Crystal Structures of Dipotassium N-methylnitrogenbis(trioxosulphate), $K_2[CH_3N(SO_3)_2]$, Potassium N-methylimido(trioxosulphate), $K[CH_3NH(SO_3)]$ and N,N-Dimethylsulphamic Acid, $[H(CH_3)_2N^+(SO_3^-)]$

ALAN J. MORRIS, COLIN H. L. KENNARD*, JOHN R. HALL
Department of Chemistry, Queensland Institute of Technology, Brisbane, Qld. 4067, Australia

and GRAHAM SMITH
Department of Chemistry, University of Queensland, Brisbane, Qld. 4000, Australia

Received January 4, 1982

The crystal structures have been determined by X-ray diffraction from diffractometer data and refined by least squares for $K_2[CH_3N(SO_3)_2]$, *[monoclinic,* $P2_1/c$, $a = 9.819(4)$, $b = 6.053(3)$, $c = 14.749(4)$ Å, $\beta = 113.17(5)^\circ$, $Z = 4$, $R = 0.075$ *using 376 unique reflections]; for* $K[CH_3NH(SO_3)]$, *[monoclinic,* $P2_1/c$, $a = 9.468(4)$, $b = 7.256(2)$, $c = 7.306(5)$ Å; $\beta = 95.01(4)^\circ$, $Z = 4$, $R = 0.039$ *using 439 unique reflections]; and for* $H(CH_3)_2$-$N^+(SO_3^-)$, *[monoclinic,* $P2_1/c$, $a = 7.704(1)$, $b = 6.136(4)$; $c = 11.900(2)$ Å, $\beta = 101.76(2)^\circ$, $Z = 4$, $R = 0.063$ *using 438 unique reflections]. Tetrahedral stereochemistry for nitrogen was observed for* $[H(CH_3)_2N^+(SO_3^-)]$ *[angle CNC, 111.5(7)°; SNC, 112.7(5)°: 112.0(5)°] and* $K[CH_3NH(SO_3)]$ *[SNC, 116.4(3)°]; the nitrogen atom is out of the acid CCS and salt CSH planes by 0.46 and 0.34 Å respectively. A flattened pyramidal geometry was found for nitrogen in* $K_2[CH_3N(SO_3)_2]$ *[angles SNS, 120(1)°; SNC, 117(2)°, 119(2)°]; the N atom is 0.17 Å out of the plane of CSS.*

Introduction

Structural work on sulphonate derivatives of methane, ammonia and hydroxylamine [1–5] has now been extended to include some methyl substituted sulphonate derivates of ammonia. They are $K_2[CH_3N(SO_3)_2]$, (*I*), $K[CH_3NH(SO_3)]$, (*II*) and $H(CH_3)_2N^+(SO_3^-)$, (*III*).

The NS_3 skeleton of the nitrilosulphonate anion, $N(SO_3)_3^{3-}$ is reported to be planar [1]. The nitrogen atom of the imidosulphonate anion, $NH(SO_3)_2^{2-}$, has pyramidal stereochemistry [2], but to a lesser extent than the sulphamate anion, $NH_2SO_3^-$ [6]. The X-ray crystal structures of the title compounds have been determined to investigate further the role of the bulk of the groups bonded to nitrogen in determining its stereochemistry, and the participation of (p → d)π bonding [7, 8] in the N–S linkages.

Experimental

a. Preparation of Compounds

I was prepared by refluxing $K_3[N(SO_3)_2]\cdot H_2O$ in 2*M* potassium hydroxide with an excess of methyl iodide [9] for 6 hours. The solid product was recrystallised from water (pH ~ 10). *Anal.* Found: K, 29.2; C, 4.5; H, 1.1; N, 5.2%. Calcd: K, 29.3; C, 4.5; H, 1.1; N, 5.2%.

II was obtained [9] by standing $K_2[CH_3N(SO_3)_2]$ in 0.5 *M* sulphuric acid for 3 hours. Sulphate and bisulphate byproducts were removed by the addition of barium hydroxide. Excess barium ion was then precipitated as carbonate by bubbling carbon dioxide through the solution. *II* was precipitated from the filtrate with ethanol and was recrystallised from water. *Anal.* Found: K, 26.3; C, 8.1; H, 2.7%. Calcd: K, 26.2; C, 8.1; H, 2.7%.

The rapid hydrolysis of dimethylamidosulphuryl chloride $[(CH_3)_2N(SO_2)Cl]$ in warm water, produced *III* [10] which was then recrystallised from hot ethanol. *Anal.* Found: C, 19.3; H, 5.7; N, 11.2%. Calcd: C, 19.2; H, 5.6; N, 11.2%.

b. Data Collection, Structure Solution, Refinement

Table I summarises the conditions used to collect data with the University of Canterbury's computer controlled Hilger-Watts four-circle diffractometer.

---

*Author to whom correspondence should be addressed.

0020-1693/82/0000-0000/$02.75

TABLE I. Experimental Data.

		$K_2[CH_3N(SO_3)_2]$	$K[CH_3NH(SO_3)]$	$H(CH_3)_2N^+(SO_3^-)$
A. *Crystal Parameters*				
		$CH_3K_2NO_6S_2$	CH_4KNO_3S	$C_2H_7NO_3S$
crystal system		monoclinic	monoclinic	monoclinic
space group		$P2_1/c$	$P2_1/c$	$P2_1/c$
a (A)		9.819(4)	9.468(4)	7.704(1)
b (A)		6.053(3)	7.256(2)	6.136(4)
c (A)		14.749(4)	7.306(5)	11.900(2)
β (°)		113.17(5)	95.01(4)	101.76(2)
V (A^3)		805.9	500.0	550.7
Z		4	4	4
Mol. Wt.		267.4	149.2	125.1
ρ(calcd) (g cm^{-3})		2.20	1.98	1.51
ρ(found) (g cm^{-3})		2.18	1.99	1.49
F(000)		528.0	300.0	264.0
B. *Measurement of Data*				
diffractometer		Hilger-Watts	Hilger-Watts	Higher-Watts
radiation		MoKα	MoKα	MoKα
		(Zr filtered)	(Zr filtered)	(Zr filtered)
reflections measured:				
2θ maximum		52	48	48
scanning mode		$2\theta - \omega$	$2\theta - \omega$	$2\theta - \omega$
reflections collected:				
total		499	552	518
unique		376	439	438
		$[I > 2\sigma(I)]$	$[I > 2.5\sigma(I)]$	$[I > 2\sigma(I)]$
μ(MoKα) (cm^{-1})		16.4	13.4	4.8
corrections applied		none	none	none
crystal size (mm)		0.25 × 0.15 × 0.05	0.30 × 0.20 × 0.10	0.20 × 0.10 × 0.10
R		0.075	0.039	0.063
Rw		0.071	0.036	0.059
background in final difference map (eA^{-3})		0.25	0.08	0.10
weighting scheme				
$A/(\sigma^2F + BF^2)$	A	2.1	2.0	1.5
	B	8×10^{-4}	4×10^{-4}	2×10^{-3}

Data were corrected for Lorentz polarization effects but not for absorption and extinction. *II* and *III* were solved using the automatic centrosymmetric Σ_2 direct methods approach of SHELX [11]. However, this method, the tangent refinement method, MULTAN [12] and the Patterson approach were unsuccessful for *I*. It was considered that the lack of significant E's with l odd in this case meant that the z parameters of the model obtained were unreliable. In order to obtain a satisfactory trial structure, the odd l reflections were given an artificially high scale factor so as to make them effective in the symbolic assignments. This technique did give an interpretable and refinable E map using the SHELX EEES. All structures were refined by full matrix anisotropic least squares, and hydrogen atoms were located from difference-Fourier syntheses. Only the hydrogen atoms of *III* were refined, with all other isotropic U's set invariant at 0.05 $Å^2$. Neutral atom scattering factors were used for both non-hydrogen [13] and hydrogen [14] atoms. Atomic positions are listed in Table II, while bond distances and angles are given in Table III. Molecular configurations and atom naming schemes for *I, II, III* are shown in Fig. 1.

TABLE II. Atomic Parameters: non-Hydrogen Atoms ($\times 10^4$), Hydrogen ($\times 10^3$), with Estimated Standard Deviations in Parentheses.

Atom	$K_2[CH_3N(SO_3)_2]$			$K[CH_3NH(SO_3)]$			$H(CH_3)_2N^+(SO_3^-)$		
	x/a	y/b	z/c	x/a	y/b	z/c	x/a	y/b	z/c
K(1)	–427(6)	7275(20)	1569(5)	3776(2)	3778(2)	–1508(2)	–	–	–
K(2)	–2712(6)	7602(18)	3365(4)	–	–	–	–	–	–
N	3108(28)	7843(62)	4524(18)	1660(5)	7292(7)	2859(6)	2709(10)	12257(9)	1487(4)
H(N)	–	–	–	184	798	168	364(10)	1276(20)	206(5)
S(1)	1573(8)	7209(24)	4741(5)	3006(2)	5957(2)	3503(2)	3038(4)	9428(3)	1832(2)
O(11)	1752(23)	4928(37)	5027(17)	4159(4)	7240(6)	3908(6)	2767(7)	9354(9)	2983(4)
O(12)	1549(25)	8559(41)	5526(17)	3280(5)	4693(6)	2034(5)	4845(10)	9111(9)	1706(4)
O(13)	375(18)	7665(45)	3834(12)	2578(5)	4961(6)	5092(6)	1717(8)	8413(9)	991(5)
S(2)	3084(8)	7525(21)	3307(6)	–	–	–	–	–	–
O(21)	2339(30)	5433(33)	2953(18)	–	–	–	–	–	–
O(22)	2181(28)	9415(41)	2790(19)	–	–	–	–	–	–
O(23)	4573(21)	7774(61)	3426(7)	–	–	–	–	–	–
C(1)	4413(40)	7871(70)	5301(26)	297(8)	6369(9)	2379(10)	3051(16)	12805(16)	320(7)
H(11)	440	759	602	36	712	162	435(10)	1211(12)	25(5)
H(12)	526	632	567	8	571	324	296(10)	1432(12)	20(5)
H(13)	345	675	512	51	539	160	247(10)	1189(13)	20(5)
C(2)	–	–	–	–	–	–	913(15)	13042(14)	1625(8)
H(21)	–	–	–	–	–	–	101(9)	1482(12)	157(5)
H(22)	–	–	–	–	–	–	11(9)	1201(13)	115(6)
H(23)	–	–	–	–	–	–	88(8)	1294(12)	248(5)

TABLE III. Molecular Geometry with Estimated Standard Deviations in Parentheses.

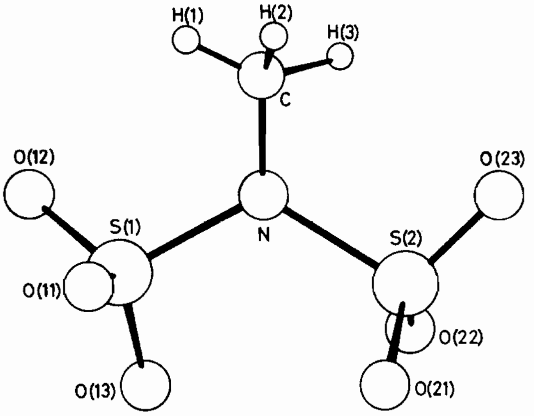
Bond Distances (Å)			
	$K_2[CH_3N(SO_3)_2]$	$K[CH_3NH(SO_3)]$	$H(CH_3)_2N^+(SO_3^-)$
N–S(1)	1.70(3)	1.637(4)	1.790(6)
N–S(2)	1.80(3)	–	–
N–C(1)	1.34(3)	1.469(6)	1.503(9)
N–C(2)	–	–	1.506(10)
N–H	–	1.02	0.94(7)
S(1)–O(11)	1.43(2)	1.446(3)	1.428(5)
S(1)–O(12)	1.42(2)	1.452(3)	1.443(5)
S(1)–O(13)	1.42(2)	1.455(3)	1.418(5)
S(2)–O(21)	1.45(2)	–	–
S(2)–O(22)	1.46(3)	–	–
S(2)–O(23)	1.41(2)	–	–
Bond Angles (°)			
C(1)–N–C(2)	–	–	111.5(7)
S(1)–N–S(2)	120(1)	–	–
S(1)–N–C(1)	117(2)	116.4(3)	112.7(5)
S(1)–N–C(2)	119(2)	–	112.0(5)
S–N–H	–	110.6(3)	96(4)
N–S(1)–O(11)	105(1)	103.5(2)	102.1(3)
N–S(1)–O(12)	109(2)	110.3(2)	101.6(3)
N–S(1)–O(13)	104(1)	105.0(2)	102.5(3)
N–S(2)–O(21)	105(1)	–	–
N–S(2)–O(22)	102(2)	–	–
N–S(2)–O(23)	105(1)	–	–
O(11)–S(1)–O(12)	111(2)	112.2(2)	115.3(4)
O(11)–S(1)–O(13)	115(1)	114.5(2)	116.0(4)

(continued overleaf)

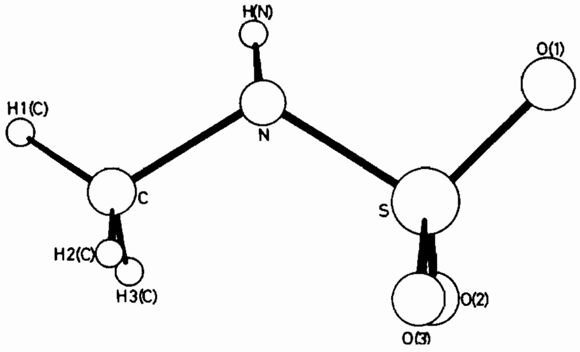
TABLE III. *(continued)*

O(12)–S(1)–O(13)	112(1)	110.9(2)	115.9(4)
O(21)–S(2)–O(22)	112(1)	–	–
O(21)–S(2)–O(23)	119(2)	–	–
O(22)–S(2)–O(23)	112(2)	–	–

I, $K_2[CH_3N(SO_3)_2]$



II, $K[CH_3NH(SO_3)]$



III, $[H(CH_3)_2N^+(SO_3^-)]$

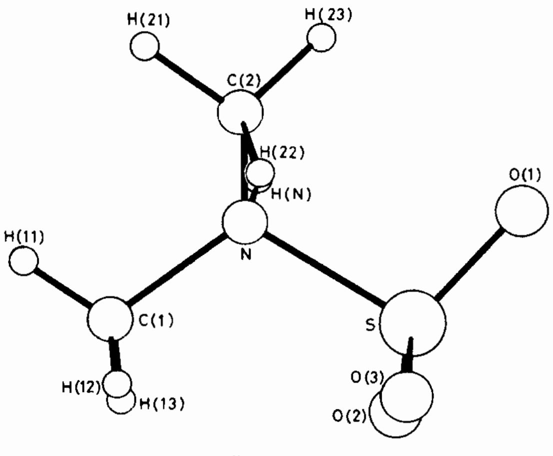


Fig. 1. Molecular configurations and naming schemes for compounds *I*, *II* and *III*.

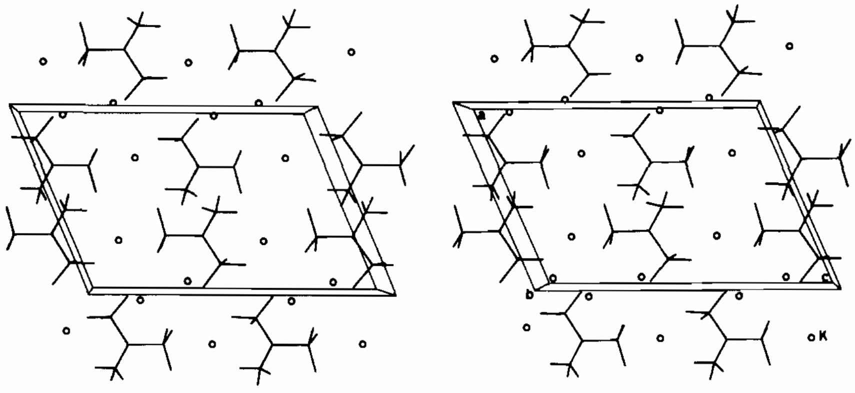
Discussion

The CNS_2 skeleton in dipotassium N-methylnitrogen bis(trioxosulphate), $K_2[CH_3N(SO_3)_2]$ (Fig. 1, *I*), approaches a planar configuration which pertains to the NS_3 skeleton of potassium nitrilotrisulphonate dihydrate, $K_3[N(SO_3)_3]\cdot 2H_2O$. The distance of the N atom above the CSS plane is 0.17 Å and the sum of the angles about N is 356°. Although $(p \rightarrow d)\pi$ bonding is available for two N–S bonds it would seem that such bonding is minimal as these distances (1.70, 1.80 Å) are large in comparison with those for $[NH(SO_3)_2^{2-}]$ [2] (1.67 Å), for which the sum of the bond angles about N is 348°, and are within the range expected for N–S single bonds [15]. Group bulk therefore appears to cause the nitrogen atom to assume a distorted trigonal planar coordination. As the standard deviations for the atomic parameters for this compound are high, it is difficult to make any definite conclusions about significance of the difference in the interatomic N–S distances [1.70(3). 1.80(3) Å]. The major feature of the packing is that the anions are in layers at $y = \frac{1}{4}, \frac{3}{4}$ (Fig. 2, *I*). The potassium cations also lie in the planes at ¼, ¾ and are surrounded by eight oxygen atoms from neighbouring molecules with K–O distances ranging from 2.72 to 3.13 Å (Table IV).

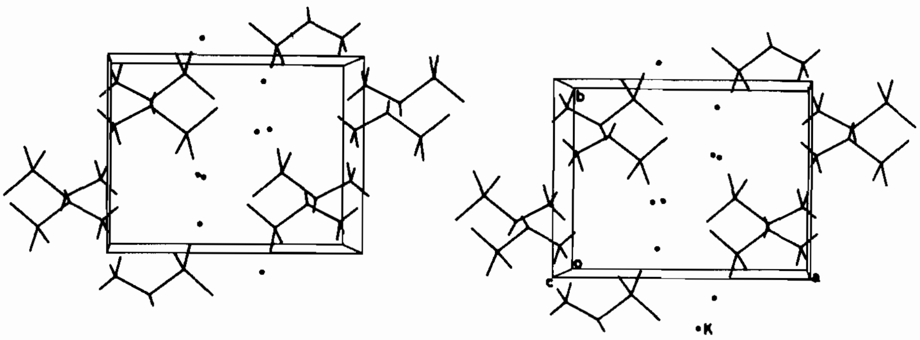
The structure of potassium N-methylimido(trioxosulphate), $K[CH_3NH(SO_3)]$ (Fig. 1, *II*), is analogous to that of potassium sulphamate $KNH_2 \cdot SO_3$ [6]. The anion assumes a tetrahedral sp^3 configuration about nitrogen with the N, 0.34 Å above the CHS plane. The sum of the angles about N is 330°. An N–S bond distance of 1.637 Å indicates the possibility of π-bonding. The $[CH_3NH(SO_3)]^-$ anions pack in layers and are arranged in a head-to-head, tail-to-tail configuration, with the potassium cations between the sulphonate oxygens (Fig. 2, *II*). One potassium is surrounded by eight oxygen atoms and the second by six, in irregular arrangements with K–O distances ranging from 2.75 to 3.20 Å (Table IV).

N,N-Dimethylsulphamic acid, $H(CH_3)_2N^+(SO_3^-)$ (Fig. 1, *III*), is analogous to sulphamic acid, $[H_3N^+(SO_3^-)]$ [16]. Both molecules exist as zwitterions with tetrahedral configuration about the nitrogen atom and comparable bond distances and angles. The N–S bond length in *III*, 1.790(6) Å is significantly longer than the calculated N–S single bond distance 1.74 Å [15] but comparable with the

I, $K_2[CH_3N(SO_3)_2]$ (perpendicular to *ac*)



II, $K[CH_3NH(SO_3)]$ (perpendicular to *ab*)



III, $H(CH_3)_2N^+(SO_3^-)$ (perpendicular to *ac*)

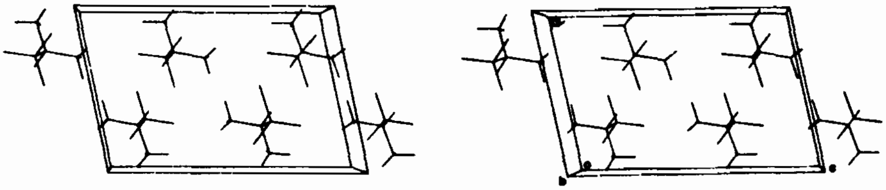


Fig. 2. Stereoscopic views of the packing in the unit cells for *I*, *II* and *III*.

TABLE IV. Intermolecular Distances (Å) Less than 3.2 Å.

$K_2[CH_3N(SO_3)_2]$, *I*-					
K(1)–O(11^{III})	2.72	K(1)–O(21^{III})	2.95	K(2)–O(12^{VI})	2.81
K(1)–O(12^{II})	2.96	K(1)–O(22^{I})	2.80	K(2)–O(13^{I})	2.83
K(1)–O(13^{I})	3.12	K(1)–O(22^{IV})	2.85	K(2)–O(21^{III})	2.72
K(1)–O(13^{IV})	2.86			K(2)–O(22^{IV})	2.76
K(1)–O(21^{I})	2.90	K(2)–O(11^{V})	2.66	K(2)–O(23^{VII})	2.70

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

I x, y, z V −x, 1 − y, 1 − z
II x, 3/2 − y, −½ + z VI −x, 2 − y, 1 − z

(continued overleaf)

TABLE IV. *(continued)*

III $-x, ½+y, ½-z$ VII $-1+x, y, z$
IV $-x, -½+y, ½-z$

$K[CH_3NH(SO_3)]$, *II*

$K-O(1^{III})$	2.92	$K-O(2^{I})$	2.75	$K-O(3^{II})$	2.78
$K-O(1^{V})$	2.84	$K-O(2^{IV})$	2.76	$K-O(3^{IV})$	3.20
$K-O(1^{VI})$	2.83	$K-O(2^{V})$	3.05		

I x, y, z IV $x, 3/2-y, -3/2+z$
II $x, y, -1+z$ V $1-x, 1-y, -z$
III $x, 3/2-y, -3/2+z$ VI $1-x, -3/2+y, 3/2-z$

TABLE V. Comparison of Mean Interatomic Distances (Å) and Angles (degrees).

	N–S	N–C	N–H	S–O	S–N–S	S–N–C	S–N–H	N–S–O	O–S–O	Reference
$K_2[CH_3N(SO_3)_2]$	1.75(3)[a]	1.34(3)	–	1.43(2)	120(1)	118(2)	–	105(2)	114(2)	this work
$K[CH_3NH(SO_3)]$	1.637(4)	1.469(6)	1.02	1.451(3)	–	116.4(3)	–	106.2(2)	112.6(2)	this work
$K_3[N(SO_3)_3]\cdot 2H_2O$	1.71(2)	–	–	1.44(2)	120(1)	–	–	104.4(10)	114(1)	1
$K_2[NH(SO_3)_2]$	1.674(5)	–	1.016(1)[b]	1.442(6)	124.4(3)	–	111.6(3)[b]	105.6(4)	113.1(4)	2
$K[NH_2(SO_3)]$	1.666(6)	–	1.007(6)[b]	1.456(4)	–	–	110.2(4)[b]	106.2(4)	113.6(5)	6
$K_3[N(SO_3)_2]\cdot H_2O$	1.604(3)	–	–	1.467(3)	121.0(1)	–	–	108.7(1)	110.2(1)	3
$K_2[O_3SONH(SO_3)]$	1.704(3)	–	0.82(4)	1.441(3)	–	–	103(3)	104.8(2)	113.7(2)[c]	4
$H(CH_3)_2N^+(SO_3^-)$	1.790(6)	1.504(10)	0.94(7)	1.430(5)	–	112.3(5)	96(4)	102.1(3)	115.8(4)	this work
$NH_3(SO_3)$	1.76(2)	–	1.02(2)	1.44(2)	–	–	111.3	–	115.1	16

[a] Standard deviation is the mean of standard deviations for the combined results. [b] Neutron. [c] Only SO_3 and not O_3SO considered.

corresponding bond length in sulphamic acid (Table V). The dimethylsulphamic acid molecules are hydrogen bonded [N···O, 2.80; H···O, 1.87 Å; N–H···O, 169°] between the imido hydrogen and a sulphonate oxygen O(2) of a neighbouring molecule (*x*, *y*, *z*; –*x*, ½ + *y*, ½ – *z*), creating infinite polymeric chains along the *b* axis. The unit cell contains four polymeric chains with spaces greater than 3 Å between the two different two-chain strands (Fig. 2, *III*).

A comparison of mean interatomic distances for the nitrogen sulphonate series is found in Table V.

Acknowledgements

The authors wish to thank the Australian Research Grants Committee for financial support, Professor B. Penfold and Dr. W. T. Robinson of the University of Canterbury for the use of the Hilger-Watts diffractometer, Professor L. F. Dahl of the University of Wisconsin for his useful comments, and Dr. K. E. Brown of D. S. I. R., Lower Hutt, New Zealand for assistance with some of the calculations. One of us (G. S.) wishes to thank the Queensland Institute of Technology for leave to work on this project.

References

1 J. V. Tillack and C. H. L. Kennard, *J. Chem. Soc., (A)*, 1637 (1970).
2 P. G. Hodgson, F. H. Moore and C. H. L. Kennard, *J. Chem. Soc. Dalton Trans.*, 1443 (1976).
3 J. R. Hall, R. A. Johnson, C. H. L. Kennard, G. Smith, B. W. Skelton and A. H. White, *J. Chem. Soc. Dalton Trans.*, 1091 (1980).
4 J. R. Hall, R. A. Johnson, C. H. L. Kennard, G. Smith, B. W. Skelton and A. H. White, *J. Chem. Soc. Dalton Trans.*, 2199 (1980).
5 J. R. Hall, R. A. Johnson, C. H. L. Kennard and G. Smith, *J. Chem. Soc. Dalton Trans.*, 149 (1980).
6 G. W. Cox, T. M. Sabine, V. M. Padmanabhan, N. T. Ban, M. K. Chung and A. J. Surjadi, *Acta Crystallogr., 23*, 578 (1967).
7 G. A. Jeffrey and D. W. Jones, *Acta Crystallogr., 9*, 283 (1956).
8 D. W. J. Cruickshank, *J. Chem. Soc.*, 5486 (1961).
9 W. Traube and M. Wolff, *Chem. Ber., 13*, 1493 (1920).
10 R. Behrend, *Liebigs J., 222*, 116 (1884).
11 G. M. Sheldrick, *SHELX 76. Program for Crystal Structure Determination*, University of Cambridge, England (1976).
12 G. Germain, P. Main and M. M. Woolfson, *Acta Crystallogr. A, 27*, 368 (1971).
13 D. T. Cromer and J. B. Mann, *Acta Crystallogr. A, 24*, 321 (1968).
14 R. F. Stewart, E. R. Davidson and W. J. Simpson, *J. Chem. Phys., 42*, 3175 (1965).
15 V. Schomaker and D. P. Stevenson, *J. Am. Chem. Soc., 63*, 37 (1941).
16 R. L. Sass, *Acta Crystallogr., 13*, 320 (1960).