

## Crystal Structure and Chemical Stabilization of the Triple Salt (KHSO<sub>5</sub>)<sub>2</sub> · KHSO<sub>4</sub> · K<sub>2</sub>SO<sub>4</sub>

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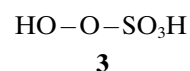
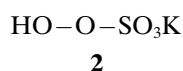
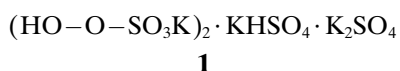
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The title compound, a versatile and chemically stabilized oxidant, which is used technologically on a large scale, builds up an intercalation-type of crystal structure with alternating sheets of sulfate and peroxomonosulfate anions, interspersed by the potassium cations. The sulfate ions are joined by a very short but nonetheless probably asymmetric hydrogen bond. At room temperature, the HSO<sub>5</sub><sup>-</sup> ions show dynamic orientational/conformational disorder in the area of the hydrogenperoxy group, which disappears at 100 K. The chemical stabilization of the triple salt is ascribed to shielding of the HSO<sub>5</sub><sup>-</sup> ions effected by the intercalation between the sulfate sheets and, furthermore, by the large and abundant K<sup>+</sup> ions of this potassium-rich compound.

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**Introduction.** – The ternary salt (KHSO<sub>5</sub>)<sub>2</sub> · KHSO<sub>4</sub> · K<sub>2</sub>SO<sub>4</sub> (**1**), the so-called ‘triple salt’, is a versatile and environmentally benign oxidant [1], which is commercially produced in large quantities and widely used for bleaching, cleaning, and disinfection purposes<sup>1)</sup>.

The salt **1** has also proved to be the oxidant of choice for the preparation of dioxiranes, which are themselves efficient oxidants for a large variety of preparatively most-valuable chemical transformations; in particular, 3,3-dimethyldioxirane may be readily obtained from acetone by exposure to **1** [2]. Compound **1** represents a convenient stabilized form of the simpler salt potassium hydrogenperoxomonosulfate KHSO<sub>5</sub> (**2**) and ultimately also of *Caro*’s acid H<sub>2</sub>SO<sub>5</sub> (**3**), a notoriously unstable and hazardous material. Crystal-structure analyses of **2** · H<sub>2</sub>O [3] and, remarkably, also of **3** [4a] have been accomplished. Preliminary X-ray-analysis results on **1** have been obtained previously, but it was merely communicated that, ‘despite problems of disorder’, HSO<sub>5</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, and HSO<sub>4</sub><sup>-</sup> species could be identified in the crystal with a very short H-bond connecting the sulfate and hydrogensulfate anions [3a]. Later on, another similarly limited, brief outline of the crystal-structure was documented [4b]. We deem it useful to report in the following the complete crystal-structure analysis of **1**




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<sup>1)</sup> Trade names: *Caroat* (Degussa), *Curox* (Peroxid-Chemie), *Oxone* (DuPont).

based on X-ray measurements at both ambient and low temperature<sup>2)</sup>). The nature of the disorder, the H-bonding pattern, and the structural basis of the chemical stabilization of **1** are considered to be of particular relevance.

**Results and Discussion.** – Large compact crystals of **1** of polyhedral shape could be easily obtained from H<sub>2</sub>O. Their space group is  $P2_1/a$  with two formula units in the unit cell<sup>2)</sup>. The crystals of **1** are structured by characteristic H-bonded building blocks comprising two central sulfate ions united through a strong H-bond and two terminal hydrogenperoxomono sulfate ions H-bonded to one each of the two sulfate species (Fig. 1). These H-bonded four-membered chains extend across (average) centers of symmetry and are seen to neatly correspond to one anionic formula unit. In the complete crystal structure of **1**, the H-bonded anionic molecular quartets are held together by the K<sup>+</sup> counter ions *via* Coulombic forces, without the interference of hydration H<sub>2</sub>O.

At room temperature the chiral hydrogenperoxomonosulfate ion of **1** is orientationally and conformationally disordered in the crystal. The disorder is chiefly located in the area of the peroxy group, which takes up two distinct unequally populated orientations and conformations, respectively. The ratio of the statistical weights of major and minor orientations results as 0.752:0.248 from the refinements. Both orientations correspond to enantiomeric HSO<sub>5</sub><sup>-</sup> conformations and are related by an approximate mirror plane (Fig. 1). The atomic positions of the SO<sub>3</sub> moiety as well as the H-atom of the peroxy group in both HOOSO<sub>3</sub><sup>-</sup> orientations do not differ much and could not be resolved in the refinements. Interestingly, on cooling to 100 K the disorder of the HSO<sub>5</sub><sup>-</sup> ions in the crystals of **1** disappears virtually completely with a relative population of the minor orientation estimated at less than *ca.* 4% (Fig. 1). A renewed X-ray measurement after rewarming the crystal to room temperature (over 2 h) reproduces the previously disordered situation. These observations, thus, correspond to a particularly clear and, as such, rather rare case of reversible dynamic disorder. Obviously, the unequal population of the HSO<sub>5</sub><sup>-</sup> orientations is due to the asymmetric environment in the crystal. Various combinations of rotational and conformational processes may be invoked to rationalize the reorientation mechanism of the HSO<sub>5</sub><sup>-</sup> ions, but the X-ray-diffraction data do not allow us to single out a specific sequence of elementary dynamic events. However, it may, nevertheless, be concluded that the key

<sup>2)</sup> Large polyhedral crystals from H<sub>2</sub>O; space group  $P2_1/a$  (No. 14),  $Z = 2$ , crystallographic symmetry of **1**,  $C_1$ . The X-ray intensities were measured on a four-circle diffractometer equipped with a CCD area detector applying Mo radiation ( $\lambda = 0.71073 \text{ \AA}$ ,  $\Theta_{\text{max}} = 30^\circ$ ). A crystal measuring *ca.*  $0.6 \times 0.6 \times 0.6 \text{ mm}^3$  was used. Structure solution was by direct methods (SHELXS97) and subsequent least-squares refinement (SHELXL97). The short H-bond uniting the sulfate ions across a center of symmetry was found to be unsymmetrical and disordered, and the bridging H-atom was refined with two half-occupied positions. Measurement at room temperature:  $a = 8.6154(4)$ ,  $b = 10.5991(5)$ ,  $c = 9.8293(5) \text{ \AA}$ ,  $\beta = 105.207(2)^\circ$ ,  $V = 866.14 \text{ \AA}^3$ ,  $d_x = 2.357 \text{ g cm}^{-3}$ ;  $R1 = 0.033$  including 2277 reflections with  $F_o > 4\sigma(F_o)$ ,  $wR2 = 0.081$  including all measured 2502 independent reflections ( $R_{\text{int}} = 0.029$ ); maximum residual electron density,  $\Delta\rho_{\text{max}} = 0.70 \text{ e \AA}^{-3}$ . Measurement at 100 K:  $a = 8.4994(2)$ ,  $b = 10.5305(2)$ ,  $c = 9.8208(2) \text{ \AA}$ ,  $\beta = 105.285(1)^\circ$ ,  $V = 847.90 \text{ \AA}^3$ ,  $d_x = 2.408 \text{ g cm}^{-3}$ ;  $R1 = 0.025$  (2414 reflections),  $wR2 = 0.063$  (2449 reflections,  $R_{\text{int}} = 0.031$ );  $\Delta\rho_{\text{max}} = 0.58 \text{ e \AA}^{-3}$ . Further details are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de) on quoting CSD-413073,413074.

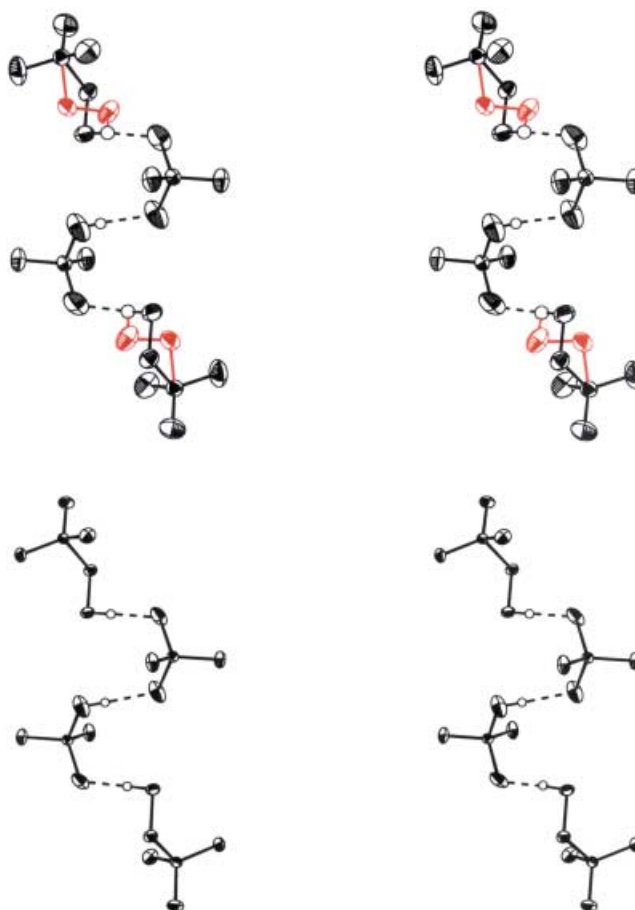


Fig. 1. Stereoview of an H-bonded four-membered chain of each two central sulfate and terminal peroxomonosulfate ions in the crystals of **1** (50% ellipsoids; isotropic temperature factors of H divided by 5; H-bonds dashed; *top*: room temperature, *below*: 100 K). The central H-bond uniting the sulfate ions represented as ordered in the diagram is, in fact, disordered across a (average) center of symmetry. The minor orientation (conformation) of the  $\text{HSO}_5^-$  ions, which are disordered at room temperature, is shown in red (see text).

enantiomerization step of the interconverting  $\text{HSO}_5^-$  orientations is of a conformational nature and corresponds to a torsional motion of the OH group around the O–O bond by ca.  $180^\circ$  (magnitude of the associated H–O–O–S torsion angle in both orientations roughly  $90^\circ$ ; see below). Possibly, this motion proceeds *via* a synplanar arrangement of the HOOS moiety since, in this way, the H-bond between the  $\text{HSO}_5^-$  and sulfate ions need not be disrupted.

The intramolecular geometry of the  $\text{HSO}_5^-$  ion in the crystals of the ‘triple salt’ **1** agrees well with that found in  $\mathbf{2} \cdot \text{H}_2\text{O}$  [3] and, not surprisingly, somewhat less well with that of **3** [4a]. The O–O distance amounts to 1.458(2) Å (all data given here from measurement at 100 K) and coincides with that observed in crystalline  $\text{H}_2\text{O}_2$  (1.458(2) Å

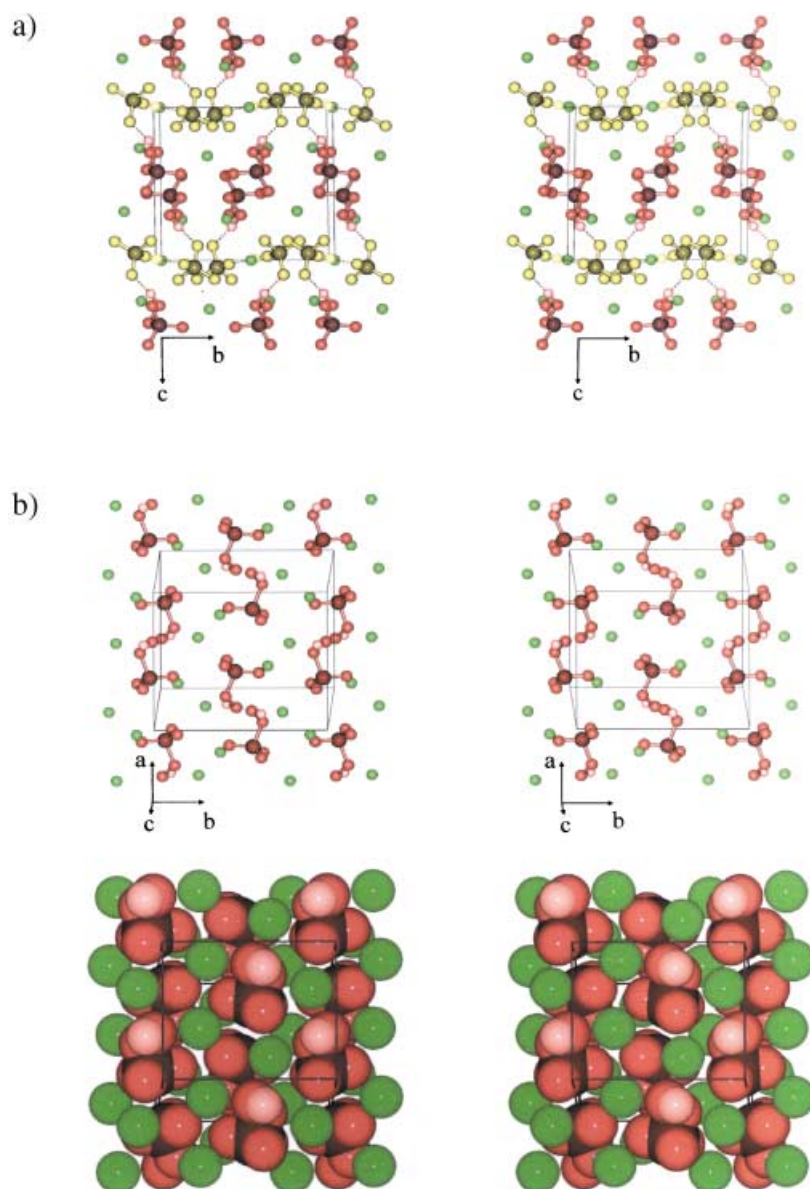


Fig. 2. a) *Ball-and-stick stereoview of the crystal structure of 1 at 100 K.*  $\text{H}(\text{SO}_4)_2^{2-}$ , yellow;  $\text{HSO}_5^-$  red;  $\text{K}^+$ , green; H-bonds between sulfate ions drawn as ordered although disordered in actual fact. The view is along the crystallographic  $a$  axis running in the plane of the alternating (horizontal) sheets of sulfate and peroxomonosulfate ions, respectively. Note the central peroxomonosulfate sheet intercalated between two sulfate sheets. b) *View along (reciprocal)  $c^*$  axis on to a sheet of  $\text{HSO}_5^-$  ions (red) interspersed with  $\text{K}^+$  ions (green).* *Top:* ball-and-stick, *below:* space-filling representation with Pauling, Van der Waals, and ionic radii. Note the shielding of the  $\text{HSO}_5^-$  ions by surrounding  $\text{K}^+$  ions in the space-filling diagram. The two views of the crystal structure shown transform into one another by a rotation of  $90^\circ$  around the horizontal  $b$  axis.

[5]). The S–O distance of the SOOH moiety is lengthened to 1.647(2) Å and exceeds the other S–O lengths (average 1.446 Å) by 0.20 Å; at the same time, the three O–S–O angles involving the peroxy O-atom are compressed (average 103.5°) relative to the tetrahedral value, whereas the three remaining O–S–O angles of the SO<sub>3</sub> moiety are correspondingly widened (average 114.7°), as if an incipient dissociation process of HSO<sub>5</sub><sup>-</sup> towards SO<sub>3</sub> and HOO<sup>-</sup> were to be observed. Expectedly, the S–O–O–H torsion angle is close to orthogonal (90(2)°).

With an observed O···O distance of 2.583(2) Å, the H-bond extending from the low-acidic OH function of the peroxy group of **1** to the sulfate ion is of average length (and strength). On the other hand, the H-bond uniting the sulfate ions across a (average) center of symmetry is short and strong as evidenced by an O···O distance of only 2.422(3) Å (2.429(3) Å at room temperature). Clearly, this H-bond benefits from the high negative charge of the H(SO<sub>4</sub>)<sub>2</sub><sup>3-</sup> units within which it is defined. For comparison, it is noted that the analogous H-bond in crystalline Na<sub>3</sub>H(SO<sub>4</sub>)<sub>2</sub> shows a similar O···O separation of 2.432(2) Å [6], whereas that in K<sub>3</sub>H(SO<sub>4</sub>)<sub>2</sub> is appreciably longer, 2.493(1) Å [7]; accordingly, the crystal structures of these salts are not isomorphous! Thus, despite the strength of the H-bond in H(SO<sub>4</sub>)<sub>2</sub><sup>3-</sup>, counterion and environmental influences on its length are not negligible. The question arises as to whether or not the bridging H-atom in H(SO<sub>4</sub>)<sub>2</sub><sup>3-</sup> is symmetrically placed between the two bonded O-atoms. Both in Na<sub>3</sub>H(SO<sub>4</sub>)<sub>2</sub> and K<sub>3</sub>H(SO<sub>4</sub>)<sub>2</sub>, the H-bond is reported to be unsymmetric [6][7], based on neutron-diffraction data for the Na salt. Our X-ray evidence on **1** tentatively points to this conclusion, too (H-bond disordered across center of symmetry with two half-populated locations of H; *Figs. 1* and *2*). However, a neutron-diffraction experiment would obviously also be required to settle this subtle problem more definitively for **1**.

A clue to the structural basis of the chemical stabilization of **1** relative to **2** should be provided by inspection of the crystal packing mode of **1**. *Fig. 2, a*, shows that the HSO<sub>5</sub><sup>-</sup> as well as the H(SO<sub>4</sub>)<sub>2</sub><sup>3-</sup> anions are arranged in alternating sheets (in the crystallographic *a, b* plane), interspersed by the K<sup>+</sup> cations. Thus, the chemically sensitive HSO<sub>5</sub><sup>-</sup> ions are intercalated between layers of chemically robust sulfate and K<sup>+</sup> species, which should confer significant shielding from attack by potential reducing agents. This shielding may be referred to as one-dimensional, which indeed is ineffective with respect to chemical attack *in* the plane of the HSO<sub>5</sub><sup>-</sup> sheets. However, as shown in *Fig. 2, b*, the K<sup>+</sup> ions in these latter sheets furnish additional shielding around the HSO<sub>5</sub><sup>-</sup> ions such that, altogether, a rather effective three-dimensional shielding ('insulation') is approached, which provides a convincing crystal-structure-based rationalization of the increased chemical stability of **1**. That this enhanced, *i.e.*, higher than one-dimensional, shielding of the HSO<sub>5</sub><sup>-</sup> ions can be realized in the crystals of **1** is clearly due to the triple salt's stoichiometric richness in K<sup>+</sup> and the comparatively large size of these cations. Recently, tetraphenylphosphonium hydrogenperoxomonosulfate was reported to be chemically well-stabilized since, here, the bulky cations assemble in the crystal to form segregated channels in which the HSO<sub>5</sub><sup>-</sup> ions are lined up [8]. Thus, in this case the hydrogenperoxomonosulfate anions are two-dimensionally shielded from chemical attack, ensuring effective protection.

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