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The Structure of Potassium Pyrosulfite and the Nature of the Pyrosulfite Ion.

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The crystal structure of $K_2S_2O_5$ has been confirmed and refined by a least-squares method. The lattice constants are $a = 6.936 \pm 0.005$, $b = 6.166 \pm 0.008$, $c = 7.548 \pm 0.006$ Å, $\beta = 102^\circ 37' \pm 6'$. The space group is $P2_1/m$, and $Z = 2$. The $S_2O_5^{2-}$ ion can best be described as a thionite-thionate ion. The bond lengths are 2.209 Å (S-S), 1.499 Å (S-O in the thionite group) and 1.431 Å, 1.472 Å (S-O in the thionate group).

The experimentally determined bond angles have been used for an exact calculation of the sulphur hybrid orbitals, assuming that these are orthogonal combinations of 3s and 3p orbitals. The results prove that this assumption is correct for the thionate group, and indicate that the bond lengths are principally determined by the s character of the hybrid orbitals which form the σ bonds.

The crystal structure of potassium pyrosulfite, $K_2S_2O_5$, was determined by Zachariasen (1932). In the discussion of the structure the author emphasizes the fact that the structure obtained (with S-S bonds) is contrary to the formula given by the chemists (with S-O-S bonds) (cf. however a discussion by Hägg, 1932). Because of the importance of this result for theoretical chemistry we found it worth while to re-investigate the structure. This study has essentially confirmed the earlier results.

Crystal data

A single crystal of the size $0.3 \times 0.1 \times 0.07$ mm.³ was enclosed in a capillary tube and used for the X-ray study. The unit cell has been redetermined, using a method first described by Weiss, Cochran & Cole (1948). Systematic errors were eliminated by a method of extrapolation worked out by Löfgren (1957).

The new results are (the old values within brackets):

$a = 6.936 \pm 0.005$ Å (6.95 Å), $b = 6.166 \pm 0.008$ Å (6.19 Å), $c = 7.548 \pm 0.006$ Å (7.55 Å) and $\beta = 102^\circ 37' \pm 6'$ ($102^\circ 41'$).

The space group is $P2_1/m$ and $Z = 2$. The calculated density is 2.34 g.cm.⁻³ (found 2.3 g.cm.⁻³).

Weissenberg photographs were taken with Cu $K\alpha$ radiation around the [110] axis (five layer lines). The intensities were visually estimated, and relative $|F|^2$ values were calculated, using Lu's (1943) curves.

Refinement of the structure

A least-squares refinement of the suggested structure was made on IBM 704 by Dr D. Sayre. The final results obtained are:

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)
K _I	0.215	0.250	0.936	1.7
K _{II}	0.639	0.250	0.673	1.2
S _I	0.027	0.250	0.329	1.4
S _{II}	0.702	0.250	0.238	1.1
O _I	0.078	0.051	0.235	2.4
O _{II}	0.632	0.053	0.314	2.5
O _{III}	0.660	0.250	0.043	2.7

The reliability factor is 0.136. A table with the observed and calculated structure factors can be obtained from this Institute.

The individual temperature factors have reasonable values. The variations obtained for the three oxygen atoms cannot easily be interpreted, but are probably not significant. The difference between K_I and K_{II} can be explained by the fact that K_{II} is more narrowly enclosed by oxygen atoms than K_I (Table I, *vide infra*). It is quite natural that S_{II} surrounded by three oxygen and one sulphur has a smaller *B* value than S_I, which is surrounded by only two oxygen and one sulphur (Fig. 1, *vide infra*).

The standard deviations in the atomic positions calculated from the residuals of the least-squares refinement would give the following standard deviations in the bond lengths: 0.002 Å for S-S, 0.004 Å for S-O and K-O, and 0.008 Å for O-O. In the struc-

Table 1. Bond distances and bond angles

The old values are within brackets								
S _I -S _{II}	2.209 Å	(2.18 Å)	K _I -O _I	2.846 Å	(2.88 Å)	O _I -S _I -O _I	110.34°	(112°)
S _I -O _I	1.499	(1.46)	K _I -O _{I'}	2.872	(2.91)	O _I -S _I -S _{II}	100.50	(102)
S _{II} -O _{II}	1.472	(1.46)	K _I -O _{II}	3.012	(3.02)	O _{II} -S _{II} -O _{II}	110.98	(108)
S _{II} -O _{III}	1.431	(1.46)	K _I -O _{III}	3.012	(3.01)	O _{II} -S _{II} -O _{III}	112.83	(116.5)
O _I -O _I	2.458	(2.41)	K _I -O _{III'}	3.209	(3.21)	O _{II} -S _{II} -S _I	106.34	(105)
O _{II} -O _{II}	2.426	(2.41)	K _{II} -O _I	2.676	(2.69)	O _{III} -S _{II} -S _I	106.84	(104)
O _{II} -O _{III}	2.418	(2.49)	K _{II} -O _{II}	2.981	(2.95)			
O _I -O _{III}	3.196		K _{II} -O _{II'}	2.669	(2.74)			
			K _{II} -O _{III}	2.770	(2.71)			

ture determination of orthorhombic sulphur (Abrahams, 1955) a standard deviation of 0.007 Å was found for each S-S bond length (and a reliability factor of 0.172). That investigation represents one of the most careful and thorough X-ray studies that have been done on compounds of this type, and it seems improbable that the difference in standard deviations could be so large. We feel that it would be safe to assign at least the following standard deviations to the bond lengths: 0.005 Å for S-S, 0.01 Å for S-O and K-O, 0.02 Å for O-O.

Description of the structure

The structure is shown in projection in Fig. 1. The bond lengths and bond angles are given in Table 1.

The existence of a S-S bond in S₂O₅²⁻ has thus been confirmed. The pyrosulphite ion can formally be described as built up by a thionite group SO₂⁻ and a

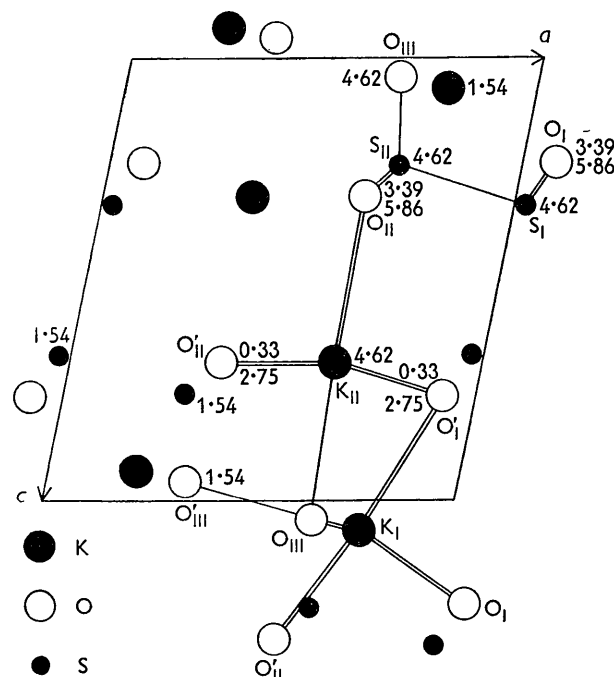


Fig. 1. The atomic arrangement projected along the *b* axis. The numbers give the height above the plane in Å. The lines are drawn to show the coordination around the sulphur and potassium atoms.

thionate group SO₃⁻. The S-O distances within the SO₂⁻ group are identical (S_I-O_I). Two of the S-O bonds in the SO₃⁻ group are identical (S_{II}-O_{II}) but the third bond (S_{II}-O_{III}) is different. The calculation of the hybrid orbitals (*vide infra*) gives results in excellent agreement. This would not be possible if the difference between S_{II}-O_{II} and S_{II}-O_{III} were not significant.

Comparison with other structures

It is natural to compare S₂O₅²⁻ with dithionite, S₂O₄²⁻, and dithionate, S₂O₆²⁻, ions. This has been done in Table 2. The values for S₂O₄²⁻ have been found by

Table 2. Comparison between S₂O₄²⁻, S₂O₅²⁻ and S₂O₆²⁻

	S ₂ O ₄ ²⁻	S ₂ O ₅ ²⁻	S ₂ O ₆ ²⁻
S-S bond length (Å)	2.389	2.209	2.15-2.16
Thionite group			
S-O (Å)	1.496, 1.515	1.499	—
S-S-O (°)	98.02, 99.38	100.50	—
Thionate group			
S-O (Å)	—	1.431, 1.472	1.43-1.45
S-S-O (°)	—	106.34	103-105

Dunitz (1956) in Na₂S₂O₄. The values for S₂O₆²⁻ are the less accurate results obtained for K₂S₂O₆ (Stanley, 1956) and Na₂S₂O₆·2 H₂O (Martínez, Garzia-Blanco & Rivoir, 1956).

This comparison shows that the thionite groups in S₂O₄²⁻ and S₂O₅²⁻ are very similar, as are the thionate groups in S₂O₅²⁻ and S₂O₆²⁻. Furthermore, the S-S bond length in S₂O₅²⁻ is intermediate between those found in S₂O₄²⁻ and S₂O₆²⁻. S₂O₅²⁻ is thus best described as a thionite-thionate ion, not only as a formalism. The name pyrosulfite ion is misleading, because it indicates an analogy with the pyrosulfate ion. The name originated from an analogy in the chemical preparation, but now we know that the structures are quite different. The pyrosulfate ion contains a S-O-S bridge and no S-S bond.

Discussion

It is obvious that the S-S as well as the S-O bond lengths vary considerably among the ions S₂O₄²⁻, S₂O₅²⁻ and S₂O₆²⁻. The S-S bond length increases from S₂O₄²⁻ to S₂O₆²⁻. The S-O bond lengths are longer and the bond angles S-S-O smaller for the thionite groups

in $S_2O_4^{2-}$ and $S_2O_5^{2-}$ than for the thionate groups in $S_2O_5^{2-}$ and $S_2O_6^{2-}$ (Table 2).

Moffitt (1950) has made a penetrating discussion of the nature of the sulphur-oxygen bonds, using molecular-orbital methods. He starts off with a σ -bond skeleton and then treats the remaining electrons as occupying non-bonding atomic orbitals, localized or non-localized molecular orbitals which may give rise to π bonds.

We will here deal only with the σ bonds, under the same assumptions as Moffitt, that only s and p orbitals are used for the S-O σ bonds. From the experimental results we will determine the nature of the hybrid orbitals used, if they are assumed to be orthogonal. For that purpose we make use of formulae given by Löwdin (1953).

Two hybrid orbitals are written as $h_1 = a_1(3s) + b_1(3p)$ and $h_2 = a_2(3s) + b_2(3p)$, where $(3s)$ and $(3p)$ are the atomic orbitals. The weight of s character is then given by a_1^2 and a_2^2 respectively. The angle between the two hybrid orbitals is denoted θ_{12} . If the hybrid orbitals are orthogonal, it follows that $\cos \theta_{12} = -a_1 a_2 / b_1 b_2$, where $b_1 = \sqrt{1 - a_1^2}$ and $b_2 = \sqrt{1 - a_2^2}$.

If h_1 and h_2 are identical, as the two $S_{II}-O_{II}$ bonds in the thionate group of $S_2O_5^{2-}$, the formula reduces to $\cos^2 \theta_{12} = a^2 / (1 - a^2)$, and a^2 can be calculated from the experimentally found bond angle.

Using the bond angles $O_{II}-S_{II}-O_{II}$ and $O_{II}-S_{II}-O_{III}$, the following a^2 values were obtained for the thionate group of $S_2O_5^{2-}$: each of the two $S_{II}-O_{II} = 0.264$ and $S_{II}-O_{III} = 0.296$. (Tetrahedral sp^3 hybridization corresponds to $a^2 = 0.25$.) In the thionite group a^2 for $S_{I}-O_I$ is 0.258.

It was next assumed that only s and p orbitals are used for the S-S σ bond. The a^2 value for the hybrid orbital of the thionate group pointing in the S-S direction is 0.181, and the value for the thionite group is 0.087.

If the assumption about orthogonal hybridization of only s and p orbitals is correct, the problem is overdetermined for the thionate group with four hybrid orbitals and the validity of the assumption can be tested. First of all the sum of all a^2 values should be exactly 1. The sum calculated from the experimental data is 1.005. A still sharper test is given by the required constancy of the products

$$\cos \theta_{12} \cdot \cos \theta_{34} = \cos \theta_{13} \cdot \cos \theta_{24} = \cos \theta_{14} \cdot \cos \theta_{23},$$

which can easily be derived. The values of $\cos \theta$ are very sensitive to variations in θ when θ is so near $\frac{1}{2}\pi$, as in this case. The products obtained are 0.104, 0.109, 0.109. It can thus be concluded that the bonding from the sulphur atom of the thionate group can be described, within the limits of experimental error, as an orthogonal hybridization of only $3s$ and $3p$ orbitals. No arbitrary simplifications have been introduced. It has not been necessary to use d orbitals.

This result implies that the S-S bond in $S_2O_6^{2-}$ is only a single bond of σ type. This is confirmed by the

fact that in $K_2S_2O_6$ (Stanley, 1956) there are two types of $S_2O_6^{2-}$ ions with different mutual configuration of the thionate groups. A third type is found in $Na_2S_2O_6 \cdot 2 H_2O$ (Martínez *et al.*, 1956).

The exact treatment of the thionate group cannot be extended to the thionite group, for which the problem is not overdetermined. It is possible, however, to obtain an idea about how some d character in the hybrid would influence the results of the calculations. The S-O hybrid orbital from sulphur in the thionite group is called $h_1 = a_1(3s) + b_1(3p)$ and the S-S hybrid orbital $h_2 = a_2(3s) + b_2(3p) + c_2(3d)$. The equation $\cos \theta_{12} = -a_1 a_2 / b_1 b_2$ is still correct but b_2 is no longer $\sqrt{1 - a_2^2}$ but equal to $\sqrt{1 - a_2^2 - c_2^2}$. The value of a_1^2 is determined from the angle O-S-O and θ_{12} is known from experiments. The equation can then be reduced to the form $a_2^2 = \text{const.} (1 - c_2^2) / (1 + \text{const.})$, where $\text{const.} = \cos^2 \theta_{12} \cdot (1 - a_1^2) / a_1^2$. If we assume that $c_2^2 = 0$, the highest possible a_2^2 value is thus obtained. There are good reasons to assume that c_2^2 is small compared with 1 and that a very reasonable value is obtained for a_2^2 by putting $c_2 = 0$. If c_2^2 is as high as 0.50, which is impossible, $a_2^2 = \frac{1}{2} a_1^2$ (max.).

The results obtained by these calculations are summarized in Table 3, where also the values calculated from the less accurate data available for $S_2O_4^{2-}$ and $S_2O_6^{2-}$ are given.

Table 3. Bond lengths and s character

	S-O (Å)	a^2	S_I-S_2 (Å)	a_1^2	a_2^2
$S_2O_4^{2-}$	1.496, 1.515	0.238	2.389	0.064	0.064
$S_2O_5^{2-}$	1.499	0.258	2.209	0.087	0.181
	1.472	0.264	—	—	—
	1.431	0.296	—	—	—
$S_2O_6^{2-}$	1.43	0.284	2.15	0.144	0.144
S_8	—	—	2.04	0.231	0.231

Within the limits of experimental error there is a direct relation between bond length and s character for the hybrid orbitals directed from the sulphur to the oxygen atoms. The orbitals from the oxygen atoms can be assumed to be pure p orbitals (following Moffitt, 1950).

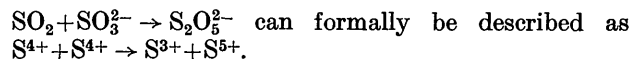
In the S-S bond lengths the same trend is obvious. If $S_2O_5^{2-}$ were a direct intermediate between $S_2O_4^{2-}$ and $S_2O_6^{2-}$, the S-S bond length should be 2.27 Å. The s character in the sulphur hybrid orbitals of this bond are larger for the thionite group as well as for the thionate group compared with corresponding groups in $S_2O_4^{2-}$ and $S_2O_6^{2-}$, and the S-S bond length is accordingly shorter: 2.21 Å. A calculation on S_8 (Abrahams, 1955), based on the same assumption of orthogonal hybridization in the σ bonds, also leads to agreement with the finding that more s character in the σ bonds gives shorter bond lengths.

This relation is purely empirical and does not exclude the possibility that there are more basic relations which in this case happen to give the same result as the s -character considerations. Moffitt (1950) in his molecular orbital treatment of the S-O bonds partly

uses d orbitals for the molecular π orbitals. In the case of the thionate group, which was not discussed by Moffitt, these assumptions must be considered as superfluous for the description of the bonding conditions. All bonds can be described by the σ bond skeleton. The thionite group, on the other hand, may very well include d orbitals and double bonds. Dunitz (1956) has actually been able to explain the eclipsed structure of $S_2O_4^{2-}$ by a simplified molecular-orbital treatment using pd hybridization. (The S-S bond in $S_2O_5^{2-}$ cannot have any double-bond character, however, because of the hybridization in the SO_3^- group.) The discussion by Moffitt (1950) about the double-bond character of the S-O bonds in SO_2 , sulfones and sulfoxides is also very convincing.

We have found it worth while, however, to enquire what information an exact discussion of the σ bonds may give, and the results seem to indicate that the bond lengths are principally determined by the σ bonds.

We have not discussed the polarity of the bonds in $S_2O_5^{2-}$ and do not feel competent to do it. The formal oxidation numbers are +3 and +5 and the reaction



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Die Kristallstruktur von Langbeinit, $K_2Mg_2(SO_4)_3$

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Langbeinite crystallizes in space group $P2_13$ with $a = 9.92_0$ Å; the unit cell contains 4 formula units $K_2Mg_2(SO_4)_3$. The structure is solved by two-dimensional methods with the aid of the isotypical $Tl_2Mn_2(SO_4)_3$ ($a = 10.22_3$ Å). After two refinements, the R index for the $hk0$ data (up to $h^2 + k^2 = 173$) is 0.14_8 . The SO_4 tetrahedra are in general position, K and Mg on the threefold axes. The coordination polyhedra around Mg are octahedra; the coordination around K is irregular. All interatomic distances are of the usual order of magnitude.

Einleitung

Die bisherigen röntgenographischen Untersuchungen an dem kubischen Salz Langbeinit beschränken sich auf Bestimmung der Gitterkonstante und Auslöschungseinheit. Gossner & Koch (1931) fanden: $a = 9,96$ kX., wahrscheinliche Raumgruppe $P2_13-T^4$. Die Gitterkonstante wurde mit dem genau gleichen Wert von Ramsdell (1935) bestätigt. Bellanca (1947) untersuchte das isotype $K_2Mn_2(SO_4)_3$ und fand dieselbe Raumgruppe; die Gitterkonstante des Mn-Langbeinit gibt er zu $a = 10,014$ Å an.

Langbeinit zeigt einen schwachen piezoelektrischen Effekt (Bond, 1943) wie auch wir feststellen konnten. Er ist jedoch nach der Literatur (Luedecke, 1898; Gossner & Koch, 1931) nicht optisch aktiv. Auch ein

eigener Versuch, an einer 20 mm. dicken Kristallplatte Zirkularpolarisation nachzuweisen, verlief erfolglos. Da jedoch eine Reihe anderer Vertreter der Raumgruppe $P2_13$ optisch aktiv sind ($NaClO_3$, $Na_3SbS_4 \cdot 9H_2O$, $NaUO_2(CH_3COO)_3$), schien es interessant die Atomanordnung in diesem Salz aufzuklären; dies noch um so mehr, als es zu Langbeinit eine ganze Reihe isotypen Verbindungen gibt.

Experimentelles

Zur Strukturanalyse dienten geschliffene Kügelchen (Bond, 1951) von natürlichen Kristallen aus Stassfurt sowie von synthetischem $Tl_2Mn_2(SO_4)_3$, welches Sulfat sich aus Pulveraufnahmen als isotyp mit $K_2Mg_2(SO_4)_3$ erwies. Von diesen wurden auf der Precession-Kamera