

## The Crystal Structure of Ammonium Pyrosulphite

BY S. BAGGIO\*

Universidad Central de Venezuela, Escuela de Química, Caracas, Venezuela

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The crystal structure of ammonium pyrosulphite has been determined by three-dimensional X-ray analysis. The crystals are orthorhombic and belong to the space group  $Pnma$ . The unit cell has dimensions  $a=7.133$ ,  $b=6.085$ ,  $c=15.062$  Å, and contains four molecules. The structure has been solved using Patterson and Fourier syntheses and refined by full-matrix least-squares methods on 744 independent reflexions. Hydrogen atoms have been located in a difference electron density map, and included in the least-squares refinement with fixed positional parameters. The final  $R$  value was 8.9%. The pyrosulphite ion has  $C_s$  (mirror) symmetry; the most important distances in the anion are: S–S=2.170, S–O (thionite group)=1.495 and S–O (thionate group)=1.454 Å.

### Introduction

The structure of the pyrosulphite ion in  $K_2S_2O_5$  was determined some years ago by Zachariassen (1932) and confirmed by Lindqvist & Mörtzell (1957), who also gave a detailed discussion of  $\sigma$ -bonding in this structure. Although Zachariassen, Lindqvist & Mörtzell detected the presence of a S–S bond in the anion, Rocchiccioli (1960) postulated a structure having S–O–S bonds from an analysis of the infrared and Raman spectra of pyrosulphite salts. More recently Herlinger & Long (1969) redetermined the infrared and Raman spectra of pyrosulphite solutions and concluded that the S–S bond is also present in solution and that the anion has  $C_s$  symmetry. The study of the crystal structure of potassium pyrosulphite showed differences between the S–O bond lengths of the thionite and thionate groups, but these differences were not significant because of the high dispersion of results.

The crystal structure determination of ammonium pyrosulphite was undertaken in order to provide more accurate data on the dimensions of the pyrosulphite ion, which are relevant to the discussion of  $\pi$ -bonding in compounds of second row elements (Cruickshank, 1961; Gillespie & Robinson, 1963).

### Experimental

Well-developed crystals of  $(NH_4)_2S_2O_5$  were prepared following the method given by Divers & Owaga (1900). The crystals were unstable when exposed to humidity and air, so all manipulations were carried out in a nitrogen atmosphere. They are trigonal prisms with the longest dimension along the  $b$  axis.

Preliminary photographs taken with  $Cu K\alpha$  radiation showed orthorhombic symmetry, with systematic

absences of  $hk0$  reflexions for  $h=2n$  and  $0kl$  reflexions for  $k+l=2n$ . These extinctions indicated the space groups  $Pnma$  or  $Pn2_1a$  and the solution of the structure confirmed  $Pnma$ .

The cell data are  $a=7.133 \pm 0.008$ ,  $b=6.085 \pm 0.016$ ,  $c=15.062 \pm 0.009$  Å,  $V=653.9$  Å<sup>3</sup>,  $D_m=1.80$  and  $D_c(Z=4)=1.83$  g.cm<sup>-3</sup>. The density was measured by flotation. The unit-cell dimensions were determined by the least-squares procedure proposed by Alcock & Sheldrick (1967) using the  $K\alpha_1-K\alpha_2$  splitting of 37 independent high-angle reflexions recorded on levels  $h2l$  to  $h5l$  by the equi-inclination Weissenberg method with  $Cu K\alpha$  radiation ( $\lambda K\alpha_1=1.54051$  Å).

As the crystals deteriorate fairly rapidly in the X-ray beam, even when enclosed in a quartz capillary, the intensities were collected with two crystals of approximately the same dimensions ( $0.4 \times 0.4 \times 0.8$  mm). They were mounted with the  $b$  axis parallel to the spindle axis. Levels  $h0l$  to  $h4l$  were recorded from crystal I by means of a Weissenberg camera, whereas levels  $h5l$  to  $h7l$  and  $0kl$  to  $2kl$  of crystal II were recorded with a Weissenberg and precession camera respectively. The Weissenberg photographs were taken using the equi-inclination technique. The number of recorded reflexions was 860, of which 744 were independent. The intensity data were obtained with zirconium-filtered molybdenum radiation, and measurements were made with a Nonius microdensitometer on mechanically integrated spots.

Corrections were applied for Lorentz and polarization factors and data from different photographs were cross-correlated and placed on the same scale using the method of Hamilton, Rollett & Sparks (1965). The discrepancy index for equivalent reflexions measured on different layers was  $R(F_o)=6.2\%$ . Absorption corrections were neglected ( $\mu_{Mo}=7.0$  cm<sup>-1</sup>).

### Solution and refinement of the structure

The structure was readily solved by analysis of a three-dimensional Patterson synthesis. The two independent

\* Present address: Universidad de Buenos Aires, Fac. de Farmacia y Bioquímica, Junin 956, Buenos Aires, Argentina.

sulphur atoms were located and a Fourier synthesis phased on the two heavy atoms revealed the positions of all the non-hydrogen atoms.

The final parameters for the non-hydrogen atoms were obtained by full-matrix least-squares refinement of the observed reflexions, the function minimized being  $\sum \omega(F_o - F_c)^2$ . With isotropic temperature factors and one scale factor for each layer line, convergence was achieved after four cycles with discrepancy indices  $R(\sum |F_o| - |F_c| / \sum |F_o|) = 0.111$  and  $R'(\sum \omega \Delta^2 / \sum \omega F_o^2) = 0.148$ . Refinement was continued allowing for anisotropic thermal motion and using just one scale factor. After three cycles refinement was ended because parameter shifts were one fifth of the estimated standard deviation. At this point it was observed that the  $F_o$  values of the strongest reflexions were

systematically lower than their corresponding  $F_c$  values. Refinement was therefore continued with the application of a secondary extinction correction as given by Zachariassen (1963), the 'C' parameter being refined together with the positional parameters. After two cycles the residuals were  $R=0.095$  and  $R'=0.120$ . The weighting scheme used in the last stages of refinement was:  $\sigma = [1.0 - 0.1(F_o - 15)]^{1/2}$  if  $F_o > 15$ ,  $\sigma = 1$  if  $15 > F_o > 6$ ,  $\sigma = [1.0 - 0.1(F_o - 6)]^{1/2}$  if  $6 > F_o$ , which gave a fairly constant value of  $\omega \Delta^2$  over ranges of  $F_o$  and  $\sin \theta$ .

With the final set of calculated structure factors a three-dimensional difference electron density map was computed in order to locate the hydrogen atoms. Since the nitrogen atoms lie on a mirror plane, two of the hydrogen atoms from each ammonium ion must also

Table 1. Observed and calculated structure factors

Values listed are  $I$ ,  $10F_o$ , and  $10F_c$ . Intensities that could not be distinguished from the background are indicated by three asterisks in the  $F_o$  column.

Table with 20 columns of data representing observed and calculated structure factors. The columns are labeled with Miller indices (hkl) and contain values for intensity (I), observed structure factor (10Fo), and calculated structure factor (10Fc). The table is organized into groups based on the Miller indices, with some values marked with asterisks to indicate background noise.

lie on the plane. The four highest peaks ( $0.4-0.6 \text{ e.}\text{\AA}^3$ ) could be assigned to these four hydrogen atoms. The hydrogen atoms lying out of the plane were less well defined, the corresponding peaks being somewhat smeared out and only slightly higher than the e.s.d. for the electron density, which was close to  $0.25 \text{ e.}\text{\AA}^{-3}$ . For this reason it was preferred to calculate the theoretical positions for the out-of-plane hydrogen atoms assuming tetrahedral bonding around the nitrogen atoms and normal N-H distances. When the hydrogen atoms were included in the structure factors calculation

and their isotropic temperature factor refined with the parameters of the heavy atoms, the residuals  $R$  and  $R'$  were reduced to 0.089 and 0.111 respectively after two cycles. No attempt was made to refine the positional parameters of the hydrogen atoms because the data were not of sufficient quality to warrant this.

The form factors for S, N, O and H used throughout the refinement were from *International Tables for X-ray Crystallography* (1962); the O atoms of the pyrosulphite ion were given a fractional charge of  $-\frac{2}{3}$  each, and their form factor obtained by interpolation.

Table 2. *Final parameters*

## (a) Fractional coordinates and isotropic temperature factors

For parameters refined in the least-squares procedure standard deviations are given in parentheses.

	$x/a$	$y/b$	$z/c$	$B$
S(1)	0.1685 (3)	0.7500	0.4061 (1)	$2.0^* \text{ \AA}^2$
S(2)	0.3924 (3)	0.7500	0.3085 (1)	$2.2^*$
O(1)	0.4926 (10)	0.5465 (12)	0.3380 (4)	$5.5^*$
O(2)	0.0600 (10)	0.5509 (13)	0.3913 (4)	$5.4^*$
O(3)	0.2632 (12)	0.7500	0.4918 (4)	$3.2^*$
N(1)	0.3058 (11)	0.2500	0.4999 (5)	$2.2^*$
N(2)	0.2989 (11)	0.2500	0.1875 (6)	$2.1^*$
H(1)	0.18	0.25	0.49	4 (4)
H(2)	0.37	0.25	0.46	2 (2)
H(3)	0.33	0.37	0.53	11 (6)
H(4)	0.36	0.25	0.14	6 (4)
H(5)	0.20	0.25	0.17	7 (6)
H(6)	0.32	0.37	0.21	9 (6)

$$* B_{\text{eq}} = \frac{4}{3} \sum_i \sum_j \beta_{ij} (\bar{a}_i \cdot \bar{a}_j).$$

(b) Thermal parameters ( $\times 10^4$ ) corresponding to the anisotropic temperature factor expression  $\exp[-(\sum_i \sum_j \beta_{ij} h_i h_j)]$ 

	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
S(1)	64 (4)	198 (6)	20 (1)	0	0 (2)	0
S(2)	101 (6)	201 (6)	17 (1)	0	-1 (2)	0
O(1)	302 (27)	383 (45)	51 (5)	-28 (33)	-21 (12)	5 (14)
O(2)	216 (21)	448 (45)	56 (5)	-48 (28)	3 (12)	-17 (15)
O(3)	216 (23)	327 (27)	14 (3)	0	-2 (9)	0
N(1)	93 (21)	163 (20)	24 (4)	0	0 (10)	0
N(2)	89 (20)	150 (21)	26 (4)	0	10 (10)	0

(c) Mean-square amplitudes of vibration ( $\times 10^4$ ) along the principal axes of the vibration tensor, and angles of these axes with respect to the crystal axes

	$U_1$	Angle	$U_2$	Angle	$U_3$	Angle
S(1)	1283 $\text{\AA}^2$	0.0°	1515 $\text{\AA}^2$	90.0°	1924 $\text{\AA}^2$	90.0°
		90.0		90.0		0.0
		90.0		0.0		90.0
S(2)	1395	85.2	1613	4.8	1939	90.0
		90.0		90.0		0.0
		4.8		94.8		90.0
O(1)	2306	64.6	2621	68.6	2933	34.2
		88.3		24.6		114.4
		25.4		101.6		112.2
		22.5		101.5		3013
O(2)	2255	68.3	2490	76.6	3013	25.8
		84.0		17.8		106.7
		87.6		2.4		2473
O(3)	1266	90.0	2061	90.0	2473	0.0
		2.4		92.4		90.0
		0.0		90.0		90.0
N(1)	1547	0.0	1660	90.0	1746	90.0
		90.0		90.0		0.0
		90.0		0.0		90.0
N(2)	1411	28.7	1675	90.0	1811	61.3
		90.0		0.0		90.0
		118.7		90.0		28.7

The observed and calculated structure factors are given in Table 1 and the final parameters are given in Table 2.

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- (1) A. Zalkin & B. Foxman: General Fourier synthesis, *FORDAP* (IBM 360);
- (2) C. T. Prewitt, B. Foxman & L. N. Becka: Full-matrix least-squares, *SFLS5* (IBM 360);
- (3) M. E. Pippy & F. R. Ahmed: Scan of interatomic distances and angles (IBM 360);
- (4) L. M. Amzel & S. Baggio: Photographic data processing and layer correlation program, *PHOTO* (IBM 360).

## Results and discussion

The projection of the structure down the *b* axis is illustrated in Fig. 1, in which short hydrogen contacts are shown by dotted lines. The structure consists of well separated  $S_2O_5^{2-}$  and  $NH_4^+$  ions; for N(1) atoms there are no contacts with non-hydrogen atoms at less than 3.0 Å, whereas for the N(2) atom there are three contacts at less than 3.0 Å. Short N-O and N-S distances in Table 3 are together with angles involving hydrogen atoms. It can be seen that there is no strong evidence of hydrogen bonding in the structure, since, with the exception of the S(2)-H(6)-N(2) angle, all angles X-H-N (X=S or O) are far from 180°.

Table 3. Intra- and inter-molecular contacts involving the  $NH_4^+$  ion

	Distance	$\sigma$		Angle
N(1)-O(2)	3.02 Å	0.01	S(1)-O(2)-H(1)	110°
N(1)-O(3)	3.06	0.01	O(2)-H(1)-N(1)	116
N(1)-O(1) (-x, -y, -z)	3.08	0.01	S(1)-O(3)-H(3)	107
N(2)-S(2)	3.608	0.004	N(3)-H(3)-N(1)	130
N(2)-O(1)	2.86	0.01	S(2)-O(1)-H(3)	110
N(2)-O(2)	2.87	0.01	O(1)-H(3)-N(1)	135
			S(1)-S(2)-H(6)	103
			S(2)-H(6)-N(2)	172
			S(2)-O(1)-H(5)	156
			N(2)-H(5)-O(1)	129
			S(1)-O(2)-H(4)	174
			N(2)-H(4)-O(2)	119

Table 4. Distances and angles in the pyrosulphite ion

For numbering of atoms see Fig. 2.

	Distance	$\sigma$	Angle	$\sigma$	
S(1)-S(2)	2.170 Å	0.004	S(2)-S(1)-O(2)	106.7°	0.3
S(1)-O(2)	1.453	0.007	S(2)-S(1)-O(3)	105.1	0.3
S(1)-O(3)	1.455	0.006	O(2)-S(1)-O(3)	112.5	0.4
S(2)-O(1)	1.495	0.007	O(2)-S(1)-O(2')	112.8	0.4
O(1)···O(1')	2.47	0.01	S(1)-S(2)-O(1)	98.5	0.3
O(2)···O(3)	2.42	0.01	O(1)-S(2)-O(1')	111.2	0.4
O(2)···O(2')	2.42	0.01			

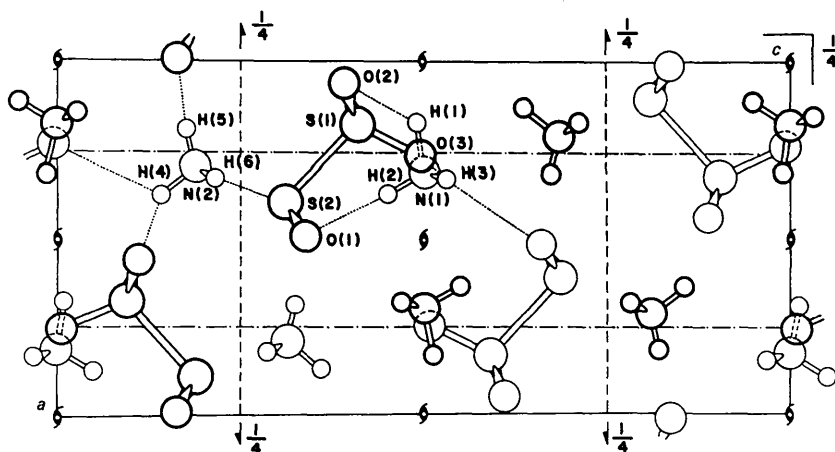


Fig. 1. Projection of the structure down the *b* axis.

Table 5. Distances and angles in some sulphur oxyanions

Anion	S-S	Thionate group			Thionite group			References
		S-O	O-S-O	S-S-O	S-O	O-S-O	S-S-O	
SO <sub>3</sub> <sup>2-</sup>		1.536 (7) Å 1.524 (6) 1.468 (5)	103.6 (6)° 104.8 (4) 110.5 (4)					Baggio & Becka (1969) Battelle & Trueblood (1965) Baggio, Amzel & Becka (1969)
S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	2.013 (3) Å		108.4 (4)°					Dumitz (1956)
S <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	2.39				1.50 Å	108.0°	98.5°	Lindqvist <i>et al.</i> (1957)
S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	2.21	1.43, 1.47	112.0	106.3	1.50	110.0	100.5	This work
S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	2.170 (4)	1.454 (6)	112.6 (4)	105.8 (3)	1.495 (6)	111.2 (4)	98.5 (3)	Berthold (1967)
S <sub>2</sub> O <sub>6</sub> <sup>2-</sup>	2.15	1.456						Berthold (1967)
S <sub>2</sub> O <sub>6</sub> <sup>2-</sup>	2.14	1.451						Rausell-Calom & Garcia-Blanco (1966)
S <sub>4</sub> O <sub>6</sub> <sup>2-</sup>	2.150 (4)	1.46 (1)	114.0 (5)	104.4 (3)				Foss & Hordvik (1964)
S <sub>4</sub> O <sub>6</sub> <sup>2-</sup>	2.116 (10)	1.46 (2)	113.3 (1.0)	104.8 (1.0)				Foss & Tjomsland (1956)
S <sub>5</sub> O <sub>6</sub> <sup>2-</sup>	2.019 (9)							Foss & Maroy (1965)
S <sub>5</sub> O <sub>6</sub> <sup>2-</sup>	2.12 (3)	1.46 (1)						Foss & Maroy (1965)
S <sub>6</sub> O <sub>6</sub> <sup>2-</sup>	2.04 (3)							Foss & Maroy (1965)
S <sub>6</sub> O <sub>6</sub> <sup>2-</sup>	2.12 (1)	1.43 (3)	114.0	103.0				
S <sub>6</sub> O <sub>6</sub> <sup>2-</sup>	2.02 (2)							
S <sub>6</sub> O <sub>6</sub> <sup>2-</sup>	2.05 (1)							

The pyrosulphite ion has  $C_s$  symmetry since it lies on the mirror plane of the space group  $Pnma$ . Distances and angles in the anion are summarized in Table 4 and Fig. 2. The S-S bond, 2.170 Å, is shorter than that reported previously for the pyrosulphite ion in  $K_2S_2O_5$  by Lindqvist & Mörtzell (1957), but considerably longer than the sum of covalent radii, 2.04 Å (taking a radius of 1.02 Å for tetrahedral sulphur; Pauling, 1960). This distance indicates that there is no double-bond character in the S-S bond of  $S_2O_5^{2-}$ . Distances and angles in some sulphur oxyanions are given in Table 5. There is a significant difference between the S-S bond length in the thiosulphate ion and that in oxyanions where both sulphur atoms are bonded to an oxygen atom. It seems reasonable to assume that  $\pi$ -bonding between  $3d$  orbitals of sulphur and  $2p$  orbitals of oxygen is responsible for the weakening of the S-S bond in the latter compounds. This effect is also observed in polythionates, where the S-S bond adjacent to oxygen atoms is longer than the inner S-S bonds.

For the discussion of the S-O bonds it is convenient to consider the thionate and the thionite groups separately. In the former the average S-O bond length is 1.454 Å, the average O-S-O angle,  $112.7^\circ$  and the average S-S-O angle,  $105.9^\circ$ . These values compare well with those reported for the dithionate and polythionates. The S-O bond length is slightly shorter than in the thiosulphate, but this might be expected because the S-S bond in the thiosulphate has some double-bond character. For the thionite group the S-O distance is 1.495 Å, the O-S-O angle,  $112.2^\circ$  and the S-S-O angle,  $98.5^\circ$ . The S-O bond length is influenced by the  $Z_{eff}$  of the sulphur atom and the availability of sulphur orbitals for  $\pi$ -bonding. Robinson (1964) discussed the effect of unshared electrons on sulphur in relation to the bond order in the sulphite ion. He suggested that the bond order in the  $SO_3^{2-}$  ion is only 1.33, as compared with 1.50 in the sulphate ion, with a lone pair replacing one of the two resonating double bonds in the valence bond formulation. He attributed this effect to a reduction of the electronegativity of the central atom by the lone pair. This can be applied to the  $-SO_2$  group in  $S_2O_5^{2-}$  where there is a double bond resonating in two S-O bonds (any double-bond character in the S-S bond can be ignored), giving a bond order of 1.50. Making use of the relation between bond order and bond distance found by Gillespie & Robinson (1963) a distance of 1.49 Å is obtained for the S-O bond in good agreement with experimental values. The effect of unshared electrons can also explain the low value obtained for the S-S-O angle in the thionite group. In the thionate group a bond order of 1.65 is obtained using the bond length *versus* bond order curve, which is compatible with the idea of two double bonds resonating between three S-O bonds.

The distance between oxygen atoms have a mean value of 2.43 Å, a value that is practically identical to that reported for sulphate, sulphite, thiosulphate, di-

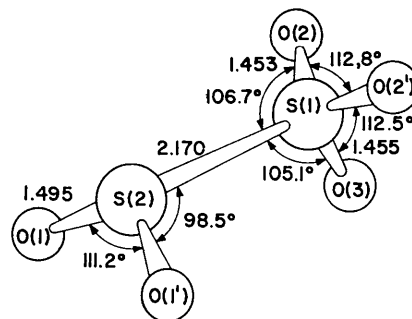


Fig. 2. Structure of the  $S_2O_5^{2-}$  ion in ammonium pyrosulphite.

and polythionates. The constancy of the  $O \cdots O$  distances provides additional support for the idea that the variation in the O-S-O angles can be explained satisfactorily by the predominance of non-bonded repulsion effects, as discussed by McDonald & Cruickshank (1967).

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