O$ (77 K)				
1.0 mol dm^{-3} $N(SO_3)_2^{3-}$ Raman (i.r. in parentheses)	Raman		Infrared		
	$^{14}N(^{15}N)$ [a]	^2H	$^{14}N(^{15}N)$ [a]	^2H	Assignment
	60w	59w			
			70w	68w	
	78w	79w			
	95vw	95vw	91w	91w	lattice modes
	100w	100w	99w	99w	
			115w	114w	
	123w	123w	126w	127w	
	134vw	133vw	139w	140 (sh)	
	151w	151w	147w		
	161w	162w	161w,br	163w,br	
	178w	174w			
	197vw	192vw			
			190w,br	183w,br	$\delta(NS_2)$ (A_1)
	219w	218w	217w	217w	$\rho(SO_3)$ (B_2)
				270vw	D_2O rock (B_2)
	339m	341m	342vw	341vw	$\rho(SO_3)$ (B_1)
			349vw		H_2O rock (B_2)
362s,p	360m	358w	360vw	354w	$\rho(SO_3)$ (A_1)
370 (sh),dp	379m	383m	375vw		$\rho(SO_3)$ (A_2)
		ca. 400w,vbr		*ca.* 380w,br	D_2O wag (B_1)
			456vw	461vw	$\delta(SO_3)$ (B_1)
	ca. 480w,vbr		487w,br	486vw	H_2O wag (B_1)
529m,p	527m	531m	525w	525w	$\delta(SO_3)$ (A_1)
545 (sh),dp	551w	552w	555w	548w	$\delta(SO_3)$ (B_2)
	577vw	578vw	580vw	579 (sh)	$\delta(SO_3)$ (A_2)
610w,dp (610 [b])	624m (619m)	622w	611s	604s	$\delta(SO_3)$ (B_2)
			618 (sh)		525 + 100 (=625)
	629 (sh)	629m			527 + 100 (=627)
687w,p	681vw	681vw	675vw	673vw	$\delta(SO_3)$ (A_1)
	(675vw)				
794s,p (780 [b])	787s (777s)	790s	775m (766m)	774m	$\nu(N-S)$ (A_1)
			964 (sh)	959w (sh)	487 + *ca.* 480 (*ca.* 967)
986w,p (983s)	983vw	984vw	982s	975s	$\nu(S-O)$ (A_1)
			1 035 (sh)		675 + 360 (=1 035)
(1 046sh)	1 044w	1 041w	1 042s	1 039s	$\nu(N-S)$ (B_2)
	(1 012w)		(1 041s)		
1 074vs,p (1 061m)	1 082vs	1 082vs	1 070m	1 066m	$\nu(S-O)$ (A_1)
	1 128w	1 125w	1 126m	1 121m	$\nu(S-O)$ (A_2)
1 158w,br,dp	1 156m	1 150m	1 157s		$\nu(S-O)$ (B_1)
(1 160s,br)	1 162m	1 160m	1 177s	1 160s,br	$\nu(S-O)$ (B_2)
	1 193m	1 191m	1 195s		$\nu(S-O)$ (B_2)
		1 208vw		1 210 (sh)	$\delta(DOD)$ (A_1)
				1 417vw	$\delta(HOD)$ (A')
				1 447vw	$\delta(HOD)$ (A')
					777 + 766 (=1 543)
			1 556vw	1 564vw	787 + 775 (=1 562)
				1 600 (sh)	1 210 + *ca.* 400 (≈1 610)
			1 635w	1 637vw	$\delta(HOH)$ (A_1)
					1 012 + 766 (=1 778)
			1 817vw	1 817vw	1 044 + 775 (=1 819)
			2 120vw,br		1 635 + *ca.* 480 (≈2 115)
		2 530m		2 520m	$\nu(O-D)$ (A_1)
				2 560 (sh)	$\nu(O-D)$ (HDO) ($2A'$)
		2 600 (sh), br		2 610m	$\nu(O-D)$ (B_2)
	3 455m		3 453m	3 455w [c]	$\nu(O-H)$ (A_1)
			3 481m		$\nu(O-H)$ (B_2)
	3 520 (sh)		3 515 (sh)	3 510 (sh)	2 × 1 635 + *ca.* 250 (*ca.* 3 520)

[a] ^{15}N frequencies given where they differ by >4 cm^{-1}. [b] Relative intensity uncertain due to contribution from H_2O libration. [c] Contains contributions from $\nu(O-H)$ (HDO) (A').

Also, bands at 1 042 and 1 044 cm^{-1} in the i.r. and Raman spectra respectively of the solid shift by 28—32 cm^{-1} on ^{15}N substitution and are therefore assigned to the antisymmetric N–S stretch (B_2). The B_2 mode is probably masked by the intense band at 1 074 cm^{-1} in the Raman spectrum of the aqueous solution, but appears as a shoulder at 1 046 cm^{-1} in the infrared.

The SO_3 and NS_2 bending and the SO_3 rocking vibrations are crowded together in the region below 700 cm^{-1} and hence considerable vibrational coupling between them is expected. However, modes having predominantly SO_3 bending character probably occur at higher frequencies than those which are predominantly SO_3 rocking. This is consistent with the frequencies [20] observed for the SO_3 bending (534 cm^{-1}) and rocking modes (374 cm^{-1}) of sulphamic acid, $NH_3^+SO_3^-$. Also, it is a reasonable assumption that the predominantly NS_2 bending mode (A_1) will occur below those involving mainly SO_3 group motion, as in the case of the symmetric N–S and S–O stretches.

On this basis, the *three* polarized bands observed below 700 cm^{-1} are assigned to the symmetric (A_1) SO_3 bending (687 and 529 cm^{-1}) and rocking (362 cm^{-1}) modes. Bands at 456 and *ca.* 340 cm^{-1} in the solid-state spectrum are tentatively assigned to the B_1 bending and rocking modes respectively.* Bands at 580 and 375 cm^{-1} in the i.r. spectrum of the solid have very weak intensity and therefore are assigned to the A_2 bending and rocking modes respectively. The depolarized bands at 610 and 545 cm^{-1} can then be assigned to the B_2 bending modes and those at *ca.* 220 cm^{-1} in the spectrum of the solid to the B_2 rocking mode.

Having accounted for the SO_3 bending and rocking modes, the broad i.r. band at 190 cm^{-1} can be assigned, in part, to the NS_2 deformation. The intensity maximum of this band, which has a counterpart in the spectrum of anhydrous $K_3[N(SO_3)_2]$ (186 cm^{-1}), shifts by 7 cm^{-1} on deuteriation. This shift is attributed to a band arising from an essentially translatory mode of the water molecule which is buried in the broad absorption envelope. Indeed, a Raman band at 197 cm^{-1}, which is absent from the spectrum of anhydrous $K_3[N(SO_3)_2]$, shows a similar shift (5 cm^{-1}) on deuteriation. No assignment is made for the SO_3 torsional modes, which are expected to occur below 50 cm^{-1}.

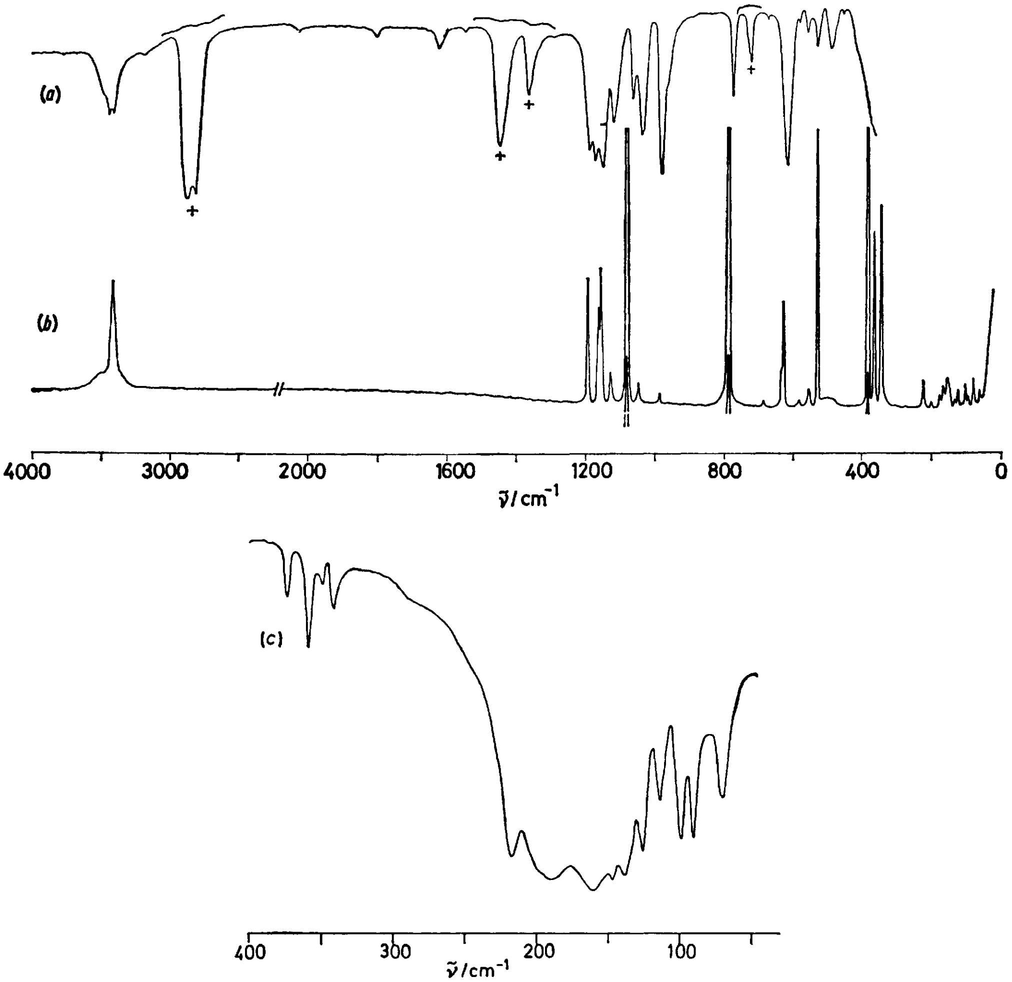


FIGURE 3 Infrared (400—4 000 cm^{-1}) (*a*), Raman (*b*), and far-i.r. (*c*) spectra of $K_3[N(SO_3)_2]\cdot H_2O$ at 77 K

The observed isotope (^{15}N) effect on the vibrational frequencies of $N(SO_3)_2^{3-}$ is in reasonable agreement with the predictions of the Teller–Redlich product rule. The observed (calculated values in parentheses) † products of the isotopic frequency ratios $[^{15}N(SO_3)_2^{3-}/^{14}N(SO_3)_2^{3-}]$ are 0.965 (0.967) (A_1), 0.993 (1.000) (A_2), 0.996 (0.977) (B_1), and 0.965 (0.968) (B_2).

Bands corresponding to the internal modes of H_2O are assigned on the basis of their isotopic (deuterium) frequency shifts and by their absence from the spectra of

---

* In the vibrational spectrum of imidosulphonate $NH(SO_3)_2^{2-}$ (C_s) (unpublished work), the five A' SO_3 bending/rocking modes (corresponding to $3A_1 + 2B_1$ under C_{2v} symmetry) are assigned the bands at 666, 525, 450, 324, and 316 cm^{-1}. A similar comparison supports the assignment of the band at 1 156 cm^{-1} to the B_1 S–O stretch.

† The calculated products were determined using the general formula given by Herzberg.[21] Each SO_3 group was regarded as a single entity of 1.33 × 10^{-25} kg with its centre of mass at the point of half-height (0.2 Å) of the SO_3 pyramid. The SO_3 torsions were neglected in these calculations.

the anhydrous salt. The shoulders at 3 515 and 3 520 cm^{-1} in the i.r. and Raman spectra respectively are absent from the spectra of the anhydrous salt, but there are no corresponding features in the O–D stretching region of $K_3[N(SO_3)_2]\cdot D_2O$. These features are probably due to combinations which gain intensity through Fermi resonance with O–H stretches. Possible combinations are those involving unobserved, essentially H_2O translatory modes at *ca.* 250 cm^{-1} and the overtone of the HOH deformation at 1 635 cm^{-1}. The frequencies of the O–H stretches and HOH deformation add further support to the proposal that the water molecule is involved in hydrogen bonding.

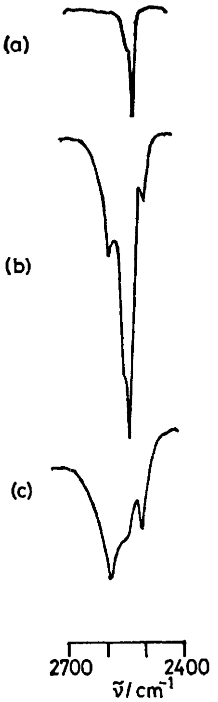


FIGURE 4 Infrared spectra (KBr discs) of partially deuteriated $K_3[N(SO_3)_2]\cdot H_2O$ at 77 K in the O–D stretching region: (*a*) 92.2, 7.6, and 0.2; (*b*) 64, 32, and 4; and (*c*) 4, 32, and 64 mol % of H_2O, HDO, and D_2O respectively

Due to the incomplete deuteriation, the O–D stretching region of $K_3[N(SO_3)_2]\cdot D_2O$ contains contributions from the HDO species. Therefore, the assignment of bands in this region is based also on the changes which occur for samples having varying degrees of deuteriation. Also, these changes are consistent with the space-group requirement that the hydrogen atoms of the water molecule are inequivalent. This inequivalance is probably associated with their involvement in hydrogen bonds of different strengths and is consistent with the $O(H)\cdots O(SO_3)$ interatomic distances.

The i.r. spectra of partially deuteriated samples of $K_3[N(SO_3)_2]\cdot H_2O$ at 77 K in the O–D stretching region are shown in Figure 4. Two features are apparent in the spectrum of the least deuteriated sample (*a*) (2 553 and 2 565 cm^{-1}). These are ascribed to the HDO species since the D_2O concentration (0.2 mol %) in this sample is negligible. Furthermore, the HDO concentration (7.6 mol %) is low enough to prevent significant correlation coupling from occurring and hence the presence of two bands is indicative of two types of HDO molecules in the crystal. Therefore, the hydrogen atoms of $K_3[N(SO_3)_2]\cdot H_2O$ must be inequivalent. On increased deuteriation [(*b*) and (*c*)], the growth of two new bands is observed. These bands, which increase in intensity relative to those of HDO, are assigned to the A_1 (2 520 cm^{-1}) and B_2 (2 610 cm^{-1}) modes of D_2O. Spectrum (*c*) represents the highest deuteriation achieved.

The assignment of i.r. bands to the H_2O wagging (B_1) (487 cm^{-1}) and rocking (B_2) (349 cm^{-1}) modes is based on their isotopic frequency ratios, $\nu(H)/\nu(D)$ (1.28 and 1.29 respectively), and their absence from the spectrum of anhydrous $K_3[N(SO_3)_2]$. The H_2O and D_2O wagging modes are observed in the Raman spectrum also. The water twisting mode (A_2) is not observed. In the i.r. spectra, the wagging modes of H_2O and D_2O are also observed in combination (2 120 and 1 600 cm^{-1} respectively) with the deformation modes. The combination of the A_g and A_u wagging modes of H_2O is also observed (964 cm^{-1}). Similar assignments of combination modes have been made for some other crystalline hydrates [22] and for ice.[23]

Seventeen lattice vibrations are observed below 200 cm^{-1} for $K_3[N(SO_3)_2]\cdot H_2O$. Some of the lower-lying modes may of course have some SO_3 torsional character. In all, 20 of the predicted 39 lattice modes are observed.

The present assignment of the intense Raman bands at 1 074 and 794 cm^{-1} to the A_1 S–O and N–S stretches respectively is in agreement with that of Siebert.[1] However, Siebert assigned an intense band at 1 000 cm^{-1} in the i.r. spectrum of $Na_3[N(SO_3)_2]\cdot 12H_2O$ to the B_2 N–S stretch (*cf.* 1 046 cm^{-1} in the present work). It is more likely that this band is due to the A_1 S–O stretch observed at 986 cm^{-1} in the present work. The B_2 N–S stretch of the sodium salt probably gives rise to an i.r. band at 1 015 cm^{-1} which was assigned to a B_2 S–O stretch by Siebert.

The authors thank the Australian Research Grants Committee for funds to purchase the i.r. and Raman spectrometers. R. A. J. acknowledges the award of a Commonwealth Postgraduate Research Scholarship. G. S. thanks the Queensland Institute of Technology for leave to carry out the project.

[9/383 *Received, 9th March*, 1979]

REFERENCES

[1] H. Siebert, *Z. anorg. Chem.*, 1957, **289**, 15.
[2] H. H. Sisler and L. F. Audrieth, 'Inorganic Syntheses,' McGraw-Hill, New York, 1946, vol. 2, p. 180.
[3] H. H. Sisler and L. F. Audrieth, *J. Amer. Chem. Soc.*, 1938, **60**, 1947.
[4] J. R. Hall and R. A. Johnson, *Phosphorus Sulfur*, 1977, **3**, 175.
[5] L. F. Audrieth, M. Sveda, H. H. Sisler, and M. J. Butler, *Chem. Rev.*, 1940, **26**, 49.
[6] J. R. Hall and R. A. Johnson, *J. Mol. Structure*, 1978, **48**, 353.
[7] V. Seidl and O. Knop, *Canad. J. Chem.*, 1969, **47**, 1361.

[8] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321; R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[9] D. T. Cromer and D. Liberman, *J. Chem. Phys.*, 1970, **53**, 1891.

[10] J. R. Hall, R. A. Johnson, C. H. L. Kennard, and G. Smith, *J.C.S. Dalton*, 1980, 149.

[11] V. Schomaker and D. P. Stevenson, *J. Amer. Chem. Soc.*, 1941, **63**, 37.

[12] D. W. J. Cruikshank, *J. Chem. Soc.*, 1961, 5489.

[13] G. J. Jeffrey and J. Stadler, *J. Chem. Soc.*, 1951, 1467.

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

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

[16] P. G. Hodgson, F. H. Moore, and C. H. L. Kennard, *J.C.S. Dalton*, 1976, 1443.

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

[18] R. L. Sass, *Acta Cryst.*, 1960, **13**, 320.

[19] M. R. Truter, *J. Chem. Soc.*, 1962, 3393.

[20] I. Nakagawa, S. Mizushima, A. J. Saraceno, T. J. Lane, and J. V. Quagliano, *Spectrochim. Acta*, 1958, **12**, 239.

[21] G. Herzberg, ' Infrared and Raman Spectra of Polyatomic Molecules,' Van Nostrand, New York, 1945, p. 232.

[22] M. Falk and O. Knop, ' Water, A Comprehensive Treatise,' ed. F. Franks, Plenum, New York, 1973, vol. 2, p. 91.

[23] P. A. Giguère and K. B. Harvey, *Canad. J. Chem.*, 1956, **34**, 798.