The Active Principle of Caro's Acid, HSO_5^-: *X*-Ray Crystal Structure of $KHSO_5{\cdot}H_2O$

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The structure of HSO_5^-, the active component in Caro's acid, in the title compound, and in the triple salt $K_5(HSO_5)_2(HSO_4)(SO_4)$, has been determined and the location of the proton on the peroxo group established.

Caro's acid[1] is one of the strongest oxidants known (E° + 1.81 V[2]); its salts $KHSO_5{\cdot}H_2O$ (**1**) and the 'triple salt' $K_5(HSO_5)_2(HSO_4)(SO_4)$ (**2**) are also powerful oxidants. Compound (**2**) particularly is used in the bleaching industry. Owing to the difficulty of isolating crystalline H_2SO_5 and its highly explosive nature, no *X*-ray data are available on Caro's acid nor are they likely to become available. We present here the first crystal structure of a 'caroate,' $KHSO_5 \cdot H_2O$. We show that the Raman spectrum of (**1**) is similar to that of Caro's acid, so that it is very likely that the structure of HSO_5^- in (**1**) is close to that in the acid.

Crystals of (**1**) and (**2**) were prepared by an improvement of the methods given in the patent literature.[3] Reaction of oleum (20%, 18 cm^3) with 86% hydrogen peroxide (11 cm^3) at -5°C generated Caro's acid. A 50% aqueous solution of potassium carbonate (24 cm^3) was then carefully added at 0 °C to give colourless crystals of (**1**) which were re-crystallised from water. A similar method using twice the amount of carbonate gave (**2**).

Some preliminary *X*-ray diffraction data on (**1**) have been reported,[4] but because of the instability of the crystals a full structure determination was not attempted.

Crystal data: $KHSO_5{\cdot}H_2O$. The unit cell reported by Kyrki and Lappalainen[4] was orthorhombic, with a = 7.62, b = 18.35, c = 7.52 Å. We found a similarly dimensioned cell which, however, was monoclinic with a = 18.392(3), b = 7.701(1), c = 7.498(1) Å, β = 90.89(1)°, U = 1061.9 Å^3 (at 20 °C), space group $C2/c$, and Z = 8. The crystal used for *X*-ray work was coated with picture varnish to prevent decomposition. *X*-Ray diffraction data were collected on a Nicolet R3m/Eclipse S140 diffractometer system using an ω scan technique with graphite-monochromated Cu-K_α radiation. A total of 717 independent reflections were measured (to θ = 57°), of which 44 were 'unobserved.' The structure was solved by direct methods and least-squares refinement has now reached R = 0.029.† The program system SHELXTL[5] was used throughout the calculations.

$KHSO_5{\cdot}H_2O$	$K_5(HSO_5)_2(HSO_4)(SO_4)$	$(NH_4)_2S_2O_8$
(**1**)	(**2**)	(**3**)

Figure 1 shows the structure of the HSO_5^- anion. The three terminal S–O distances are in the range 1.435—1.444(2) Å. The longest of these involves an oxygen atom forming two hydrogen bonds, and therefore a mean of the two shorter distances (1.436 Å) is probably closer to a true bond length for terminal S—O. The S—O (peroxo) distance is 1.632(2) Å. These bond lengths can be compared to those found for $S_2O_8^{2-}$ in $(NH_4)_2S_2O_8$ (**3**),[6] where the mean terminal S–O is 1.427(3) Å, while S–O (peroxo) is 1.644(5) Å. The O–O distance in (**1**) is 1.460(3) Å and is appreciably shorter than the 1.497(8) Å found in (**3**), but is comparable to 1.453(7) Å in solid hydrogen peroxide.[7] The dihedral angle at the O–O moiety is *ca.* 90°, again similar to that in solid H_2O_2.

We have obtained preliminary *X*-ray data on (**2**), and, despite problems of disorder, it is clear that the anionic species present are 'caroate' ions HSO_5^-, sulphate, and bisulphate ions; the latter pair connected by a very short hydrogen bond. The 'triple salt' is more stable than the title compound, and it is the 'caroate' ion which is the active component within it.

We have measured the Raman and i.r. spectra of normal and deuteriated (**1**) and (**2**) in the solid state; there are published Raman data on Caro's acid[8] and i.r. data on (**1**).[9]

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† The atomic co-ordinates for this work are available on request from Prof. Dr. G. Bergerhoff, Institut für Anorganische Chemie, Universität, Gerhard-Domagk-Str. 1, D-5300 Bonn 1, W. Germany. Any request should be accompanied by the full literature citation for this communication.

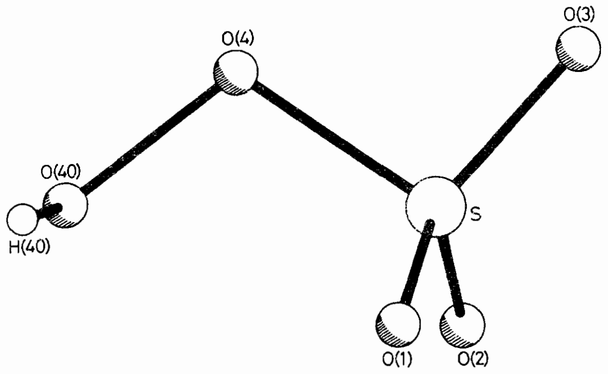

Figure 1. Structure of the HSO_5^- anion in (**1**). Bond lengths: S–O(1), 1.444(2); S–O(2), 1.437(2); S–O(3), 1.435(2); S–O(4), 1.632(2); O(4)–O(40), 1.460(3) Å. Bond angles: O(1)–S–O(2), 113.1(1); O(1)–S–O(3), 115.0(1); O(1)–S–O(4) 105.9(1); O(2)–S–O(3), 115.2(1); O(2)–S–O(4), 106.8(1); O(3)–S–O(4), 99.0(1); S–O(4)–O(40), 109.4(2)°.

The profiles of the Raman spectra of H_2SO_5, (**1**), and (**2**) show considerable similarities suggesting closely related structures for HSO_5^- in all three [additional features are also observed for (**2**) arising from the other anions present]. Apart from S=O stretching vibrations near 1250 and 1070 cm^{-1} and deformations near 570 cm^{-1}, the O–O stretch is clearly observed in Caro's acid at 893 cm^{-1},[8] at 897 and 885 in (**1**), at 893 in (**2**), and at 854 in $S_2O_8^{2-}$.[10]

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