Crystal Structure of Dipotassium Pentasulphide

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Crystals of K_2S_5 are orthorhombic, space group $P2_12_12_1$ with $Z = 4$ in a unit cell of dimensions: $a = 6.494(1)$, $b = 6.600(2)$, $c = 17.414(5)$ Å. The structure has been elucidated by vector methods from 656 independent diffracted intensities measured on a four-circle diffractometer and refined to R 0.045. The $[S_5]^{2-}$ anion exists as a contorted but unbranched chain in which successive S–S bond lengths are 2.037, 2.074, 2.075, and 2.050(5) Å, and the bond angles are close to tetrahedral. The torsions in the chain around the S(2)–S(3) and S(3)–S(4) bonds are 74 and 69° respectively. The potassium ions are evenly distributed between the S_5 units with minimum K · · · S 3.215(4) Å, and a nearest-neighbour K · · · K of just under 4 Å.

THE only precise structural study of a polysulphide is of Na_2S_4,[1] although earlier work has established the crystal arrangements in Na_2S_2,[2] BaS_3,[3] $BaS_4{\cdot}H_2O$ [4] (since redetermined), and Cs_2S_6.[5] All polysulphide ions so far investigated comprise unbranched non-linear chains of S atoms. The pentasulphides are of potential industrial interest because the $[S_5]^{2-}$ ion is believed to be the favoured species during the sulphur-rich stages of discharge of the sodium–sulphur battery, and hitherto there has been no structural study of a pentasulphide.†

EXPERIMENTAL

Crystals of K_2S_5 were prepared by first dissolving potassium metal in ethanol and then saturating the solution of potassium ethoxide so formed with hydrogen sulphide gas to give KHS; addition of the stoicheiometric quantity of sulphur indicated by reaction (1) gave the required product,

$$2KHS + 4S \longrightarrow K_2S_5 + H_2S \qquad (1)$$

which could be recrystallised from ethanol. All reactions were performed in a Schlenck tube under dry nitrogen.

Crystals of K_2S_5 are red-orange prisms which decompose rapidly in air. Diffracted intensities were collected from a crystal of dimensions $0.17 \times 0.12 \times 0.10$ mm mounted in nitrogen in a Lindemann capillary on a Syntex $P2_1$ four-circle diffractometer, according to methods described earlier.[6] Of the total 806 independent reflections for $3.7° < 2\theta < 50.0°$, 656 satisfied the criterion $I > 2.5\sigma(I)$, and only these were used in the solution and refinement of the structure.

RESULTS

Crystal Data.—K_2S_5, $M = 238.5$, Orthorhombic, $a = 6.494(1)$, $b = 6.600(2)$, $c = 17.414(5)$ Å, $D_c = 2.08$ g cm^{-3}, $Z = 4$, $2.98 > D_m > 1.33$ g cm^{-3}, $F(000) = 472$. Space group $P2_12_12_1$. Mo-K_α X-radiation (graphite monochromator), $\lambda = 0.710\,69$ Å; μ(Mo-K_α) = 5.2 cm^{-1}.

The structure was solved by vector methods and refined by full-matrix least-squares with anisotropic thermal parameters for all atoms. Weights were applied according to the scheme $1/w = x\,.\,y$, where $x = b/\sin\theta$ if $\sin\theta < b$,

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† After this work was complete, a structural study of Tl_2S_5 was published by B. Leclerc and T. S. Kabré (ref. 12). The two crystals K_2S_5 and Tl_2S_5 have closely similar structures; in order to convert parameters for Tl_2S_5 to the corresponding ones for K_2S_5 the transformation $a \rightarrow b$, $b \rightarrow c$, $c \rightarrow a$ should be carried out.

[1] R. Tegman, *Acta Cryst.*, 1973, **B29**, 1463.

[2] H. Föppl, *Angew. Chem.*, 1958, **70**, 401.

[3] W. S. Miller and A. J. King, *Z. Krist.*, 1936, **94A**, 439.

[4] S. C. Abrahams, *Acta Cryst.*, 1954, **7**, 423; S. C. Abrahams and J. L. Bernstein, *Acta Cryst.*, 1969, **B25**, 2365.

[5] S. C. Abrahams and E. Grison, *Acta Cryst.*, 1953, **6**, 206.

[6] A. Modinos and P. Woodward, *J.C.S. Dalton*, 1974, 2065.

$x = 1$ if $\sin\theta \geqslant b$, and $y = F/a$ if $F > a$, $y = 1$ if $F \leqslant a$ ($a = 40.0$, $b = 0.22$). No corrections for X-ray absorption were applied as the crystal was very small and $\mu < 10$ cm^{-1}.

Refinement converged at R 0.045 (R' 0.050), and a final electron-density difference synthesis showed no peaks >0.6 or <-0.5 eÅ^{-3}. Positional and thermal parameters are in Table 1, interatomic parameters in Table 2, and torsion angles between calculated least-squares planes are given in the text of the Discussion. Atomic scattering factors were those of ref. 7. All computational work was carried out at the University of London Computing Centre with the 'X-Ray System' of programmes.[8] Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21662 (6 pp., 1 microfiche).*

TABLE 1

Atomic positional (fractional co-ordinates) and thermal * parameters, with standard deviations in parentheses

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
K(1)	0.624 8(5)	0.415 5(4)	0.512 7(2)	37(2)	27(1)	37(2)	−4(1)	5(1)	−4(1)
K(2)	0.079 9(5)	0.262 7(4)	0.835 1(2)	35(2)	32(1)	35(1)	−0(1)	−2(1)	−2(1)
S(1)	0.587 4(5)	−0.084 8(5)	0.528 4(2)	31(2)	31(2)	36(2)	1(2)	−0(1)	−6(1)
S(2)	0.424 7(5)	−0.130 7(5)	0.626 8(2)	32(2)	29(2)	45(2)	−0(2)	−0(2)	12(2)
S(3)	0.446 6(5)	0.123 5(6)	0.696 4(2)	30(2)	57(2)	29(2)	0(2)	−3(1)	−9(2)
S(4)	0.263 8(6)	0.344 3(5)	0.646 0(2)	39(2)	29(2)	42(2)	−5(2)	11(2)	−6(2)
S(5)	−0.038 7(5)	0.259 4(5)	0.655 8(2)	33(2)	25(2)	33(2)	4(2)	−2(1)	2(2)

* Anisotropic thermal parameters (× 10³) in the form: $\exp\{-2\pi^2[U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl]\}$.

TABLE 2

Interatomic distances (Å) and bond angles (°)

(a) The S_5 chain

S(1)–S(2)	2.037(4)	S(1)–S(2)–S(3)	109.7(1)
S(2)–S(3)	2.074(4)	S(2)–S(3)–S(4)	106.4(1)
S(3)–S(4)	2.075(4)	S(3)–S(4)–S(5)	108.7(1)
S(4)–S(5)	2.050(5)		

Dihedral angles

S(1),S(2),S(3)/S(2),S(3),S(4)	73.6
S(2),S(3),S(4)/S(3),S(4),S(5)	68.7

(b) K • • • S distances <3.57 Å

K(1) · · · S(1)	3.321(4)	K(2) · · · S(1^{IV})	3.368(4)
K(1) · · · S(4)	3.332(4)	K(2) · · · S(2^{IV})	3.357(4)
K(1) · · · S(5^{I})	3.471(4)	K(2) · · · S(2^{V})	3.418(4)
K(1) · · · S(1^{II})	3.319(4)	K(2) · · · S(5^{V})	3.294(4)
K(1) · · · S(1^{III})	3.285(4)	K(2) · · · S(5^{VI})	3.335(4)
K(1) · · · S(2^{III})	3.426(4)	K(2) · · · S(3)	3.515(4)
K(1) · · · S(4^{III})	3.378(4)	K(2) · · · S(4)	3.541(4)
K(1) · · · S(5^{III})	3.327(4)	K(2) · · · S(4^{VI})	3.567(4)
K(2) · · · S(5)	3.215(4)		

(c) K · · · K distances

K(1) · · · K(2^{IV})	3.996(4)	K(1) · · · K(1^{VIII})	3.936(4)
K(1) · · · K(2^{VII})	3.981(4)		

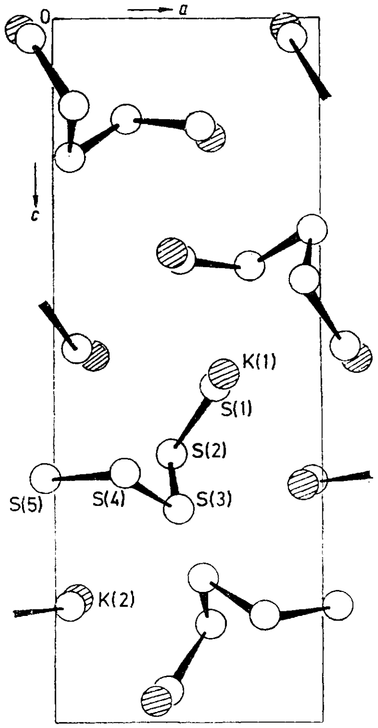
Roman superscripts indicate the following symmetry operations as applied to the co-ordinates of Table 1:

I	$1 + x, y, z$	V	$-x, \frac{1}{2} + y, 1\frac{1}{2} - z$
II	$x, 1 + y, z$	VI	$-x, y - \frac{1}{2}, 1\frac{1}{2} - z$
III	$\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$	VII	$\frac{1}{2} - x, 1 - y, z - \frac{1}{2}$
IV	$1 - x, \frac{1}{2} + y, 1\frac{1}{2} - z$	VIII	$x - \frac{1}{2}, \frac{1}{2} - y, 1 - z$

DISCUSSION

Crystals of K_2S_5 comprise a three-dimensional array of discrete K^+ cations and $[S_5]^{2-}$ anions in which the five sulphur atoms are covalently linked into a contorted but unbranched chain. The structure is illustrated in the Figure which shows the unit cell in projection down b. The potassium ions all lie close to planes parallel to (203); indeed, those planes give rise to the strongest diffracted beam (F_o *ca.* 200, for a structure in which only 9 of the $F_o > 100$). The closest approach of K^+ ions to one another is just <4 Å (Table 2); the distance is of course much greater where a $[S_5]^{2-}$ ion lies between two K^+ ions.

Interest centres on the configuration of the $[S_5]^{2-}$ unit. The bond lengths along the chain [2.037, 2.074, 2.075, and 2.050(5) Å] and the angles between the bonds [109.7, 106.4, and 108.7(2)°] are indicative of covalent bonding and do not themselves suggest any significant localisation of the electronic charge within the $[S_5]^{2-}$ unit. The torsions in the chain are best indicated by



The orthorhombic unit cell of K_2S_5 seen in projection down b looking towards the origin

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Dalton*, 1975, Index issue. (Items less than 10 pp. are supplied as full-size copies.)

[7] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[8] Technical Report TR 192, Computer Science Center, University of Maryland, U.S.A., June 1972.

the angles between successive planes: S(1),S(2),S(3)/S(2),S(3),S(4) 74° and S(2),S(3),S(4)/S(3),S(4),S(5) 69°. It can be argued [9,10] that the bond length S–S should vary according to the dihedral angle, being a maximum (*ca.* 2.10 Å) for a *cis* planar disulphide and a minimum (*ca.* 2.03 Å) when the dihedral angle is 90°. In the latter case repulsion between electron lone pairs is at a minimum and any possible p–d π-interaction is enhanced. Experimental studies indicate [9] the overall truth of this, and further indicate that a dihedral angle of *ca.* 70° should give a bond length of *ca.* 2.07 Å. If the electronic charge were considered to be localised at the two ends of the $[S_5]^{2-}$ chain, a shortening of the terminal bonds by some 0.04 Å might be envisaged (the covalent radii of S and Cl differ by about this, and S^- is isoelectronic with Cl^0). Our results do not conflict with this interpretation.

The $[S_5]^{2-}$ chain has approximate two-fold symmetry (not required crystallographically), the direction of the two-fold axis bisecting the angle S(2)–S(3)–S(4). Inspection of the components of the anisotropic temperature factors shows that the thermal motion also has approximate two-fold symmetry for the non-terminal atoms of the chain, the principal axis of the ellipsoid lying in each case close to the bisector of the angle at the appropriate sulphur atom. For terminal atoms S(1) and S(5) the principal motion is approximately perpendicular to the terminal bond but in directions not related by the two-fold axis. The crystal environments of these two atoms are, of course, different. [The direction cosines of the principal axes of the ellipsoids for each of the S atoms of the chain [11] are: S(1) −0.239, 0.827, 0.510; S(2) 0.028, 0.879, −0.477; S(3) 0.487, 0.234, 0.842; S(4) 0.218, 0.957, 0.192; S(5) −0.406, 0.874, −0.268.]

The contact distances between the K^+ ions and the individual S atoms of the chains indicate that the closest distances (*ca.* 3.3 Å) occur between the terminal atoms and their nearest K^+ neighbours. Then there are several contacts involving S(2) and S(4) between 3.3 and 3.5 Å, but the shortest contact between the central sulphur atom S(3) and K^+ is >3.5 Å [K(2)···S(3) 3.515(4) Å]. In our view, however, it is meaningless to discuss ' co-ordination polyhedra ' in structures such as this, and the interpretation of the Tl_2S_5 structure [12] which ascribes to each Tl^+ ion a ' tetrahedral ' environment (comprising three S atoms and the inert Tl^+ electron pair) obviously cannot be held to apply here, even though the structure is closely similar.

We thank the S.R.C. for financial help, and Dr. P. Moseley of A.E.R.E., Harwell, Didcot, Berks., for supervision of the preparation of the crystals.

[5/1521 *Received, 1st August,* 1975]

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[9] A. Hordvik, *Acta Chem. Scand.*, 1966, **20**, 1885.

[10] A. Hordvik and E. Sletten, *Acta Chem. Scand.*, 1968, **22**, 3029.

[11] R. Goddard, unpublished WATFOR programme.

[12] B. Leclerc and T. S. Kabré. *Acta Cryst.*, 1975, **B31**, 1675.