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Refinements of Structures Containing Bonds between Si, P, S or Cl and O or N. IX. $(NO_2^+)_2 . S_3O_{10}^{2-}$

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The crystallographic data given by Eriks & MacGillavry (1954) have been used in a structure refinement. The dimensions of the $S_3O_{10}^{2-}$ ion are similar to those of the $P_3O_{10}^{5-}$ ion in $Na_5P_3O_{10}$, phase II. The nitronium ions appear to be slightly bent.

The crystal structure of $(NO_2^+)_2.S_2O_{10}^{2-}$ was determined by Eriks & MacGillavry (1954) from the *hk*0, *h*0*l* and *h*1*l* reflexions. Although the intensity statistics indicated a centre of symmetry, no normal structure in the space group *C*2/*c* could be found. The actual structure with symmetry *Cc* showed a strong pseudosymmetry which introduced a false centre in the *b*-axis projection. The general features of the structure with discrete nitronium and S_3O_{10} ions were clearly established by Eriks & MacGillavry, but they did not aim at a precision determination. The coordinates given by them are nearer the pseudosymmetry than is necessary, for most of the pairs of atoms in the left and right hand halves of the structure are given coordinates of the types (x,y,z) and $(-x,y,z')$. The two halves may both have general coordinates. The present calculations with Eriks & MacGillavry's data represent some refinement of the structure (one atom, O(5), has shifted 0·6 Å) and confirm its general features. An accurate determination would require extensive three-dimensional data to overcome the effects of the pseudosymmetry.

Table 1. *Atomic coordinates* (Å)

Atom	*x*	*y*	*z*
S(1)	−0·01	1·95	1·88
S(2)	2·85	2·32	2·94
O(1)	1·23	2·93	2·42
O(2)	3·50	3·50	2·95
O(3)	2·97	1·58	4·09
O(4)	2·94	1·55	1·89
O(5)	0·06	1·89	0·57
O(6)	1·80	−1·37	2·62
O(7)	4·06	−1·05	3·05
N	2·90	−1·12	2·93
S(2′)	−2·85	2·32	1·73
O(1′)	−1·18	2·86	1·92
O(2′)	−3·52	3·62	1·44
O(3′)	−2·98	1·45	2·98
O(4′)	−2·87	1·49	0·52
O(5′)	−0·03	0·79	2·69
O(6′)	−1·83	−1·33	1·80
O(7′)	−4·03	−0·93	1·48
N′	−2·91	−1·19	1·76

The space group is *Cc*, with cell dimensions $a=19·54$, $b=7·30$, $c=7·56$ Å and $\beta=102°$. The data used in the refinement were the 226 non-zero $|F_o|$ given by Eriks (1952). Seven cycles of least-squares refinements were carried out. Most of the coordinate shifts were less than 0·1 Å, except for O(5), whose *y* coordinate changed by 0·61 Å. This shift is considered to be genuine because after an initial substantial increase of the mean-square vibration amplitude *U* to 0·11 Å^2 at the original position, it fell to the reasonable value of 0·05 Å^2 at the new position. The final value of the residual *R* was 14·3%. The revised atomic coordinates are given in Table 1. The approximate e.s.d.'s in the *x*, *y* and *z* directions are; sulphur, 0·02, 0·03, 0·02 Å; oxygen, 0·04, 0·08, 0·05 Å; nitrogen, 0·06, 0·10, 0·07 Å. Individual isotropic vibrations were allowed; nearly all of these were around $U=0·03$ Å^2, except for O(5), O(5′) and some of the atoms of the nitronium ions, which had $U=0·05$ Å^2. If the $|F_o|$ listed by Eriks are for $\frac{1}{8}$th of the cell contents, the $|F_o|$ scale factor determined by the least-squares process was $1·28 \pm 0·02$. The weighting scheme used was

$$w = 1(24+|F_o|+|F_o|^2/154)\ ,$$

with the $|F_o|$ appropriate to the whole cell, but without the factor 1·28.

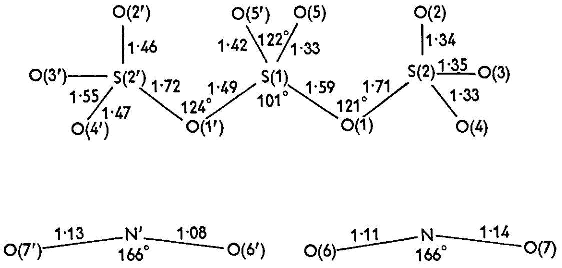

Fig. 1. Dimensions of the ions.

The revised molecular dimensions are shown in Fig. 1. The coordinate e.s.d.'s derived directly from the least-squares matrix, but without any allowance for interatomic interactions, indicate e.s.d.'s in the

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S–O bonds of about 0·05 Å. Owing to the pseudosymmetry of the structure this is likely to be an underestimate, an impression which is confirmed by the fact that the three equivalent S–O bonds of the S(2) tetrahedron are all much shorter than those of the S(2′) tetrahedron. Accurate dimensions can probably be obtained only with full three-dimensional data, which would minimize the effects of the pseudosymmetry. The best course for the present is to average the chemically equivalent bonds and angles; these averages are shown in Fig. 2. The precise details are probably not very reliable, but the general features of the $S_3O_{10}^{2-}$ ion are similar to those of the isoelectronic $P_3O_{10}^{5-}$ ion (Davies & Corbridge, 1958; Cruickshank, 1964). The angles all correspond within 6° and the four distinct bond lengths show the same sequence, though the evidence from the much more accurate $P_3O_{10}^{5-}$ suggests that the difference between the lengths of S(1)–O(1) and S(2)–O(1) should be appreciably less. The angles between the planes S(2)–O(1)–S(1) and S(2′)–O(1′)–S(1) and the plane O(1)–S(1)–O(1′) are about 13° and 10° respectively, so that the five atoms S(2), O(1), S(1), O(1′) and S(2′) are roughly coplanar (indeed this is a plane of a pseudosymmetry for the whole ion) and the $p\pi$ orbitals on O(1) and O(1′) belong to essentially the same π-orbital system (Cruickshank, 1961).

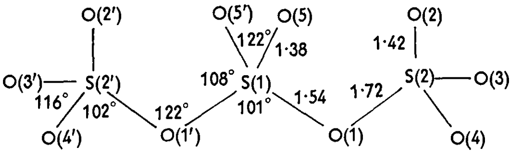

Fig. 2. Averaged dimensions of the $S_4O_{10}^{2-}$ ion.

The four N–O bonds in the nitronium ions average 1·12 Å, which is sufficiently close to the expected 1·14 Å (Truter, Cruickshank & Jeffrey, 1960). Both O–N–O angles are 166°; despite the rather large probable errors this is probably significantly different from 180° and agrees with Gerding & Eriks's (1952) interpretation of the Raman spectra in terms of slightly bent NO_2^+ ions.

One unsatisfactory feature of the interionic contacts obtained by Eriks & MacGillavry was the short 2·34 Å distance for the O(3)–N and O(3′)–N′ approaches. With the revised coordinates the minimum contact distance is 2·54 Å between O(4′) and N′. Further the original structure had a contact of 2·70 Å between an O(5) and an O(5′) of neighbouring $S_3O_{10}^{2-}$ ions; this has satisfactorily lengthened to 3·14 Å with the revised coordinates.

The main interionic contacts are between nitronium ions and oxygen atoms of the terminal sulphate groups. N is approached by five oxygen atoms from four $S_3O_{10}^{2-}$ ions: O(3) (2·93 Å) and O(4) (2·87 Å) of the same molecule, another O(4) (2·76 Å), an O(3) (2·68 Å) and an O(2) (2·75 Å). N′ is similarly approached by five oxygen atoms: O(3′) (2·92 Å) and O(4′) (2·96 Å), another O(4′) (2·54 Å) an O(3′) (2·56 Å) and an O(2′) (2·57 Å). These sulphate oxygen atoms also approach one or both of the nitronium oxygen atoms at distances down to 2·62 Å. There are also several contacts of about 3 Å between a terminal sulphate oxygen atom and the terminal oxygen atom only of a nitronium ion. As mentioned, O(5) and O(5′) of neighbouring ions approach to within 3·14 Å. In addition O(5) lies between the ends O(6) (2·75 Å) and O(6′) (2·89 Å) of two nitronium ions, and O(5′) between O(6) (2·84 Å) and O(6′) (2·80 Å) of other ions.

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Refinements of Structures Containing Bonds between Si, P, S or Cl and O or N. X. β–Ca_2SiO_4

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The crystallographic data given by Midgley (1952) have been used in a structure refinement. The revised bond length in the orthosilicate ion is $Si-O = 1{\cdot}62 \pm 0{\cdot}02$ Å.

The crystal structure of β dicalcium silicate, Ca_2SiO_4, was determined by Midgley (1952) from the three principal Fourier syntheses. Owing to overlapping, the orthosilicate tetrahedron was assumed to be nearly regular. Because of this and of the paucity of values for the Si–O bond lengths in orthosilicates, it

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