

## Note on the Structure of the Trithionate Group, (S<sub>3</sub>O<sub>6</sub>)—2

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## Note on the Structure of the Trithionate Group, $(S_3O_6)^{-2}$

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The structure of the trithionate group is found from a complete determination of the crystal lattice of the potassium compound. Two of the sulphur atoms form four bonds each, three bonds with oxygen atoms and one with sulphur. The four bonds are directed towards the corners of a tetrahedron. The third sulphur atom forms only two bonds, both with sulphur atoms; the bond angle is  $103^\circ$ . The S—O distance is 1.50Å and the S—S distance 2.15Å. Some features of the binding in sulphur-oxygen radicals are briefly discussed.

UNTIL three years ago the sulphate radical remained the only sulphur oxygen group the structure of which was known. Since then we have in this laboratory determined the structures of the sulphite,<sup>1</sup> the pyro-sulphite<sup>2</sup> and the persulphate<sup>3</sup> groups, while that of the dithionate<sup>4</sup> was found elsewhere. We are now in position to add a sixth group to this list, namely the trithionate group.

The structure of the trithionate group was obtained through a complete determination of the crystal lattice of the potassium compound. Crystals of potassium trithionate have orthorhombic symmetry. The unit cell contains four molecules and have dimensions  $a = 9.77 \pm 0.04\text{Å}$ ,  $b = 13.63 \pm 0.04\text{Å}$ ,  $c = 5.76 \pm 0.02\text{Å}$ . The space group is  $Pnam(V_h^{16})$ . Two sets of 8 oxygen atoms are lying in general positions of the space group, while there are two sets of four equivalent potas-

sium atoms, three sets of four sulphur atoms and two sets of four oxygen atoms all lying in the reflection planes. Thus there are 20 degrees of freedom in the crystal lattice. By suitable methods of attack and somewhat tedious calculations we succeeded in determining the values of all 20 parameters with considerable accuracy (see Table I).

TABLE I. *Parameter values.*

	$2\pi x$	$2\pi y$	$2\pi z$		$2\pi x$	$2\pi y$	$2\pi z$
$K_I$	$47^\circ$	$32^\circ$	$90^\circ$	$O_I$	$-45^\circ$	$110^\circ$	$90^\circ$
$K_{II}$	65	-85	90	$O_{III}$	125	210	90
$S_I$	12	115	90	$O_{I'}$	30	100	15
$S_{II}$	30	170	90	$O_{III'}$	130	150	15
$S_{III}$	110	170	90				

In agreement with chemical knowledge three sulphur atoms and six oxygen atoms are grouped together in the lattice so as to form the trithionate radicals. It should be remarked that this is a direct experimental result of our investigation, as we in solving the structure did not rely upon any other chemical evidence than the result of chemical analyses.

<sup>1</sup> W. H. Zachariasen and H. E. Buckley, *Phys. Rev.* **37**, 1295 (1931).

<sup>2</sup> W. H. Zachariasen, *Phys. Rev.* **40**, 923 (1932).

<sup>3</sup> W. H. Zachariasen and R. C. L. Mooney, *Zeits. f. Krist.* (in press). Compare *Phys. Rev.* **44**, 327 (1933).

<sup>4</sup> M. L. Huggins and Glenn O. Frank, *Am. Mineral.* **16**, 580 (1931).

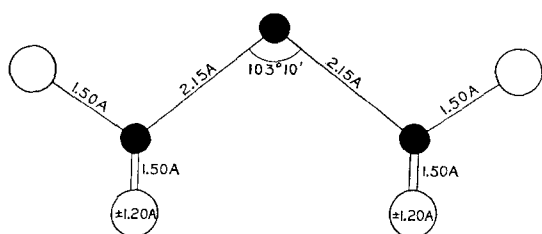


FIG. 1. The structure is shown of the trithionate group. The small circles represent sulphur atoms, the large circles oxygen atoms. Unless indicated by attached numbers the atoms lie in the plane of the paper. The connection lines indicate the bonds.

The structure of the trithionate radical is shown in Fig. 1. One will notice that the symmetry of the group is fairly high, there being two reflection planes. Only one of these planes was found for the crystal lattice as a whole, namely the plane passing through the three sulphur atoms. Two of the sulphur atoms form four bonds each, three of the bonds being with oxygen atoms and one with the third sulphur atom. The angles between the bonds were found to be practically equal to the tetrahedral angle. The third sulphur atom forms only two bonds, both with other sulphur atoms. The angle between these two bonds was found to be  $103^\circ$ , definitely lower than the tetrahedral angle. The distance between sulphur and oxygen is on the average 1.50 Å (the individual values lying between 1.42 Å and 1.57 Å). The sulphur to sulphur distance is 2.15 Å (individual values 2.14 Å and 2.17 Å). This last value compares favorably with the distance 2.18 Å found in the pyrosulphite group and the distance 2.14 Å found in  $\text{FeS}_2$ . In  $\text{K}_2\text{S}_2\text{O}_6$  M. L. Huggins found an S-S distance of 2.06 Å. Also the S-O distance has been found to be essentially constant in all sulphur oxygen radicals and equal to a value somewhere between 1.45 Å and 1.50 Å.

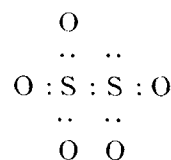
Like all other sulphur oxygen radicals of the form  $(\text{S}_m\text{O}_n)^{-2}$  the trithionate group may be satisfactorily interpreted in terms of only single electron pair bonds. Following Pauling<sup>5</sup> and Slater<sup>6</sup> we can account for the observed structure if we assume all the oxygens to be present as  $\text{O}^{-1}$ , two of the sulphur atoms to be present as  $\text{S}^{+2}$  and the third as a neutral atom. The  $\text{S}^{+2}$  ions should be capable of forming four electron pair

bonds directed towards the corners of a tetrahedron, while the neutral sulphur atom may form two bonds which tend to be at right angles to each other. The fact that the observed angle between the two latter bonds is  $103^\circ$  instead of the predicted value of  $90^\circ$ , may be attributed to the repulsion between sulphur atoms and between oxygen atoms, as is apparent from Fig. 1.

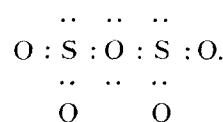
A detailed account of the investigation will appear later in *Zeitschrift für Kristallographie*. A discussion of the structures of the sulphur oxygen groups in general also will be reserved for a later paper; on this occasion I shall only point out a few rules which seem to hold.

In order to explain the fact that sulphur in the sulphur oxygen groups forms one, two, three or four bonds, Pauling and Slater assume that sulphur is present as  $\text{S}^{-1}$ ,  $\text{S}$ ,  $\text{S}^{+1}$  or  $\text{S}^{+2}$ . In addition to the valence binding we will therefore often have ionic binding tending to increase the strength of the bond. With respect to oxygen sulphur can form two, three or four bonds as in sulphur mono-oxide, the sulphite group or the sulphate group. No group is known, however, in which only one sulphur-oxygen bond is formed. Thus we do not know the radical  $(\text{SO})^{-2}$ , which would correspond to the hypochlorite group. This, of course, becomes explicable when we consider that we in this case will have ionic repulsion opposing the valence binding. (It fits in with the same principle that we have no group  $(\text{PO}_2)^{-3}$  corresponding to the sulphylic or the chlorite groups.) It is highly significant, however, that we have groups  $(\text{S}_2)^{-2}$  as in  $\text{Na}_2\text{S}_2$ .

The experimental determination of the structures shows that S-S binding occurs whenever the stoichiometric ratio permits, as if an S-S binding is preferred for an S-O bond. Thus the structure of the pyrosulphite radical was shown to be



rather than



<sup>5</sup> L. Pauling, J. Am. Chem. Soc. **53**, 1367 (1931).

<sup>6</sup> J. C. Slater, Phys. Rev. **37**, 481 (1931).

No group is known, however, in which sulphur forms more than two bonds with other sulphur atoms (a double bond being considered equivalent to two single bonds). Furthermore, if sulphur forms two bonds with other sulphur atoms, no additional bonds can be formed, while a sulphur atom may form one S—S bond and three S—O bonds. According to this rule oxygen atoms can be attached only to the sulphur atoms at either end in a chain of sulphur atoms. This gives a nice explanation of the polythionates and of the nonexistence of groups like  $(S_3O_7)^{-2}$  and  $(S_3O_8)^{-2}$  and so on. The significance of this rule seems to be that we always have to consider the sulphur atom as neutral as far as binding with other

sulphur atoms is concerned. That is to say: sulphur cannot form more than two bonds with other sulphur atoms (corresponding to the two unpaired  $p$  electrons) and if it forms two bonds with other sulphur atoms, it has become saturated. From reasoning of analogy we would expect that chlorine can only form one bond with other chlorine atoms in the chlorine-oxygen groups, and that a chlorine atom is saturated if one such bond is formed. This means that there should be no chlorine-oxygen groups involving chlorine-chlorine binding. This fits with observations, the oxides  $Cl_2O_3$ ,  $Cl_2O_4$ ,  $Cl_2O_5$ ,  $Cl_2O_6$ ,  $Cl_nO_6$  and so on all being non-existent.