

References

- BECKER, P. J. & COPPENS, P. (1974a). *Acta Cryst.* **A30**, 129–147.
 BECKER, P. J. & COPPENS, P. (1974b). *Acta Cryst.* **A30**, 148–153.
 BECKER, P. J. & COPPENS, P. (1975). *Acta Cryst.* **A31**, 417–425.
 IKEDA H. & HIRAKAWA, K. (1973). *J. Phys. Soc. Jpn*, **35**, 722–728.
International Tables for X-ray Crystallography (1967). Vol. II. Birmingham: Kynoch Press.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
 IWATA, M. (1977). *Acta Cryst.* **B33**, 59–69.
 IWATA, M. & SAITO, Y. (1973). *Acta Cryst.* **B29**, 822–832.
 JOHANSEN, H. (1976). *Acta Cryst.* **A32**, 353–355.
 KADOTA, S., YAMADA, I., YONEYAMA, S. & HIRAKAWA, K. (1967). *J. Phys. Soc. Jpn*, **23**, 751–756.
 KANAMORI, J. (1960). *J. Appl. Phys.* **31**, suppl. 14S–23S.
 MCWEENY, R. (1951). *Acta Cryst.* **4**, 513–519.
 MARUMO, F., ISOBE, M. & AKIMOTO, S. (1977). *Acta Cryst.* **B33**, 713–716.
 MARUMO, F., ISOBE, M., SAITO, Y., YAGI, T. & AKIMOTO, S. (1974). *Acta Cryst.* **B30**, 1904–1906.
 MIYAMAE, H., SATO, S. & SAITO, Y. (1977). *Acta Cryst.* **B33**, 3391–3396.
 OKAZAKI, A. (1969a). *J. Phys. Soc. Jpn*, **26**, 870.
 OKAZAKI, A. (1969b). *J. Phys. Soc. Jpn*, **27**, 518.
 OKAZAKI, A. & SUEMUNE, Y. (1961). *J. Phys. Soc. Jpn*, **16**, 176–183.
 SHOEMAKER, D. P. (1968). *Acta Cryst.* **A24**, 136–142.
 TANAKA, K. (1978). *Acta Cryst.* **B34**, 2487–2492.
 TANAKA, K., KONISHI, M. & MARUMO, F. (1977). *Rep. Res. Lab. Eng. Mater., Tokyo Inst. Technol.* **3**, 19–26.
 TORIUMI, K., OZIMA, M., AKAOGI, M. & SAITO, Y. (1978). *Acta Cryst.* **B34**, 1093–1096.
 WEISS, R. J. & FREEMAN, A. J. (1959). *J. Phys. Chem. Solids*, **10**, 147–161.

Acta Cryst. (1979). **B35**, 1308–1312

Crystal Structure of $\text{K}_3\text{N}(\text{SO}_3)_2 \cdot \text{H}_2\text{O}$ (I) and Refinement of the Crystal Structure of $\text{K}_2\text{NH}(\text{SO}_3)_2$ (II)

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Abstract

Crystal (I) is triclinic, space group $P\bar{1}$, with $a = 8.126(4)$, $b = 7.978(3)$, $c = 6.762(4)$ Å, $\alpha = 103.36(3)$, $\beta = 90.98(3)$, $\gamma = 97.86(3)^\circ$, $Z = 2$. The structure was refined to $R = 0.029$ for 2067 reflexions. The bond lengths are $\text{S}-\text{N} = 1.606$ and $\text{S}-\text{O} = 1.468$ Å, and bond angles are $\text{S}-\text{N}-\text{S} = 120.83(11)$ and $\text{N}-\text{S}-\text{O} = 108.70^\circ$. The structure of (II) has been refined to a final $R = 0.043$ over 1113 reflexions. The H atom was observed, and its coordinates agree well with those obtained earlier by neutron diffraction.

Introduction

Studies of various S- and N-containing compounds, e.g. SO_3NH_3 , $[\text{SO}_3\text{NH}_2]^-$, $[(\text{SO}_3)_2\text{NH}]^{2-}$, have shown that $\text{S}-\text{O}$ and $\text{S}-\text{N}$ lengths vary over a wide range. Cruickshank (1961) explained the contraction of the $\text{S}-\text{O}$ and $\text{S}-\text{N}$ bonds by the formation of two strong π -bonding

molecular orbitals. The formation of such orbitals is possible only if there are p orbitals available for the π systems on the bridge atom.

Thus, if the bridge atom (N) in $\text{K}_3\text{N}(\text{SO}_3)_2$ is replaced by NH in $\text{K}_2\text{NH}(\text{SO}_3)_2$, we should observe $\text{S}-\text{O}$ and $\text{S}-\text{N}$ bond-length variations, since the number of p orbitals available on the N atom is different in the two compounds.

For this reason we have undertaken the X-ray structural analysis of the two compounds. The crystal structure of $\text{K}_3\text{N}(\text{SO}_3)_2 \cdot \text{H}_2\text{O}$ is unknown, but that of $\text{K}_2\text{NH}(\text{SO}_3)_2$ has been determined by X-ray diffraction (Jeffrey & Jones, 1956). Further refinement of the data was made by Cruickshank & Jones (1963). More recently, Hodgson, Moore & Kennard (1976) redetermined the structure by neutron diffraction. They showed that the N atom is surrounded tetrahedrally by two SO_3 groups and two half H atoms. As crystals of good quality were available, we have refined the structure of this salt, and determined that of $\text{K}_3\text{N}(\text{SO}_3)_2 \cdot \text{H}_2\text{O}$.

Crystal structure of $K_3N(SO_3)_2 \cdot H_2O$

Experimental

$K_3N(SO_3)_2 \cdot H_2O$ was prepared by addition of a small excess of KOH to a warm solution of $K_2NH(SO_3)_2$. The solid was obtained after addition of ethanol to the cooled solution. The crystal selected for the structural analysis was a parallelepiped $0.25 \times 0.25 \times 0.20$ mm. The cell parameters were determined by least squares from the setting angles of 25 reflexions measured on a Philips PW 1100 automatic four-circle diffractometer with graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.7107 \text{ \AA}$). This study showed that the crystal is triclinic with $a = 8.126 (4)$, $b = 7.978 (3)$, $c = 6.762 (4) \text{ \AA}$, $\alpha = 103.36 (3)$, $\beta = 90.98 (3)$, $\gamma = 97.86 (3)^\circ$, $Z = 2$.

The intensities of 2460 independent reflexions with $3 \leq \theta \leq 30^\circ$ in the $h > 0$ hemisphere were collected by the ω -scan technique with a $0.035^\circ \text{ s}^{-1}$ scanning speed and a 1.80° scan width. The background was measured for half the scan time at each end of the scan. Three standard reflexions were monitored at regular intervals and showed no systematic variation. The intensities were corrected for Lorentz and polarization effects but not for absorption ($\mu = 2.0 \text{ mm}^{-1}$).

The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1971). Statistics from normalized structure factors showed that the space group was $P\bar{1}$; this was confirmed by the successful refinement. 499 reflexions with $|E| > 1.28$ were included in the phase-determining process with sixteen sets of starting phases. The E map corresponding to the solution with the best figure of merit (COMBINED FOM maximum) revealed the positions of 9 of the 15 atoms in the cell: the three K^+ ions, three O, two S, and the N. The remaining O atoms and the H atoms of the water

Table 1. $K_3N(SO_3)_2 \cdot H_2O$: atomic coordinates (for K, S $\times 10^5$, for N, O $\times 10^4$, for H $\times 10^3$) with e.s.d.'s in parentheses

	x	y	z
K(1)	24092 (6)	-5563 (6)	31290 (7)
K(2)	93601 (6)	65553 (6)	80156 (7)
K(3)	57642 (6)	32638 (6)	33233 (8)
N	8774 (2)	8734 (2)	2492 (3)
S(1)	72283 (6)	93780 (6)	15114 (7)
S(2)	85435 (6)	69344 (6)	31988 (7)
O(1)	6625 (2)	8143 (2)	-404 (3)
O(2)	7903 (2)	11064 (2)	1139 (3)
O(3)	5896 (2)	9582 (2)	2952 (3)
O(4)	8024 (2)	5430 (2)	1462 (2)
O(5)	7322 (2)	6938 (2)	4784 (2)
O(6)	10198 (2)	6825 (2)	4007 (2)
O(w)*	3906 (2)	5995 (3)	2284 (3)
H(1)	356 (4)	562 (4)	120 (5)
H(2)	462 (4)	665 (4)	209 (5)

* Oxygen of the water molecule.

molecule were revealed by difference maps. These H atoms were included in the last stages of refinement but their thermal vibrations were constrained to the isotropic thermal parameter of the carrier atom. The final R and R_w [$w = 1/\sigma^2(F_o)$] were 0.029 and 0.038 respectively for the 2067 independent reflexions with $I > 3\sigma(I)$. Atomic scattering factors were taken from Cromer & Waber (1965) for the heavy atoms and from Stewart, Davidson & Simpson (1965) for H. The atomic coordinates are given in Table 1.*

Description of the structure and discussion

A perspective view of the molecule with the atomic numbering is given in Fig. 1. Fig. 2 shows the packing. Table 2 gives the bond lengths and angles. The S—O lengths are not significantly different in the two SO_3 groups [maximum spreads are 0.008 and 0.016 \AA in S(1)O₃ and S(2)O₃ respectively]. The mean S—O length = 1.468 and mean S—N = 1.606 \AA . The O—S—O

* Lists of structure factors and thermal parameters for (I) and (II) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34277 (31 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

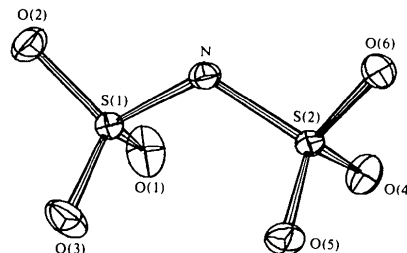


Fig. 1. Perspective drawing of $[N(SO_3)_2]^{3-}$ showing the numbering scheme (thermal ellipsoids are drawn at the 50% probability level).

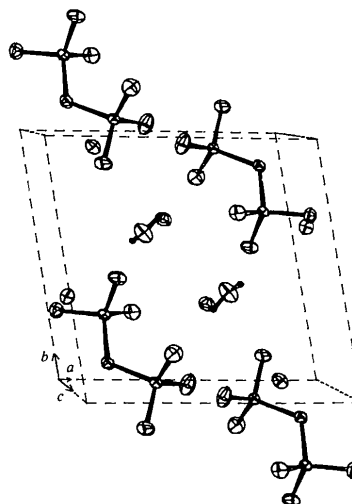


Fig. 2. Packing in the $K_3N(SO_3)_2$ unit cell.

angles are very close to tetrahedral (mean $110 \cdot 20^\circ$), and N—S—O angles range between $104 \cdot 26$ and $111 \cdot 50^\circ$ (mean $108 \cdot 70^\circ$). Nevertheless, the N—S(1)—O(2) ($104 \cdot 78^\circ$) and N—S(2)—O(6) ($104 \cdot 26^\circ$) bond angles are slightly smaller than the others.

The K^+ ions are essentially surrounded by O atoms. The shortest $K \cdots O$ distances are shown in Table 3. There is also a $K^+(1) \cdots N$ separation ($2 \cdot 936 \text{ \AA}$) slightly shorter than some $K^+ \cdots O$ contacts. For $K^+(2)$ and $K^+(3)$, the shortest $K \cdots N$ distances are $3 \cdot 2$ and $>4 \text{ \AA}$ respectively.

The bridging N atom is not involved in any electrostatic or van der Waals interaction with O atoms. The shortest N—O distances are N—O(2) 2/210 (coding in Table 3) $3 \cdot 693 \text{ \AA}$ and N—O(6) 2/121 $3 \cdot 754 \text{ \AA}$.

The geometries of the water molecule and the hydrogen bonds are given in Table 4. The O—H \cdots O(3) 1/000 hydrogen bond is very weak. The analysis of the thermal vibration of the anion was carried out in the TLS approximation to rigid-body motion (Schomaker & Trueblood, 1968). Smaller parts of the anion were successively checked. The values of the r.m.s. and e.s.d.'s criteria with the T, L and S tensors are given in Table 5. The results obtained for each $N(SO_3)$ moiety were retained. The corrections to the bond distances for atomic libration were calculated by the Busing & Levy (1964) method. The observed and corrected values are reported in Table 2. Table 6 shows the deviations of atoms from the mean plane through N, S(1), S(2), O(2) and O(6).

Structure refinement of $K_2NH(SO_3)_2$

The intensities of 1426 independent reflexions with $3 \leq \theta \leq 30^\circ$ were collected in much the same way as for $K_3N(SO_3)_2 \cdot H_2O$. The scanning speed and the scan width were $0 \cdot 030^\circ \text{ s}^{-1}$ and $1 \cdot 40^\circ$ respectively. Three standard reflexions showed no significant change in intensity. The cell dimensions are in good agreement with those of Hodgson *et al.* (1976): $a = 12 \cdot 456 (5)$, $b = 7 \cdot 483 (4)$, $c = 7 \cdot 185 (4) \text{ \AA}$, $\beta = 91 \cdot 24 (2)^\circ$.

The non-hydrogen atoms were refined by full-matrix least squares to an R of $0 \cdot 044$, starting from the atomic coordinates given by Cruickshank & Jones (1963). A difference map revealed the H atom. Its coordinates were very close to Hodgson's. The isotropic thermal parameter of the H atom was fixed to that of the carrier atom. In the final cycles, one scale factor, the atomic coordinates of all the atoms and the anisotropic thermal parameters for the non-hydrogen atoms were varied. The final $R = 0 \cdot 043$ and $R_w = 0 \cdot 061$ with 1113 $I >$

Table 4. *Geometry of the water molecule and the hydrogen bonds*

O(w)—H(1)	0.76 (4) Å	H(1)—O(w)—H(2)	99 (4)°
O(w)—H(2)	0.76 (3)		
		O \cdots O	\angle O—H \cdots O
O(w)—H(2) \cdots O(3)	1/000	3.020 (3) Å	146 (3)°
O(w)—H(1) \cdots O(4)	2/110	2.866 (3)	165 (4)

Table 2. *Molecular dimensions for $K_3N(SO_3)_2 \cdot H_2O$ and bond distances corrected for rigid-body motion*

	Observed	Corrected				
N—S(1)	1.608 (2) Å	1.627 Å	S(1)—N—S(2)	120.83 (11)°	O(1)—S(1)—O(2)	110.50 (10)°
N—S(2)	1.604 (2)	1.616			O(1)—S(1)—O(3)	111.01 (10)
\langle N—S \rangle	1.606	1.621	N—S(1)—O(1)	109.93 (10)	O(2)—S(1)—O(3)	110.16 (10)
S(1)—O(1)	1.464 (2)	1.481	N—S(1)—O(2)	104.78 (9)	O(4)—S(2)—O(5)	109.30 (9)
S(1)—O(2)	1.460 (2)	1.477	N—S(1)—O(3)	110.27 (10)	O(4)—S(2)—O(6)	109.72 (9)
S(1)—O(3)	1.469 (2)	1.486	N—S(2)—O(4)	111.50 (9)	O(5)—S(2)—O(6)	110.49 (9)
S(2)—O(4)	1.480 (2)	1.491	N—S(2)—O(5)	111.50 (9)	\langle O—S—O \rangle	110.20
S(2)—O(5)	1.473 (2)	1.484	N—S(2)—O(6)	104.26 (9)		
S(2)—O(6)	1.464 (2)	1.475	\langle N—S—O \rangle	108.70		
\langle S—O \rangle	1.468	1.482				

Table 3. *Interionic distances (Å) about K^+ for $K_3N(SO_3)_2 \cdot H_2O$*

Coding of equivalent positions: (1) x, y, z ; (2) $\bar{x}, \bar{y}, \bar{z}$. K^+ cations are in position 1. O(6) 1/0 $\bar{1}$ 0 means that O(6) is in position 1, translated by $0a, 1b, 0c$.

$K^+(1) \cdots O(6)$	1/ $\bar{1}$ $\bar{1}$ 0	2.744 (2)	$K^+(2) \cdots O(2)$	2/221	2.680 (2)	$K^+(3) \cdots O(1)$	2/110	2.679 (2)
O(2)	2/110	2.822 (2)	O(6)	2/211	2.802 (2)	O(2)	1/0 $\bar{1}$ 0	2.829 (2)
O(3)	1/0 $\bar{1}$ 0	2.826 (2)	O(1)	1/00 $\bar{1}$	2.813 (2)	O(5)	2/111	2.837 (2)
O(3)	2/111	2.855 (2)	O(5)	1/000	2.817 (2)	O(4)	2/111	2.857 (2)
O(5)	2/111	2.882 (2)	O(6)	1/000	2.855 (2)	O(w)	2/111	2.892 (2)
N	1/ $\bar{1}$ $\bar{1}$ 0	2.936 (2)	O(4)	2/112	2.864 (2)	O(3)	1/0 $\bar{1}$ 0	2.907 (2)
O(1)	2/110	3.000 (2)	O(4)	1/100	2.882 (2)	O(5)	1/000	2.962 (2)
O(w)	1/0 $\bar{1}$ 0	3.096 (2)	O(w)	2/111	3.089 (2)	O(w)	1/000	3.016 (2)

Table 5. Analysis of molecular thermal motion: translational T (\AA^2), rotational L (rad^2) and their correlation S (\AA rad) tensors

The tensors are referred to a Cartesian system defined by X parallel to \mathbf{a} , Y parallel to $\mathbf{c}^* \wedge \mathbf{a}$, Z parallel to \mathbf{c}^* . The origin is at the center of mass. The trace of S has been set to 0.

(I) $\text{K}_3\text{N}(\text{SO}_3)_2 \cdot \text{H}_2\text{O}$ NS(2) O_3 group

T ($\text{\AA}^2 \times 10^4$)			L ($\text{rad}^2 \times 10^4$)			S ($\text{\AA rad} \times 10^4$)		
140 (4)	-9 (6)	2 (4)	44 (4)	4 (9)	10 (3)	1 (8)	-3 (3)	-10 (2)
	139 (4)	4 (4)		67 (4)	-14 (4)	6 (4)	0 (7)	-4 (3)
		129 (5)			37 (7)	22 (3)	5 (3)	-2 (6)
r.m.s. = 0.0003 \AA^2			e.s.d. = 0.0006 \AA^2					

NS(1) O_3 group

T ($\text{\AA}^2 \times 10^4$)			L ($\text{rad}^2 \times 10^4$)			S ($\text{\AA rad} \times 10^4$)		
145 (8)	-5 (7)	1 (5)	106 (10)	-44 (10)	35 (6)	12 (11)	10 (5)	-16 (3)
	140 (7)	-6 (7)		80 (7)	-30 (9)	-10 (5)	-3 (9)	21 (5)
		125 (8)			51 (10)	-15 (3)	-17 (6)	-9 (10)
r.m.s. = 0.0005 \AA^2			e.s.d. = 0.0010 \AA^2					

(II) $\text{K}_2\text{NH}(\text{SO}_3)_2$ NSO₃ group

T ($\text{\AA}^2 \times 10^4$)			L ($\text{rad}^2 \times 10^4$)			S ($\text{\AA rad} \times 10^4$)		
143 (10)	-5 (6)	19 (7)	108 (10)	-11 (4)	27 (7)	-1 (12)	63 (3)	7 (4)
	169 (10)	0 (6)		44 (15)	-15 (5)	-6 (3)	1 (13)	14 (4)
		125 (10)			76 (13)	-16 (5)	-28 (4)	1 (11)
r.m.s. = 0.0007 \AA^2			e.s.d. = 0.0011 \AA^2					

Table 6. Deviations (\AA) of atoms from the least-squares plane in the $[\text{N}(\text{SO}_3)_2]^{3-}$ anion

The plane equation is of the form $AX + BY + CZ + D = 0$ where X , Y and Z refer to the Cartesian system defined in Table 5. The atoms defining the plane are marked by an asterisk.

$A = 0.3210$	*N(1)	0.0161 (19)	O(1)	1.2213 (19)
$B = -0.2598$	*S(1)	0.0079 (5)	O(3)	-1.1965 (19)
$C = -0.9107$	*S(2)	-0.0079 (5)	O(4)	1.1920 (14)
$D = 1.2235$	*O(2)	-0.0125 (19)	O(5)	-1.2163 (14)
	*O(6)	-0.0031 (14)		

Table 7. $\text{K}_2\text{NH}(\text{SO}_3)_2$: atomic coordinates (for $\text{K}, \text{S} \times 10^5$, for $\text{N}, \text{O} \times 10^4$ for $\text{H} \times 10^3$) with their e.s.d.'s

	x	y	z
K	34740 (5)	64093 (9)	64259 (9)
S	39915 (5)	17775 (8)	63899 (9)
N	5000	735 (4)	7500
O(1)	4437 (2)	2718 (4)	4819 (3)
O(2)	3287 (2)	316 (3)	5864 (3)
O(3)	3524 (2)	2996 (3)	7711 (3)
H	477 (8)	-33 (11)	826 (10)

$3\sigma(I)$. * The atomic coordinates, intraionic lengths and angles, and interionic distances about K^+ are reported in Tables 7, 8 and 9 respectively. The results are in good agreement with Cruickshank's and Hodgson's.

* See previous footnote.

Discussion

This refinement enables us to confirm by X-ray diffraction the result obtained by neutron diffraction. The H atom is found to be statistically distributed on either side of the diad axis. The N-H (0.907 \AA) length and S-N-H (111 $^\circ$) angle agree well with Hodgson's values (1.016 \AA and 111.5 $^\circ$).

The results of the analysis of the thermal vibration carried out in the TLS approximation to rigid-body motion are reported in Table 5. The bond distances were corrected for libration from the results obtained with the $\text{N}(\text{SO}_3)$ moiety which fit the rigid-body model better than the whole anion $\text{N}(\text{SO}_3)_2$. The values of the corrected bond distances are reported in Table 8.

Comparison of the two structures

Observed S-O lengths in many oxyanions in crystalline solids range from 1.40 to 1.80 \AA (Louisnathan, Hill & Gibbs, 1977). The S-O length is, for example, 1.40 \AA in sulfonyl diamide $\text{SO}_2(\text{NH}_2)_2$ (Trueblood & Mayer, 1956) and the S-O (bridge) is 1.645 \AA in the pyrosulfate ion (Lynton & Truter, 1960). The S-N length varies in the same way from 1.60 \AA in $\text{K}(\text{SO}_3\text{NH}_2)$ (Jeffrey & Stadler, 1951) to 1.761 \AA in sulfamic acid (Sass, 1960). Several authors have tried to interpret these bond-length variations. According to Cruickshank (1961), the shortness of the S-O bond in

Table 8. *Intraionic lengths (Å) and angles (°) for $K_2NH(SO_3)_2$*

	Observed	Corrected				
S—N	1.669 (2)	1.683	S—N—S	124.2 (1)	O(1)—S—O(2)	113.8 (1)
S—O(1)	1.451 (2)	1.464	S—N—H(1)	121 (5)	O(1)—S—O(3)	111.8 (1)
S—O(2)	1.446 (3)	1.460	S—N—H(2)	101 (5)	O(2)—S—O(3)	113.4 (1)
S—O(3)	1.448 (2)	1.461	N—S—O(1)	107.6 (1)	⟨O—S—O⟩	113.0
⟨S—O⟩	1.449	1.462	N—S—O(2)	102.6 (1)		
N—H	0.91 (9)		N—S—O(3)	106.9 (1)		
			⟨N—S—O⟩	105.7		

Table 9. *Interionic distances about K^+ for $K_2NH(SO_3)_2$*

Coding of equivalent positions: (1) x, y, z ; (2) $\bar{x}, \bar{y}, \bar{z}$; (3) $x, \bar{y}, \frac{1}{2} + z$; (4) $\frac{1}{2} - x, \frac{1}{2} - y, \bar{z}$; (5) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$.

$K^+ \dots O(3)$	3/011	2.709 (2)	$K^+ \dots O(2)$	1/010	2.960 (3)
O(3)	1/000	2.717 (2)	O(2)	4/001	3.005 (2)
O(1)	3/010	2.773 (2)	O(2)	5/001	3.075 (2)
O(3)	5/001	2.838 (2)	O(1)	1/000	3.236 (2)
O(1)	2/111	2.846 (3)			

SO_4^{2-} , together with the considerable variability of S—O lengths as the intramolecular environment is changed, is taken to be symptomatic of strong $d\pi-p\pi$ interactions. Bartell, Su & Yow (1970) showed that Hückel molecular-orbital calculations omitting π orbitals and neglecting d orbitals gave a good account of structural trends in a series of S compounds with various monovalent ligands. Nevertheless, the addition of a small amount of d character to the wave function increased the bond overlap populations to more plausible magnitudes and improved the correlation between overlap populations and bond lengths. They conclude that there is little to choose between the two approaches.

The values obtained for the S—O and S—N lengths in the two compounds agree well with Cruickshank's $d\pi-p\pi$ valence-bond scheme, particularly for the S—O bond. If we assume a linear bond-length—bond-order relation determined by 1.69 Å for a bond of π order zero (Cruickshank) and 1.49 Å for a bond of π order $\frac{1}{2}$, the theoretical lengths for S—O in (I) and (II) are, respectively, 1.48 and 1.45 Å, values very close to those obtained: 1.468 and 1.448 Å (uncorrected values). For the S—N bond, comparison with other compounds is not so easy, owing to the lack of available data. If we assume that the bond length for the pure single S—N bond is 1.76 Å, the value obtained for

NH_3SO_3 (N has no orbitals available for π bonding) and 1.60 Å for a bond of π order $\frac{1}{4}$, the observed values of 1.669 and 1.606 Å are correctly shorter and longer than the two values.

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References

- BARTELL, L. S., SU, L. S. & YOW, H. (1970). *Inorg. Chem.* **9**, 1903–1912.
- BUSING, W. R. & LEVY, H. A. (1964). *Acta Cryst.* **17**, 142–146.
- CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.
- CRUICKSHANK, D. W. J. (1961). *J. Chem. Soc.* pp. 5486–5503.
- CRUICKSHANK, D. W. J. & JONES, D. W. (1963). *Acta Cryst.* **16**, 877–883.
- GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368–376.
- HODGSON, P. G., MOORE, F. H. & KENNARD, C. H. L. (1976). *J. Chem. Soc. Dalton Trans.* pp. 1443–1445.
- JEFFREY, G. A. & JONES, D. W. (1956). *Acta Cryst.* **9**, 283–289.
- JEFFREY, G. A. & STADLER, H. P. (1951). *J. Chem. Soc.* pp. 1467–1474.
- LOUISNATHAN, S. J., HILL, R. J. & GIBBS, G. V. (1977). *Phys. Chim. Miner.* **1**, 53–69.
- LYNTON, H. & TRUTER, M. R. (1960). *J. Chem. Soc.* pp. 5112–5118.
- SASS, R. L. (1960). *Acta Cryst.* **13**, 320–324.
- SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* **B24**, 63–76.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
- TRUEBLOOD, K. N. & MAYER, S. W. (1956). *Acta Cryst.* **9**, 628–634.