

Reinvestigation of the Structure of Potassium Pyrosulfite, $K_2S_2O_5$

BY I-CHIA CHEN AND YU WANG*

Department of Chemistry, National Taiwan University, Taipei, Taiwan

(Received 31 March 1984; accepted 17 July 1984)

Abstract. $M_r = 444.63$, monoclinic, $P2_1/m$, $a = 6.921(1)$, $b = 6.160(1)$, $c = 7.537(1)$ Å, $\beta = 102.79(1)^\circ$, $V = 313.33$ Å³, $Z = 2$, $D_m = 2.36$, $D_x = 2.356$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.7093$ Å, $\mu = 20.94$ cm⁻¹, $F(000) = 188$, $T = 298$ K, $R = 0.040$ for 780 observed reflections. The molecule contains a plane symmetry (S–S–O) and a long S–S bond [2.2194(9) Å] between the thionite and thionate groups. The S–O distances are 1.4870(8) Å in the thionite group and 1.453(1) and 1.4602(8) Å in the thionate group. A comparison with other compounds containing the $S_2O_5^{2-}$ ion is made.

Introduction. The structure of the title compound has been reported by Lindqvist & Mörtzell (1957) using film data. They showed that the molecule has an unusually long S–S bond [2.209(7) Å]. We are particularly interested in different types of S–S bond. In order to obtain more accurate parameters we have reinvestigated the structure with diffractometer data.

Experimental. Crystal $0.13 \times 0.13 \times 0.3$ mm, CAD-4 diffractometer, unit cell: 17 reflections, 2θ range 40 to 50° . D_m by flotation ($\text{CHCl}_3/\text{CHBr}_3$). No absorption correction. $2\theta_{\text{max}} = 60^\circ$ ($-9 \leq h \leq 9$, $k \leq 8$, $l \leq 10$). Three standard reflections monitored every 0.5 h; variation 2%. 992 unique reflections, 780 observed with $I \geq \sigma(I)$. Atoms refined anisotropically, function minimized $\sum w(F_o - F_c)^2$; $R = 0.040$, $R_w = 0.023$, $S = 1.54$; weighting scheme from counting statistics. $(\Delta/\sigma)_{\text{max}} = 0.07$. Peaks on final $\Delta\rho$ map $+0.5$ to -0.6 e Å⁻³. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Programs from NRCC SDP PDP-11 package (Gabe & Lee, 1981).

Discussion. The atomic coordinates and equivalent isotropic temperature factors are listed in Table 1.† Our data confirm the previous work (Lindqvist & Mörtzell,

Table 1. Atomic coordinates and equivalent isotropic temperature factors (Å²) of potassium pyrosulfite

$$B_{\text{eq}} = \frac{1}{3}\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq}
K(1)	0.2131 (1)	0.25	0.93530 (5)	2.35 (2)
K(2)	0.6398 (1)	0.25	0.67278 (4)	1.79 (2)
S(1)	0.0291 (1)	0.25	0.3300 (1)	1.81 (2)
S(2)	0.7014 (1)	0.25	0.2384 (1)	1.57 (2)
O(1)	0.0741 (1)	0.0515 (1)	0.2343 (1)	2.44 (4)
O(2)	0.6350 (1)	0.0530 (1)	0.3147 (1)	2.77 (4)
O(3)	0.6555 (1)	0.25	0.0407 (1)	2.98 (8)

Table 2. Comparison between $(\text{NH}_4)_2\text{S}_2\text{O}_5$, $\text{K}_5(\text{HSO}_3)_3(\text{S}_2\text{O}_5)$ and $\text{K}_2\text{S}_2\text{O}_5$

	$(\text{NH}_4)_2\text{S}_2\text{O}_5$ (Baggio, 1971)	$\text{K}_5(\text{HSO}_3)_3(\text{S}_2\text{O}_5)$ (Magnusson, Johansson & Lindqvist, 1983)	$\text{K}_2\text{S}_2\text{O}_5$ (This work)
S(1)–S(2)*	2.170 (4) Å	2.226 (2) Å	2.2194 (9) Å
S(2)–O(3)	1.453 (7)	1.463 (3)	1.453 (1)
S(2)–O(2) (thionate)	1.455 (6)	1.462 (4)	1.4602 (8)
S(1)–O(1) (thionite)	1.495 (7)	1.489 (3)	1.4870 (8)
S(2)–S(1)–O(1)	98.5 (3)°	98.9 (1)°	99.12 (3)°
S(1)–S(2)–O(2)	105.1 (3)	105.5 (2)	105.47 (3)
S(1)–S(2)–O(3)	106.7 (3)	106.7 (1)	107.16 (5)
O(1)–S(1)–O(1)	111.2 (4)	112.3 (1)	110.63 (5)
O(2)–S(2)–O(2)	112.5 (4)	112.5 (1)	112.45 (5)
O(2)–S(2)–O(3)	112.8 (4)	110.5 (1)	112.78 (4)

* Atoms labeled according to this work.

1957), but the S–S bond is slightly longer. The S–S value of 2.2194(9) Å is significantly longer than the S–S single bond (2.046–2.052 Å) (Coppens, Yang, Blessing, Cooper & Larsen, 1977), but slightly shorter than that in $\text{ZnS}_2\text{O}_4\cdot\text{py}$ [2.386(2) Å] (Kiers & Vos, 1978). The bond length of S–O in the thionite group is 1.4870(8) Å, which is longer than the corresponding values in the thionate group 1.4602(8), 1.453(1) Å. A comparison of $\text{K}_5(\text{HSO}_3)_3(\text{S}_2\text{O}_5)$, $(\text{NH}_4)_2\text{S}_2\text{O}_5$ and $\text{K}_2\text{S}_2\text{O}_5$ is given in Table 2.

The authors would like to express their appreciation for the support of this work from the National Science Council for both the research grant and the use of the CAD-4 diffractometer.

* To whom correspondence should be addressed.

† Lists of anisotropic thermal parameters and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39625 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure, Deformation Density and Atomic Charges in Potassium Hydrogenperoxomonosulfate Monohydrate, $\text{KHSO}_5 \cdot \text{H}_2\text{O}$

BY E. O. SCHLEMPER, R. C. THOMPSON, C. KAY FAIR AND F. K. ROSS

Department of Chemistry, University of Missouri, Columbia, MO 65211, USA

AND E. H. APPELMAN AND L. J. BASILE

Department of Chemistry, Argonne National Laboratory, Argonne, IL, USA

(Received 9 January 1984; accepted 20 July 1984)

Abstract. $M_r = 170.2$, monoclinic, $C2/c$, $a = 18.226$ (3), $b = 7.662$ (1), $c = 7.420$ (5) Å, $\beta = 90.83$ (2)°, $V = 1036.1$ (8) Å³, $Z = 8$, $D_x = 2.182$ (1) g cm⁻³, Mo $K\alpha$, $\lambda = 0.7107$ Å, $\mu = 13.5$ cm⁻¹, $F(000) = 608$, $T = 130$ (2) K, $R = 0.023$, 4144 independent reflections. Sulfur has tetrahedral coordination with the average sulfate-type S–O distance of 1.445 (5) Å, the peroxo S–O distance of 1.634 (1) Å, the peroxo O–O distance of 1.463 (1) Å and the S–O–O–H torsion angle of 87 (1)°. Electron deformation density maps reveal the expected bonding features and lone-pair density. Atomic charge calculations are presented and compared with theoretical calculations for $\text{S}_2\text{O}_8^{2-}$.

Introduction. Although potassium hydrogenperoxomonosulfate is sold in an impure form commercially, pure salts of peroxomonosulfate have not been previously available. We have developed a procedure involving hydrolysis of $\text{K}_2\text{S}_2\text{O}_8$ that affords highly pure $\text{KHSO}_5 \cdot \text{H}_2\text{O}$. This product yielded crystals suitable for the first determination of the structure of the HSO_5^- ion. An earlier X-ray study (Kyrki & Lappalainen, 1965) reported an orthorhombic unit cell but did not include a structure determination.

Because of the difference in chemistry of oxidation–reduction in comparison with H_2O_2 [i.e. a tendency for peroxide-bond breakage in HSO_5^- upon oxidation (Thompson, 1981)], we were interested not only in comparison of the O–O distance with that in $\text{S}_2\text{O}_8^{2-}$ and in H_2O_2 but also a comparison of deformation density with that observed for H_2O_2 (Savariault & Lehmann, 1980), for SO_4^{2-} (Kirfel & Will, 1980, 1981), and for $\text{S}_2\text{O}_3^{2-}$ (Elerman, Bats & Fuess, 1983).

Experimental. Concentrated solution of sodium peroxodisulfate was converted to the acid by passage through a column of Dowex 50X8 cation-exchange resin in the hydrogen form. The solution was concentrated in a rotary evaporator and hydrolyzed by heating at 323 K until no peroxodisulfate was detected. The solution was then neutralized to pH 3.5 by addition of KHCO_3 in an ice bath, filtered and freeze-dried. The residue was redissolved in a small quantity of water at room temperature and filtered. The filtrate was chilled in an ice bath and the crystals that formed were filtered, washed with a small quantity of absolute ethanol and dried between sheets of filter paper. Iodometric analysis indicated a bulk composition approximating $\text{KHSO}_5 \cdot \text{H}_2\text{O}$. Plate-like crystal; $\sim 0.07 \times 0.23 \times 0.27$ mm; Enraf–Nonius CAD-4 diffractometer; T maintained by constant flow of N_2 gas; 24 reflections, $\theta = 9$ – 15° , used for cell dimensions; empirical ψ -scan absorption (range of transmission = 0.83–1.00, average = 0.95); graphite monochromator; max. $2\theta = 89^\circ$; hkl and $h\bar{k}l$ ($2\theta = 3$ – 89°), $\bar{h}kl$ and $\bar{h}\bar{k}l$ ($2\theta = 2$ – 27.5°); 3 standard reflections every 3600 s ($\sim 1\%$ variation, no correction); 5842 reflections measured; θ – 2θ scan method; scan speed to obtain 2% statistics to a maximum scan time of 120 s; 4144 unique; $R_{\text{int}} = 0.024$ (measures agreement of the lower-angle data); 933 reflections with $F_o^2 < 2.0\sigma(F_o^2)$ considered unobserved; structure solved with *MULTAN* (Germain, Main & Woolfson, 1971) and difference Fourier syntheses; refinement minimized $\sum w(|F_o| - |F_c|)^2$; 85 variables (all positional parameters and anisotropic temperature factors except isotropic for hydrogen atoms); $R = 0.023$; $wR = 0.030$; $S = 1.21$; $w^{-1} = [\sigma_{\text{counting}}^2 + (0.03F_o^2)^2]/4F_o^2$; max. Δ/σ in last cycle = 0.20; max. difference density