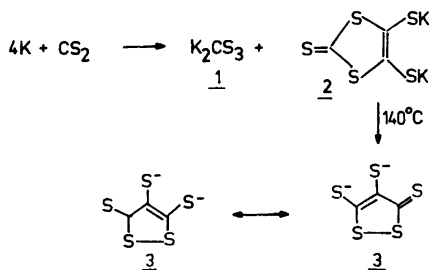# Short Communication

Trithione- and Isotrithionedithiolate. A New Class of Unsaturated 1,2-Dithiolates. IV. The Crystal Structure of Dipotassium 1,2-Dithiole-3-thion-4,5-Dithiolate, $K_2C_3S_5$

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A mixture of alkali metal and carbon disulfide in dimethylformamide (DMF) reacts to give 1,3-dithiole-2-thion-4,5-dithiolate:[1]

$$4K + CS_2 \longrightarrow K_2CS_3 \; (\underline{1}) + \underline{2}$$

(scheme: formation of $\underline{2}$, then $140\,^{\circ}C$ isomerization to $\underline{3}$)

Compound $\underline{2}$ isomerizes quantitatively to 1,2-dithiole-3-thion-4,5-dithiolate ($\underline{3}$) in dimethylformamide solution after 1−2 h at elevated temperatures (120−140 °C). The structure of the two isomeric anions has been determined by X-ray diffraction analysis of the Ni (II) chelates.[3-5] The structure analysis of $K_2C_3S_5$ will provide valuable information concerning the nature of bonding in the $C_3S_5^{2-}$ anion and the potassiumsulfur coordination.

Experimental. Compound $\underline{3}$ was isolated from the DMF solution by addition of $ZnCl_2$ and $[N(C_2H_5)_4]Br$. The resulting zinc complex enables the preparation of 4,5-bis(benzoyl-thio)-1,2-dithiole-3-thione from methanolic solution by treatment with benzoyl chloride.[1,2] 30 ml of a 1 M solution of potassium methanolate in methanol were poured upon 4.06 g (0.01 mol) solid 4,5-bis(benzoylthio)-1,2-dithiole-3-thione and the mixture was stirred for about 10 min. The resulting potassium salt of the mercaptane precipitated as a red powder. The product was filtered off and washed several times with anhydrous ether and dried in a desiccator. The powder was then dissolved in a minimum amount of water. The solution was allowed to concentrate at about 50 °C. After 24 h deep red crystals of capped, square bipyramidal shape, suited for X-ray diffraction studies, were formed. X-ray data were collected on a Syntex P2$_1$ diffractometer, using graphite monochromated Mo$K\alpha$ radiation. Three-dimensional data (1177 reflections with $2\theta \leqslant 70°$) were measured using $\omega-2\theta$ scan technique. Integrated intensity values were obtained by the Lehmann−Larsen profile analysis method.[6] Those 816 reflections having $I > 3\sigma(I)$ were used for the structure determination and refinement. The intensities were corrected for Lorentz and polarisation effects, using the program GECOR,[7] but not for absorption or extinction ($K_2C_3S_5$;
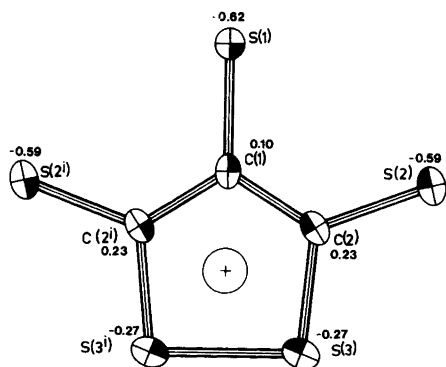
Fig. 1. Structure and atomic labelling for the $C_3S_5^{2-}$ anion. Symmetry code: (*i*) $\bar{x},y,z$. The charges calculated from the meso-ionic form are given at each atom.

M_r=274.5; D_c=1.98 g cm^{-3}; μ(Mo$K\alpha$)=20.1 cm^{-1}. Cell: a=14.436(2) Å, b=7.616(2) Å, c=8.383(2) Å and Z=4).

The positions of the potassium and sulfur atoms were obtained by direct methods (MULTAN 80)[8] and those of the carbon atoms from a subsequent electron density map. The centric space group *Cmcm* as well as the non-centric space groups *Ccm2₁* and *Ama2* possible from the extinctions gave the same results with MULTAN. However, the best refinement results were obtained i space group *Cmcm*.

Positional and thermal parameters were subjected to several cycles of block-diagonal least squares refinement.[7] The final refinement included anisotropic temperature factors for all atoms. The resulting $R(=\Sigma||F_o|-|F_c||/\Sigma|F_o|)$ value was 0.058.

A list of structure factors is available from the authors on request. The positional and thermal parameters are given in Table 1.

Discussion. The molecular structure of the $C_3S_5^{2-}$ anion is shown in Fig. 1 and bond lengths and angles are given in Table 2.

Table 1. Fractional coordinates and thermal parameters (x10^4). The anisotropic temperature factor is of the form exp $\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl$. Estimated standard deviations are given in parentheses.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
K	0.1609(1)	0	0	23(1)	138(2)	70(2)	0	0	0
S(1)	0	0.0763(3)	0.250	16(1)	64(3)	87(3)	0	0	0
S(2)	0.1932(1)	0.3250(2)	0.250	15(1)	97(2)	110(3)	−11(2)	0	0
S(3)	0.0716	0.6287(2)	0.250	26(1)	61(2)	238(5)	−15(2)	0	0
C(1)	0	0.3047(10)	0.250	12(3)	80(11)	69(11)	0	0	0
C(2)	0.0833(4)	0.4038(8)	0.250	16(2)	74(8)	91(9)	−20(8)	0	0

Table 2. Bond lengths (Å) and angles (°) in the $C_3S_5^{2-}$ anion. Standard deviations are given in parentheses. Symmetry code (*i*):$\bar{x},y,z$.

C(1)−S(1)	1.739(8)	C(2)−C(1)−S(1)	122.1(4)
C(1)−C(2)	1.420(7)	C(2)−C(1)−C(2^i)	115.8(6)
C(2)−S(2)	1.696(6)	S(2)−C(2)−C(1)	127.2(5)
C(2)−S(3)	1.721(6)	C(1)−C(2)−S(3)	116.5(3)
S(3)−S(3^i)	2.067(3)	S(2)−C(2)−S(3)	116.4(4)
		C(2)−S(3)−S(3^i)	95.6(2)

Table 3. The sulfur coordination of the potassium ion in $K_2C_3S_5$. The symmetry operation for generating atom 2 from the coordinates listed in Table 1 is given after each distance.

K(1)−S(1)	(2×)	3.182(1)	$(0, y, \frac{1}{4}; 0, -y, -\frac{1}{4})$
K(1)−S(2)	(2×)	3.277(1)	$(x, y, \frac{1}{4}; x, -y, -\frac{1}{4})$
K(1)−S(2)	(2×)	3.256(1)	$(\frac{1}{2}-x, \frac{1}{2}-y, -\frac{1}{4}; \frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{4})$
K(1)−S(3)	(2×)	3.748(1)	$(x, -1+y, \frac{1}{4}; x, 1-y, -\frac{1}{4})$

The $C_3S_5^{2-}$ anion has exact C_{2v} symmetry. The distances C(2)−S(3) 1.721(6) Å and C(1)−C(2) 1.420(7) Å in the 1,2-dithiolium ring are intermediate between double and single bond values.[9] The S(3)−S(3)^i) distance corresponds to a single bond which is also consistent with the C(2)−S(3)−S(3^i) angle of 95.6°.

Of the two terminal carbon−sulfur distances, C(1)−S(1) of 1.739(8) Å, is significantly longer than C(2)−S(2) of 1.696(6) Å. In the CS_3^{2-} ion,[10] the mean carbon−sulfur distance was found to be 1.712 Å, being in excellent agreement with the corresponding value in $K_2C_3S_5$.

A quantum chemical calculation using the CNDO method with complete optimization of the atomic positions agreed with the results of X-ray structure analysis. The molecule has C_{2v} symmetry and the C(1)−S(1) and C(2)−S(2) distances are significantly different. The charge distribution (Fig. 1) is also different for S(1) and S(2). It thus follows from the CNDO and X-ray analyses that the mesoionic form (Fig. 1) is useful in describing the bond situation in the $C_3S_5^{2-}$ ion.

The packing of $K_2C_3S_5$ is shown in Fig. 2. The $C_3S_5^{2-}$ anions are arranged in the mirror plans perpendicular to the z axis $(z=\frac{1}{4}, z=\frac{3}{4})$. The $C_3S_5^{2-}$ anions related by centers of symmetry between layers are piled up in the z direction to form channels containing the potassium cations at a separation of 4.191 Å. The potassium ion is coordinated by eight sulfur atoms (Table 3). The coordination polyhedron is a strongly distorted tetragonal antiprism. The shortest potassium sulfur distance, 3.182(1) Å between K(1)−S(1), is caused
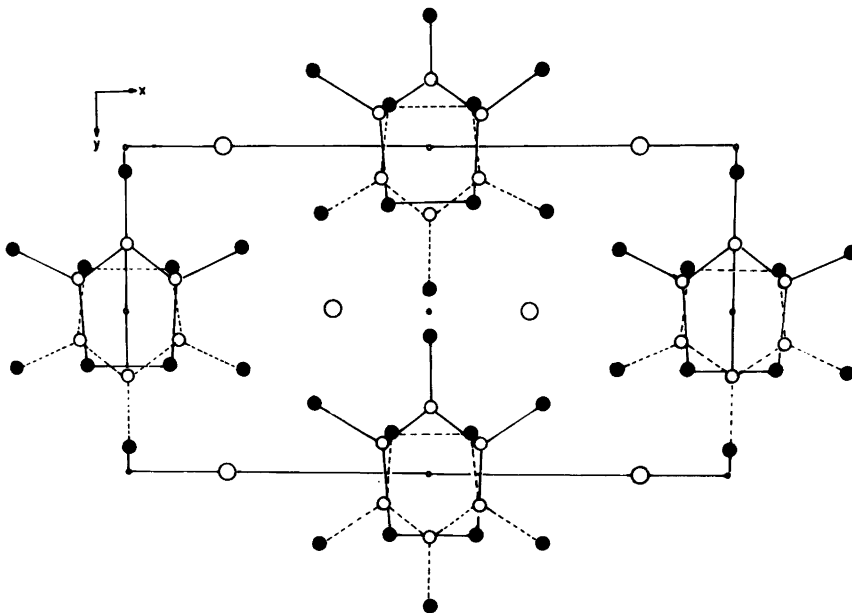

Fig. 2. The packing of the $K_2C_3S_5$ structure.

by the higher atomic charges of the S(1) atom in comparison with S(2). This value is in good agreement with the sum of the ionic radii of potassium and sulfur[9] (3.17 Å).

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