# **987.** *An Accurate Determination of the Crystal Structure of Potassium Pyrosulphate.*

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Potassium pyrosulphate, $K_2S_2O_7$, has been investigated by three-dimensional *X*-ray crystal-structure analysis. Refinement of the co-ordinates and anisotropic thermal motion parameters reduced the agreement index to 0·076. The bond lengths in the pyrosulphate ion, corrected for rotational oscillations, are S–O (bridge) = 1·645 ± 0·005 Å, and S=O = 1·437 ± 0·004 Å, the mean of three independent values; the S–O–S angle is 124·2° ± 0·5°.

THE pyrosulphate ion, $S_2O_7^{2-}$, might be expected to consist of two $SO_4$ tetrahedra sharing one oxygen atom as in the other pyro-ions $X_2O_7^{n-}$ of which the structures are known.[1] Although a few pyro-ions having an X–O–X angle of 180° have been reported, the more accurate determinations usually give values in the range 110—140°. The hydrogen pyrosulphate ion in the nitronium salt was found [2] to have an angle of about 125°.

A number of accurate determinations of S–O bond lengths have now been made, and the pyrosulphate ion is of particular interest because it contains bonds involving both shared and unshared oxygen atoms. Conclusive proof that there is a significant difference in the distances from sulphur to unshared and to shared oxygen atoms was first obtained in a study [3] of potassium ethyl sulphate, $KO_3S{\cdot}O{\cdot}C_2H_5$. The present analysis was undertaken for comparison with the ethyl sulphate ion and with the isoelectronic iminodisulphonate ion, $(SO_3{\cdot}NH{\cdot}SO_3)^{2-}$.

Preparation of the crystals was very difficult; this probably explains why the structure has not been determined previously. From the system $R_2O$–$H_2O$–$SO_3$ (where R = Na, K, or $NH_4$) one of the authors (H. L.) obtained a variety of products; details of their preparation and preliminary *X*-ray investigation are available elsewhere.[4] Eventually, crystals of potassium pyrosulphate were obtained by heating " potassium octasulphate " prepared by Weber's procedure.[5] The structure determination proved to be easy because

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[1] Barclay, Cox, and Lynton, *Chem. and Ind.*, 1956, 178.
[2] Steeman and MacGillavry, *Acta Cryst.*, 1954, **7**, 402.
[3] Jarvis, *Acta Cryst.*, 1953, **6**, 327; Truter, *ibid.*, 1958, **11**, 680.
[4] Lynton, 1955, Ph.D. Thesis, University of Leeds.
[5] Weber, *Ber.*, 1884, **17**, 2497.

preliminary measurements indicated that potassium pyrosulphate and potassium iminodisulphonate[6] were probably iso-structural. Essentially the task was to collect observations, apply a refinement procedure, and determine the dimensions of the anion as accurately as possible.

*Crystal Data.*—$K_2S_2O_7$, $M = 254{\cdot}33$. Monoclinic, $a = 12{\cdot}35$, $b = 7{\cdot}31$, $c = 7{\cdot}27$ all $\pm 0{\cdot}005$ Å, $\beta = 93° 7' \pm 4{\cdot}5'$. $U = 655{\cdot}3$ Å$^3$, $Z = 4$, $D_c = 2{\cdot}58$, $F(000) = 504$. Space group, $C2/c$ ($C_{2h}^6$, No. 15). Cu-$K_\alpha$ radiation, single-crystal oscillation and Weissenberg photographs, absorption coefficient, $\mu = 184$ cm.$^{-1}$. The pyrosulphate ion must lie on a two-fold axis or a centre of symmetry.

*Refinement.*—The close resemblance between the unit-cell dimensions and those of potassium iminodisulphonate[6] ($a = 12{\cdot}430$, $b = 7{\cdot}458$, $c = 7{\cdot}175$ Å, $\beta = 91° 11'$), and the discovery that the space groups are the same, suggested that the two compounds were iso-structural. This was confirmed by calculating the agreement index $R$ ($R = \sum|(|F_o| - |F_c|)|/\sum|F_o|$) between the observed structure factors and those calculated for the iminodisulphonate; this value was 0·25 for all ($hkl$) reflections.

Refinement was carried out by the method of least squares; the atomic co-ordinates and the anisotropic thermal parameters for each atom were adjusted until, after five cycles, the shifts indicated were less than one-quarter of the corresponding standard deviations. Refinement was complete with $R = 0{\cdot}076$.

TABLE 1. *Atomic co-ordinates.*

| | $x/a$ | $y/b$ | $z/c$ | $X'$ (Å) | $\sigma(X)$ (Å) | $Y'$ (Å) | $\sigma(Y)$ (Å) | $Z'$ (Å) | $\sigma(Z)$ (Å) |
|---|---|---|---|---|---|---|---|---|---|
| K ...... | 0·353 | 0·651 | 0·647 | 4·110 | 0·002 | 4·756 | 0·002 | 4·693 | 0·002 |
| S ...... | 0·398 | 0·183 | 0·641 | 4·663 | 0·002 | 1·338 | 0·002 | 4·654 | 0·002 |
| O(1) ... | 0·444 | 0·287 | 0·498 | 5·281 | 0·007 | 2·098 | 0·008 | 3·611 | 0·007 |
| O(2) ... | 0·332 | 0·032 | 0·581 | 3·876 | 0·006 | 0·235 | 0·007 | 4·220 | 0·008 |
| O(3) ... | 0·350 | 0·296 | 0·777 | 4·014 | 0·007 | 2·164 | 0·007 | 5·639 | 0·007 |
| O(4) ... | 0·500 | 0·078 | 0·750 | 5·879 | 0 | 0·573 | 0·008 | 5·445 | 0 |

TABLE 2. *Thermal parameters* (*all units are* $10^{-4}$ Å$^2$).

| | $U_{11}$ | $\sigma$ | $U_{22}$ | $\sigma$ | $U_{33}$ | $\sigma$ | $U_{12}$ | $\sigma$ | $U_{23}$ | $\sigma$ | $U_{13}$ | $\sigma$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| K ...... | 229 | 10 | 244 | 10 | 202 | 10 | 24 | 9 | 41 | 9 | 31 | 8 |
| S ...... | 122 | 9 | 141 | 9 | 165 | 10 | −12 | 7 | 9 | 9 | 31 | 8 |
| O(1) ... | 223 | 33 | 334 | 38 | 208 | 35 | −26 | 30 | 106 | 31 | 39 | 27 |
| O(2) ... | 180 | 30 | 237 | 36 | 379 | 39 | −67 | 27 | −48 | 33 | −102 | 28 |
| O(3) ... | 266 | 36 | 270 | 35 | 234 | 34 | 144 | 30 | −10 | 31 | 47 | 27 |
| O(4) ... | 223 | 42 | 88 | 36 | 249 | 49 | 0 | 0 | 0 | 0 | 68 | 36 |

Analysis of the anisotropic thermal motion was carried out by assuming that the pyrosulphate ion could be regarded as a rigid body. From this the corrections in the atomic co-ordinates to allow for systematic errors due to rotational oscillation[7] were calculated.

*Results.*—The structure as a whole is shown in Fig. 1; the bridging oxygen atoms of the pyrosulphate ions lie on 2-fold axes by which the two $SO_3$ groups in each anion are related. Figs. 1 and 2 show the numbering of the atoms. The atomic co-ordinates are shown in Table 1 both as fractions and in Å where $X'$, $Y'$, and $Z'$ refer to orthogonal axes parallel to $a$, $b$, and $c^*$ respectively; their standard deviations are also shown. Table 2 shows the thermal parameters and their standard deviations; $U_{11}$, $U_{22}$, and $U_{33}$ are the mean-square amplitudes of vibration parallel to the $a^*$, $b^*$, and $c^*$ axes respectively and, with $U_{12}$, $U_{23}$, and $U_{13}$, give the magnitude and orientation of the ellipsoid of vibration with respect to the crystallographic axes. Table 3 consists of the observed and calculated structure factors.

Analysis of the thermal motion was made after the determination of the position of the mass centre (5·879, 1·356, 5·445 Å) and the direction cosines of the principal axes of inertia, I, II, and III, of the pyrosulphate ion. These direction cosines, with respect to the orthogonal system of Table 1, are:

$$\text{I},\ 0{\cdot}84,\ 0{\cdot}00,\ 0{\cdot}54;\quad \text{II},\ 0{\cdot}00,\ 1{\cdot}00,\ 0{\cdot}00;\quad \text{III},\ 0{\cdot}54,\ 0{\cdot}00,\ \overline{0{\cdot}84}$$

Jeffrey and Jones, *Acta Cryst.*, 1956, **9**, 283.
Cruickshank, *Acta Cryst.*, 1956, **9**, 757.

TABLE 3. *Observed and calculated structure factors* (×10).

(*Reflections which are too weak to be observed have been omitted.*)

| *h* | *k* | *l* | $\|F_o\|$ | $F_c$ | *h* | *k* | *l* | $\|F_o\|$ | $F_c$ | *h* | *k* | *l* | $\|F_o\|$ | $F_c$ | *h* | *k* | *l* | $\|F_o\|$ | $F_c$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 6 | 0 | 0 | 618 | 704 | 2 | 2 | 2 | 950 | −975 | −6 | 4 | 2 | 301 | −275 | −4 | 8 | 4 | 182 | −256 |
| −8 | 0 | 0 | 464 | 394 | −2 | 2 | 2 | 230 | −154 | 8 | 4 | 2 | 261 | −224 | −1 | 9 | 0 | 165 | 142 |
| −10 | 0 | 0 | 371 | −310 | 4 | 2 | 2 | 915 | −975 | −8 | 4 | 2 | 229 | 209 | −3 | 9 | 0 | 98 | 71 |
| −12 | 0 | 0 | 361 | 282 | −4 | 2 | 2 | 230 | −196 | 10 | 4 | 2 | 195 | −193 | 1 | 1 | 1 | 523 | −499 |
| −0 | 0 | 2 | 483 | −491 | 6 | 2 | 2 | 700 | 717 | 12 | 4 | 2 | 228 | 217 | −1 | 1 | 1 | 606 | −663 |
| 2 | 0 | 2 | 2119 | 2287 | −6 | 2 | 2 | 80 | −81 | −12 | 4 | 2 | 226 | −225 | 3 | 1 | 1 | 582 | 601 |
| −2 | 0 | 2 | 1894 | −1995 | 8 | 2 | 2 | 526 | 518 | −14 | 4 | 2 | 94 | 119 | −3 | 1 | 1 | 657 | −795 |
| 4 | 0 | 2 | 141 | 122 | −8 | 2 | 2 | 223 | −207 | −0 | 4 | 4 | 519 | 521 | 5 | 1 | 1 | 1154 | 1155 |
| −4 | 0 | 2 | 675 | 720 | 10 | 2 | 2 | 277 | −239 | 2 | 4 | 4 | 314 | 295 | −5 | 1 | 1 | 435 | −439 |
| 6 | 0 | 2 | 1111 | −1281 | −10 | 2 | 2 | 159 | 144 | −2 | 4 | 4 | 381 | −381 | −7 | 1 | 1 | 495 | 497 |
| −6 | 0 | 2 | 412 | 469 | −12 | 2 | 2 | 313 | 295 | 4 | 4 | 4 | 543 | −581 | 9 | 1 | 1 | 874 | −871 |
| 8 | 0 | 2 | 484 | −450 | −0 | 2 | 4 | 159 | 138 | −4 | 4 | 4 | 187 | −164 | 11 | 1 | 1 | 256 | −207 |
| −8 | 0 | 2 | 652 | −687 | 2 | 2 | 4 | 426 | 406 | −6 | 4 | 4 | 288 | 297 | −11 | 1 | 1 | 688 | −698 |
| −10 | 0 | 2 | 182 | −153 | −2 | 2 | 4 | 277 | −273 | 8 | 4 | 4 | 250 | 274 | 13 | 1 | 1 | 476 | 435 |
| −12 | 0 | 2 | 257 | −203 | 4 | 2 | 4 | 316 | −293 | −8 | 4 | 4 | 158 | −150 | −15 | 1 | 1 | 527 | 544 |
| 14 | 0 | 2 | 209 | 189 | −4 | 2 | 4 | 236 | −245 | 10 | 4 | 4 | 261 | −286 | 1 | 1 | 3 | 629 | 642 |
| −14 | 0 | 2 | 480 | −439 | 6 | 2 | 4 | 292 | −280 | −10 | 4 | 4 | 256 | −273 | −1 | 1 | 3 | 301 | −312 |
| −0 | 0 | 4 | 745 | −755 | 8 | 2 | 4 | 351 | 346 | −0 | 4 | 6 | 250 | −250 | 3 | 1 | 3 | 232 | −217 |
| −2 | 0 | 4 | 665 | 665 | −8 | 2 | 4 | 406 | 414 | 2 | 4 | 6 | 379 | 385 | −3 | 1 | 3 | 308 | −305 |
| 4 | 0 | 4 | 712 | 778 | 10 | 2 | 4 | 308 | 289 | 4 | 4 | 6 | 167 | 185 | 5 | 1 | 3 | 115 | −112 |
| −4 | 0 | 4 | 1143 | 1330 | −10 | 2 | 4 | 423 | 439 | −4 | 4 | 6 | 364 | 375 | −5 | 1 | 3 | 621 | 714 |
| 6 | 0 | 4 | 324 | 303 | −14 | 2 | 4 | 158 | −186 | 6 | 4 | 6 | 359 | −368 | 7 | 1 | 3 | 909 | 1072 |
| −6 | 0 | 4 | 260 | −222 | −0 | 2 | 6 | 529 | −541 | −0 | 4 | 8 | 173 | −141 | −7 | 1 | 3 | 266 | −272 |
| 8 | 0 | 4 | 214 | −197 | 2 | 2 | 6 | 368 | 325 | 2 | 4 | 8 | 167 | −174 | 9 | 1 | 3 | 353 | 322 |
| −8 | 0 | 4 | 543 | −566 | −2 | 2 | 6 | 610 | −602 | −2 | 4 | 8 | 282 | 280 | −9 | 1 | 3 | 843 | −916 |
| 10 | 0 | 4 | 310 | −325 | 4 | 2 | 6 | 282 | 236 | −3 | 5 | 0 | 274 | 264 | 11 | 1 | 3 | 775 | −796 |
| −14 | 0 | 4 | 246 | 207 | −4 | 2 | 6 | 162 | 149 | −5 | 5 | 0 | 458 | 450 | −11 | 1 | 3 | 349 | 321 |
| −0 | 0 | 6 | 574 | 538 | 6 | 2 | 6 | 246 | −219 | −7 | 5 | 0 | 199 | 157 | 13 | 1 | 3 | 277 | −258 |
| 2 | 0 | 6 | 743 | −723 | −6 | 2 | 6 | 309 | 296 | −9 | 5 | 0 | 387 | −357 | −13 | 1 | 3 | 744 | 798 |
| −2 | 0 | 6 | 1020 | 1011 | −0 | 2 | 8 | 340 | −302 | −11 | 5 | 0 | 379 | −336 | 1 | 1 | 5 | 163 | −156 |
| 4 | 0 | 6 | 479 | −419 | 2 | 2 | 8 | 416 | −398 | −13 | 5 | 0 | 217 | 190 | 3 | 1 | 5 | 434 | 402 |
| −4 | 0 | 6 | 561 | −503 | −2 | 2 | 8 | 345 | 310 | 1 | 5 | 2 | 467 | −408 | −3 | 1 | 5 | 431 | 381 |
| 6 | 0 | 6 | 248 | 206 | 4 | 2 | 8 | 266 | 244 | −1 | 5 | 2 | 444 | 416 | 5 | 1 | 5 | 213 | −180 |
| −6 | 0 | 6 | 757 | −785 | 6 | 2 | 8 | 225 | 269 | 3 | 5 | 2 | 276 | −255 | −5 | 1 | 5 | 731 | −778 |
| 10 | 0 | 6 | 146 | −133 | −1 | 3 | 0 | 523 | −546 | −3 | 5 | 2 | 641 | 633 | 7 | 1 | 5 | 454 | −423 |
| −0 | 0 | 8 | 596 | 547 | −3 | 3 | 0 | 1036 | 978 | −5 | 5 | 2 | 373 | −352 | −7 | 1 | 5 | 740 | −823 |
| 2 | 0 | 8 | 743 | 716 | −5 | 3 | 0 | 577 | −644 | −7 | 5 | 2 | 657 | −652 | 9 | 1 | 5 | 470 | 460 |
| −2 | 0 | 8 | 487 | −442 | −7 | 3 | 0 | 791 | −881 | 9 | 5 | 2 | 170 | 153 | −9 | 1 | 5 | 491 | 493 |
| 4 | 0 | 8 | 294 | −286 | −9 | 3 | 0 | 883 | 925 | 1 | 5 | 4 | 586 | 668 | 11 | 1 | 5 | 357 | 325 |
| −4 | 0 | 8 | 269 | −240 | −11 | 3 | 0 | 693 | 667 | −1 | 5 | 4 | 462 | 485 | −11 | 1 | 5 | 565 | 569 |
| 6 | 0 | 8 | 464 | −455 | −13 | 3 | 0 | 535 | −520 | −3 | 5 | 4 | 289 | −319 | −13 | 1 | 5 | 264 | −245 |
| −6 | 0 | 8 | 364 | 347 | −15 | 3 | 0 | 285 | −355 | 5 | 5 | 4 | 264 | −286 | 1 | 1 | 7 | 249 | 194 |
| −1 | 1 | 0 | 238 | −229 | 1 | 3 | 2 | 502 | −451 | −5 | 5 | 4 | 272 | −281 | 3 | 1 | 7 | 312 | 270 |
| −3 | 1 | 0 | 261 | −317 | −1 | 3 | 2 | 312 | 287 | 7 | 5 | 4 | 132 | −150 | −3 | 1 | 7 | 510 | −451 |
| −5 | 1 | 0 | 137 | −140 | −3 | 3 | 2 | 646 | −674 | 11 | 5 | 4 | 119 | 223 | 5 | 1 | 7 | 321 | 290 |
| −7 | 1 | 0 | 265 | 267 | 5 | 3 | 2 | 779 | 761 | 0 | 6 | 0 | 798 | 803 | −5 | 1 | 7 | 369 | −332 |
| −9 | 1 | 0 | 365 | −305 | −5 | 3 | 2 | 602 | −614 | −2 | 6 | 0 | 135 | −126 | 7 | 1 | 7 | 230 | −195 |
| −11 | 1 | 0 | 586 | −553 | 7 | 3 | 2 | 355 | −339 | −4 | 6 | 0 | 810 | −824 | −7 | 1 | 7 | 430 | 403 |
| −13 | 1 | 0 | 225 | 177 | −7 | 3 | 2 | 976 | 1117 | −8 | 6 | 0 | 276 | 252 | 9 | 1 | 7 | 328 | −298 |
| −15 | 1 | 0 | 281 | 257 | 9 | 3 | 2 | 602 | −588 | −0 | 6 | 2 | 143 | −126 | −9 | 1 | 7 | 351 | 334 |
| −1 | 1 | 2 | 193 | 163 | −9 | 3 | 2 | 613 | 596 | 2 | 6 | 2 | 843 | 832 | −0 | 2 | 1 | 1566 | 1473 |
| 3 | 1 | 2 | 535 | 557 | 11 | 3 | 2 | 423 | 386 | −2 | 6 | 2 | 763 | −710 | 2 | 2 | 1 | 954 | −921 |
| −3 | 1 | 2 | 739 | 802 | −11 | 3 | 2 | 662 | −734 | 4 | 6 | 2 | 284 | 244 | −2 | 2 | 1 | 1275 | 1219 |
| 5 | 1 | 2 | 189 | −184 | 13 | 3 | 2 | 523 | 503 | −4 | 6 | 2 | 266 | 237 | 4 | 2 | 1 | 331 | −306 |
| −5 | 1 | 2 | 228 | 231 | −13 | 3 | 2 | 316 | −279 | 6 | 6 | 2 | 381 | −342 | −4 | 2 | 1 | 1126 | −1084 |
| 7 | 1 | 2 | 120 | −71 | 1 | 3 | 4 | 372 | −366 | −6 | 6 | 2 | 537 | 522 | 6 | 2 | 1 | 767 | 804 |
| −7 | 1 | 2 | 314 | −316 | −1 | 3 | 4 | 213 | −195 | −0 | 6 | 4 | 624 | −697 | −6 | 2 | 1 | 415 | −444 |
| 9 | 1 | 2 | 590 | 600 | 3 | 3 | 4 | 480 | −445 | 2 | 6 | 4 | 316 | −335 | 8 | 2 | 1 | 292 | 246 |
| −9 | 1 | 2 | 166 | −163 | −3 | 3 | 4 | 218 | −203 | −2 | 6 | 4 | 162 | 160 | −8 | 2 | 1 | 486 | 484 |
| −11 | 1 | 2 | 357 | 317 | 5 | 3 | 4 | 395 | 391 | 4 | 6 | 4 | 360 | 406 | −10 | 2 | 1 | 162 | 141 |
| 13 | 1 | 2 | 393 | −385 | −5 | 3 | 4 | 543 | 572 | −4 | 6 | 4 | 412 | 391 | −12 | 2 | 1 | 158 | 157 |
| −13 | 1 | 2 | 300 | 270 | 7 | 3 | 4 | 562 | 563 | 6 | 6 | 4 | 87 | 152 | 14 | 2 | 1 | 193 | −182 |
| 15 | 1 | 2 | 194 | 206 | −7 | 3 | 4 | 399 | 386 | −6 | 6 | 4 | 199 | −204 | −14 | 2 | 1 | 241 | 219 |
| −15 | 1 | 2 | 158 | −135 | 9 | 3 | 4 | 189 | −187 | 8 | 6 | 4 | 167 | −188 | −0 | 2 | 3 | 662 | 716 |
| 1 | 1 | 4 | 298 | −287 | −9 | 3 | 4 | 617 | −643 | −8 | 6 | 4 | 244 | −235 | 2 | 2 | 3 | 1112 | 1063 |
| −1 | 1 | 4 | 278 | 273 | 11 | 3 | 4 | 439 | −421 | −1 | 7 | 0 | 225 | 210 | −2 | 2 | 3 | 1594 | −1632 |
| −5 | 1 | 4 | 515 | −573 | −11 | 3 | 4 | 297 | −247 | −3 | 7 | 0 | 261 | −237 | 4 | 2 | 3 | 677 | −692 |
| 7 | 1 | 4 | 539 | −571 | −13 | 3 | 4 | 480 | 521 | −7 | 7 | 0 | 327 | 328 | −4 | 2 | 3 | 654 | −716 |
| −7 | 1 | 4 | 137 | −163 | 1 | 3 | 6 | 82 | 94 | −9 | 7 | 0 | 112 | 125 | 6 | 2 | 3 | 467 | −487 |
| −9 | 1 | 4 | 246 | 233 | 3 | 3 | 6 | 177 | −157 | 1 | 7 | 2 | 155 | 159 | −6 | 2 | 3 | 602 | 691 |
| 11 | 1 | 4 | 379 | 381 | −3 | 3 | 6 | 282 | 240 | −1 | 7 | 2 | 530 | −537 | 8 | 2 | 3 | 225 | 215 |
| 13 | 1 | 4 | 178 | −167 | 5 | 3 | 6 | 462 | −419 | −3 | 7 | 2 | 336 | −312 | −10 | 2 | 3 | 273 | −237 |
| −13 | 1 | 4 | 284 | −260 | −5 | 3 | 6 | 215 | 195 | 5 | 7 | 2 | 345 | −338 | −12 | 2 | 3 | 189 | 154 |
| −1 | 1 | 6 | 367 | 314 | 7 | 3 | 6 | 185 | 158 | −5 | 7 | 2 | 333 | 333 | 14 | 2 | 3 | 116 | 108 |
| −3 | 1 | 6 | 300 | −231 | −7 | 3 | 6 | 537 | −541 | 9 | 7 | 2 | 177 | 192 | −14 | 2 | 3 | 206 | −194 |
| 5 | 1 | 6 | 447 | 405 | 9 | 3 | 6 | 534 | 530 | 1 | 7 | 4 | 399 | −451 | −0 | 2 | 5 | 867 | −921 |
| −7 | 1 | 6 | 476 | 439 | −9 | 3 | 6 | 126 | −127 | 3 | 7 | 4 | 225 | 235 | 2 | 2 | 5 | 355 | 308 |
| 9 | 1 | 6 | 384 | −400 | −11 | 3 | 6 | 549 | 663 | −3 | 7 | 4 | 387 | 445 | 4 | 2 | 5 | 867 | 910 |
| −11 | 1 | 6 | 308 | −286 | −1 | 3 | 8 | 143 | 139 | 5 | 7 | 4 | 270 | 336 | −4 | 2 | 5 | 753 | 788 |
| 1 | 1 | 8 | 116 | 141 | −5 | 3 | 8 | 440 | −457 | 7 | 7 | 4 | 119 | −163 | 8 | 2 | 5 | 337 | −304 |
| 3 | 1 | 8 | 163 | −150 | −0 | 4 | 0 | 300 | −278 | −0 | 8 | 0 | 423 | −413 | −8 | 2 | 5 | 268 | −247 |
| 5 | 1 | 8 | 170 | −151 | −4 | 4 | 0 | 319 | 342 | −2 | 8 | 0 | 205 | −179 | −10 | 2 | 5 | 149 | 179 |
| −5 | 1 | 8 | 312 | 283 | −6 | 4 | 0 | 205 | −172 | −4 | 8 | 0 | 248 | 228 | 2 | 2 | 7 | 602 | −595 |
| 7 | 1 | 8 | 205 | 233 | −8 | 4 | 0 | 373 | −376 | −6 | 8 | 0 | 310 | 256 | −2 | 2 | 7 | 482 | 474 |
| −0 | 2 | 0 | 1254 | −1326 | −10 | 4 | 0 | 100 | 80 | −8 | 8 | 0 | 149 | −141 | −4 | 2 | 7 | 143 | −124 |
| −2 | 2 | 0 | 341 | −368 | −14 | 4 | 0 | 183 | −194 | −0 | 8 | 2 | 177 | 134 | 6 | 2 | 7 | 403 | 401 |
| −4 | 2 | 0 | 685 | 867 | −0 | 4 | 2 | 383 | 355 | 2 | 8 | 2 | 207 | −183 | −6 | 2 | 7 | 430 | −414 |
| −6 | 2 | 0 | 439 | 479 | 2 | 4 | 2 | 388 | −369 | −2 | 8 | 2 | 296 | 282 | −0 | 2 | 9 | 332 | 466 |
| −8 | 2 | 0 | 198 | −167 | −2 | 4 | 2 | 612 | 641 | 4 | 8 | 2 | 298 | −195 | −1 | 3 | 1 | 310 | 293 |
| −12 | 2 | 0 | 132 | 117 | −4 | 4 | 2 | 161 | −149 | −4 | 8 | 2 | 187 | 187 | 3 | 3 | 1 | 1008 | −956 |
| −0 | 2 | 2 | 298 | 253 | 6 | 4 | 2 | 385 | 368 | 6 | 8 | 2 | 143 | 139 | −3 | 3 | 1 | 141 | −149 |

TABLE 3. (*Continued.*)

| *h* | *k* |  | $\lvert F_o\rvert$ | $F_c$ | *h* | *k* | *l* | $\lvert F_o\rvert$ | $F_c$ | *h* | *k* | *l* | $\lvert F_o\rvert$ | $F_c$ |  | *k* |  | $\lvert F_o$ | $F_c$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 5 | 3 | 1 | 577 | −534 | −4 | 4 | 1 | 598 | 573 | 3 | 5 | 1 | 499 | 417 | 8 | 6 | 3 | 27 | −302 |
| −5 | 3 | 1 | 159 | −139 | −6 | 4 | 1 | 945 | 994 | −3 | 5 | 1 | 459 | 386 | −8 | 6 | 3 | 240 | 244 |
| 7 | 3 | 1 | 211 | 199 | 8 | 4 | 1 | 427 | −413 | 5 | 5 | 1 | 740 | −647 | −1 | 7 | 1 | 479 | −436 |
| 1 | 3 | 3 | 230 | 228 | −10 | 4 | 1 | 426 | −402 | 7 | 5 | 1 | 155 | −165 | 3 | 7 | 1 | 380 | 347 |
| 3 | 3 | 3 | 344 | 321 | 12 | 4 | 1 | 215 | 203 | −7 | 5 | 1 | 885 | −832 | 5 | 7 | 1 | 325 | 280 |
| −3 | 3 | 3 | 292 | 254 | 14 | 4 | 1 | 234 | 288 | 9 | 5 | 1 | 555 | 581 | −5 | 7 | 1 | 340 | 317 |
| 5 | 3 | 3 | 348 | −330 | −0 | 4 | 3 | 522 | −534 | −11 | 5 | 1 | 554 | 515 | 9 | 7 | 1 | 369 | −354 |
| −5 | 3 | 3 | 262 | 249 | 2 | 4 | 3 | 1083 | −1218 | 13 | 5 | 1 | 333 | −424 | 1 | 7 | 3 | 256 | −278 |
| 7 | 3 | 3 | 159 | −169 | −2 | 4 | 3 | 790 | 880 | 1 | 5 | 3 | 225 | −214 | 3 | 7 | 3 | 174 | −167 |
| −7 | 3 | 3 | 250 | 259 | −4 | 4 | 3 | 495 | 492 | −1 | 5 | 3 | 232 | 220 | −3 | 7 | 3 | 335 | 329 |
| 9 | 3 | 3 | 254 | 255 | 6 | 4 | 3 | 447 | 477 | 3 | 5 | 3 | 447 | 405 | −5 | 7 | 3 | 233 | 199 |
| −9 | 3 | 3 | 258 | 228 | −6 | 4 | 3 | 455 | −421 | −3 | 5 | 3 | 242 | 229 | 7 | 7 | 3 | 277 | 326 |
| 11 | 3 | 3 | 126 | 110 | 8 | 4 | 3 | 199 | −216 | −5 | 5 | 3 | 589 | −562 | −7 | 7 | 3 | 241 | −246 |
| 13 | 3 | 3 | 120 | 94 | −8 | 4 | 3 | 380 | −375 | 7 | 5 | 3 | 414 | −376 | −0 | 8 | 1 | 443 | 378 |
| −13 | 3 | 3 | 114 | −116 | 10 | 4 | 3 | 178 | −175 | 9 | 5 | 3 | 145 | −150 | 2 | 8 | 1 | 484 | −478 |
| 1 | 3 | 5 | 332 | −294 | −0 | 4 | 5 | 831 | 976 | −9 | 5 | 3 | 610 | 628 | −2 | 8 | 1 | 336 | 196 |
| −1 | 3 | 5 | 365 | −337 | −2 | 4 | 5 | 177 | 132 | 11 | 5 | 3 | 337 | 354 | 4 | 8 | 1 | 310 | −303 |
| −5 | 3 | 5 | 265 | 245 | 4 | 4 | 5 | 723 | −870 | −2 | 6 | 1 | 211 | 207 | −4 | 8 | 1 | 446 | −412 |
| 7 | 3 | 5 | 211 | −215 | −4 | 4 | 5 | 392 | −349 | 4 | 6 | 1 | 165 | 146 | 6 | 8 | 1 | 260 | 245 |
| −9 | 3 | 5 | 157 | −163 | 8 | 4 | 5 | 418 | 436 | 6 | 6 | 1 | 215 | −205 | −8 | 8 | 1 | 165 | 198 |
| 1 | 3 | 7 | 297 | −260 | −8 | 4 | 5 | 158 | 156 | −6 | 6 | 1 | 488 | −432 | −0 | 8 | 3 | 209 | 209 |
| −1 | 3 | 7 | 309 | 308 | −10 | 4 | 5 | 142 | 150 | 8 | 6 | 1 | 155 | 151 | 2 | 8 | 3 | 254 | 250 |
| 3 | 3 | 7 | 163 | −166 | −0 | 4 | 7 | 147 | −126 | −8 | 6 | 1 | 253 | −221 | −2 | 8 | 3 | 277 | −249 |
| −3 | 3 | 7 | 314 | 297 | 2 | 4 | 7 | 359 | 446 | 10 | 6 | 1 | 360 | 400 | 4 | 8 | 3 | 202 | −207 |
| 5 | 3 | 7 | 201 | 187 | −2 | 4 | 7 | 412 | −461 | −10 | 6 | 1 | 377 | 349 | −6 | 8 | 3 | 280 | 335 |
| −9 | 3 | 7 | 124 | 125 | 6 | 4 | 7 | 430 | −437 | −0 | 6 | 3 | 265 | 230 | 1 | 9 | 1 | 181 | 180 |
| −0 | 4 | 1 | 470 | −387 | −6 | 4 | 7 | 219 | 225 | 2 | 6 | 3 | 123 | 89 | −1 | 9 | 1 | 483 | 481 |
| 2 | 4 | 1 | 408 | 370 | −8 | 4 | 7 | 139 | 133 | −2 | 6 | 3 | 202 | −189 | 3 | 9 | 1 | 336 | −386 |
| −2 | 4 | 1 | 458 | −442 | 1 | 5 | 1 | 108 | 113 | 4 | 6 | 3 | 153 | 155 |  |  |  |  |  |
| 4 | 4 | 1 | 641 | 622 | −1 | 5 | 1 | 633 | −592 | −4 | 6 | 3 | 454 | −476 |  |  |  |  |  |

FIG. 1. *The structure projected along* [001]. *Large circles represent potassium ions, medium circles sulphur atoms, and small circles oxygen atoms. Atoms which lie between* $z = 0$ *and* $z = \frac{1}{2}$ *are shown as single circles and those between* $z = \frac{1}{2}$ *and* $z = 1$ *as double circles. The numbers are distances in* Å *from the potassium to the neighbours indicated by the dotted lines.*

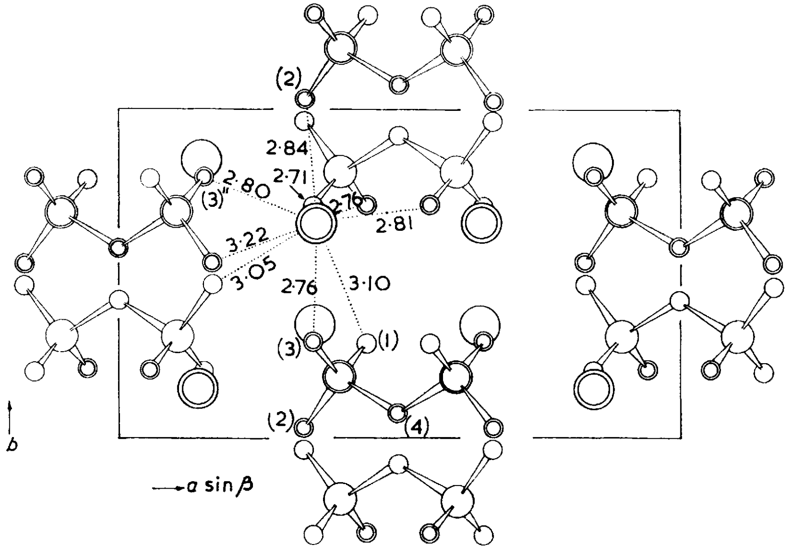


TABLE 4. *Atomic co-ordinates of the anion corrected for rotational oscillation* (*all in* Å).

|  | S | O(1) | O(2) | O(3) | O(4) |
|---|---|---|---|---|---|
| *X′* ........................... | 4·658 | 5·279 | 3·865 | 4·001 | 5·879 |
| *Y′* ........................... | 1·337 | 2·101 | 0·232 | 2·168 | 0·567 |
| *Z′* ........................... | 4·656 | 3·609 | 4·222 | 5·642 | 5·444 |

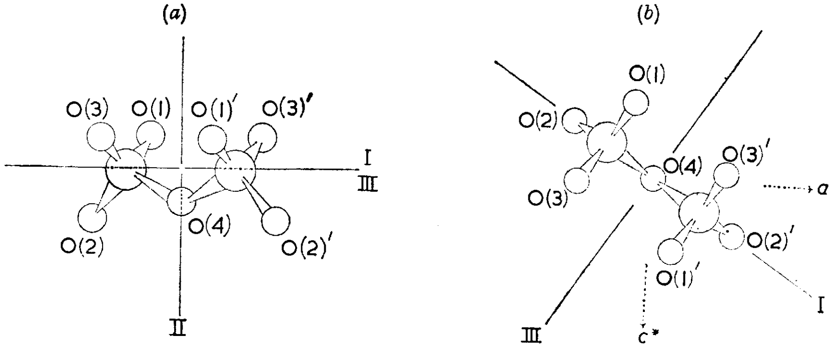
TABLE 5. *Bond lengths* (Å) *and angles in the pyrosulphate ion.*

|  |  |  |
|---|---|---|
| S–O(1) | 1·438 ± 0·007 | 1·437 ± 0·004 |
| S–O(2) | 1·428 ± 0·007 |  |
| S–O(3) | 1·447 ± 0·007 |  |
| S–O(4) | 1·645 ± 0·005 |  |

|  |  |  |
|---|---|---|
| O(1)–S–O(2) | 115·5° | all ±0·4° |
| O(1)–S–O(3) | 112·8 |  |
| O(2)–S–O(3) | 113·6 |  |
| O(1)–S–O(4) | 106·1 |  |
| O(2)–S–O(4) | 101·3 |  |
| O(3)–S–O(4) | 106·2 |  |
| S–O(4)–S | 124·2 ± 0·5° |  |

as illustrated in Fig. 2. Solution of the appropriate equations [8] gave the mean-square amplitudes of translation of the ion as 0·0171 Å$^2$ parallel to I, 0·0070 Å$^2$ parallel to II, and 0·0087 Å$^2$ parallel to III; for the rotational oscillations the r.m.s. angular displacements were 6·4° about I, 2·8° about II, and 3·3° about III. The atomic co-ordinates corrected for error due to rotational oscillation are shown, with respect to the orthogonal system, in Table 4. These corrections increased the bond lengths by 0·006 or 0·007 Å and, as the corrections are small, the error in them caused by assuming that the ion is rigid is negligible.

FIG. 2. *A pyrosulphate anion viewed (a) along the c axis and (b) down the b axis of the crystal. The directions of the axes of inertia are indicated by full lines, while the orientation of (b) with respect to the crystallographic axes is indicated by dotted lines.*



*Interatomic Distances and Angles.*—From the co-ordinates in Table 4, the bond lengths and angles were calculated and are shown, with their standard deviations, in Table 5, where the mean of the chemically indistinguishable bond lengths is also given with its standard deviation. In Fig. 1 the distances, less than 3·5 Å, from the potassium ion to its neighbours are shown. The shortest oxygen–oxygen distance is 3·04 Å from O(2) to O(3)″ [related to O(3) by a screw axis at $\frac{1}{4}$, $y$, $\frac{1}{4}$].

## DISCUSSION

The results show unequivocally that the pyrosulphate ion is bent, the bridging angle being 124·2° ± 0·5°. There is no important difference between the dimensions of the pyrosulphate and the bipyrosulphate ion,[2] but the accuracy of the results for the latter is inadequate to permit a detailed comparison.

As has been found in several other compounds containing the group $X{\cdot}SO_3{}^{n-}$, the angles about the sulphur atom have trigonal rather than tetrahedral symmetry, the X–S–O angles being less than the tetrahedral angle, and the O–S–O angles greater. The distortion of the expected configuration probably arises from repulsion between the charged oxygen atoms.

Detailed comparison of our results with those of comparable accuracy for potassium ethyl sulphate [3] and potassium iminodisulphonate [6] provides some interesting and unexpected results. The corresponding bond lengths and their standard deviations in the three anions are:

$$^{*}\,C_2H_5\text{–}O\,\frac{1{\cdot}603}{(0{\cdot}007)}\,S\,\frac{1{\cdot}464}{(0{\cdot}004)}\,O_3$$

$$O_3S\text{–}O\,\frac{1{\cdot}645}{(0{\cdot}005)}\,S\,\frac{1{\cdot}437}{(0{\cdot}004)}\,O_3$$

$$O_3S\text{–}NH\,\frac{1{\cdot}655}{(0{\cdot}007)}\,S\,\frac{1{\cdot}447}{(0{\cdot}005)}\,O_3$$

* These differ slightly from the published values [3] because they have now been corrected more accurately for rotational oscillation on the assumption that the ion is a rigid body.

[8] Cruickshank, *Acta Cryst.*, 1956, **9**, 754.

In the pyrosulphate ion the difference between the distances from sulphur to shared and unshared oxygen atoms is greater than in the ethyl sulphate. The possibility that this difference arises through random errors is statistically extremely remote. More surprisingly, there is a significant difference between the S–O lengths in the ethyl sulphate and in the pyrosulphate ions, and correspondingly also in the S–O bonds; for these $\Delta/\sigma = 4{\cdot}8$ and $4{\cdot}5$ respectively (where $\Delta$ is the difference between the two lengths and $\sigma$ is the vector sum of their standard deviations), so that the chance that the lengths are equal is less than one in $10^5$. As the sulphur atom has the same environment in both ions, it seems reasonable to suppose that the $\sigma$-bond skeleton is the same. Hence the S–O bond in the ethyl sulphate is probably not a pure single bond. There are no significant differences between the dimensions of the isoelectronic ions pyrosulphate and iminodisulphonate, although the single-bond radii of oxygen and nitrogen differ by 0·04 Å. This suggests that the central bonds may not be pure single bonds, in agreement with Cruickshank's [9] theory that all the bonds have some double-bond character arising from overlap of the $p\pi$-orbitals on oxygen or nitrogen with the $d\pi$-orbitals of sulphur. Cruickshank's theory, which also explains the changes in the lengths of the S–O bonds, covers all the groups $XO_4^{n-}$ and $X_2O_7^{m-}$ (where X = Si, P, S, or Cl) and its application to the pyrosulphate ion will be given in more detail in his paper.[9]

As the bond lengths in the iminodisulphonate and pyrosulphate ions differ by only 0·01 Å, the differences in the unit-cell dimensions of the potassium salts must arise from differences in the interionic contacts. Fig. 1 shows the contacts from the potassium ion to its nine nearest neighbours, and in the Table below the corresponding values for the iminodisulphonate are given. In each compound the K···O distances have standard deviations of 0·01 Å, so that some of the differences are statistically highly significant. There appears to be no chemical explanation for these variations and they are not related simply to the changes in unit-cell dimensions.

*Comparison of interionic distances* (*all in* Å).

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $K_2S_2O_7$ ............ | 2·84 | 2·87 | 3·22 | 3·05 | 2·76 | 3·10 | 2·76 | 2·81 | 2·61 |
| $NH(SO_3)_2K_2$ ...... | 2·96 | 2·80 | 3·07 | 2·99 | 2·71 | 3·23 | 2·74 | 2·87 | 2·70 |

## EXPERIMENTAL

It was impossible to obtain pure $K_2S_2O_7$ from solution in sulphuric acid or oleum by any of the many methods tried; the crystalline products usually contained solvated sulphuric acid.

Crystals were finally obtained by heating "potassium octasulphate," $K_2O,8SO_3$, prepared by Weber's method,[5] in an oven to 450°, whereupon sulphur trioxide was liberated and a melt of the pyrosulphate formed. Slow cooling of the melt gave a deliquescent solid which was broken up under dry carbon tetrachloride. Several large lath-like crystals were formed which showed parallel extinction. One of these was cut to give two crystals of approximately square cross-section with their long axes parallel and perpendicular to the original long axis, *c*. Each crystal was sealed in a lithium borate glass capillary tube.

The unit-cell dimensions were determined by the Straumanis method. Equi-inclination Weissenberg photographs were taken about the three principal axes for all the layer lines accessible to copper $K_\alpha$ radiation. Of the 750 possible reflections, 483 gave measurable intensities. After correction for Lorentz and polarisation effects the intensities were correlated and their square roots extracted. An approximate scale factor was obtained by making $\sum|F_o| = \sum|F_{c'}|$ where $F_{c'}$ was the calculated structure factor for the iminodisulphonate.[6] The scale factor was one of the parameters in the least-squares refinement.

The scattering factors used were those of Tomiie and Stam [10] for S and of Berghuis *et al.*[11] for $K^+$ and O. Refinement was carried out by the method of least squares on the Leeds University Ferranti Pegasus computer with programmes [12] devised by Dr. D. W. J. Cruickshank and Miss D. E. Pilling. The function minimised is

$$R' = \sum w(|F_o| - |F_c|)^2$$

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[9] Cruickshank, in preparation.

[10] Tomiie and Stam, *Acta Cryst.*, 1958, **11**, 126.

[11] Berghuis, Haanappel, Potters, Loopstra, MacGillavry, and Veenendaal, *Acta Cryst.*, 1955, **8**, 478.

[12] Cruickshank and Pilling and in part Bujosa, Lovell, and Truter, "Proceedings of a Conference on Crystallographic Computing," Pergamon Press, 1960.

where $w$ is the weighting factor. After the first cycle (for which $w$ was taken as $1/|F_o|$) the value of $w$ was taken as $1/(8 + |F_o| + 0{\cdot}025|F_o|^2)$. This proved satisfactory by the criterion that $R'/n$, where $n$ is the number of planes within a given range of $|F_o|$, should be constant for different ranges.

Analysis of the thermal motion and calculation of the corrections for rotational oscillation were carried out on the Pegasus computer with programmes written by Mr. A Bujosa.[12]

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