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## The Structure of Cesium Hydrogensulfite

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### Abstract

The structure of the hydrogensulfite ion has been determined for the first time in  $\text{CsHSO}_3$ , which crystallizes in space group  $R\bar{3}m$  with  $a = 4.6721$  (7) Å,  $\alpha = 85.31$  (1)°,  $Z = 1$ . The absolute configuration of the structure was refined to  $R = 0.014$  for 506 independent reflections. The S atom has tetrahedral coordination, with three pyramidal S–O bonds and an S–H bond in the fourth direction. The S–O distance is 1.454 (2) Å and the O–S–O angle 113.1 (2)°. The bond distance is similar to that in the  $\text{SO}_4^{2-}$  ion, while it differs markedly from that in the  $\text{SO}_3^{2-}$  ion. The  $\text{Cs}^+$  ion is nine-coordinated with Cs–O distances of 3.231 (4)–3.249 (4) Å.

### Introduction

The existence of crystalline hydrogensulfites has long been a subject of controversy. Foerster, Brosche & Norberg-Scholtz (1924) proposed that the crystalline bisulfites of sodium and potassium were not hydrogensulfites but pyrosulfites of composition  $\text{Na}_2\text{S}_2\text{O}_5$  and  $\text{K}_2\text{S}_2\text{O}_5$ . Simon & Schmidt (1960) reported the synthesis of solid hydrogensulfites,  $\text{RbHSO}_3$  and  $\text{CsHSO}_3$ , and Beck (1959) reported the existence of a salt of composition  $\text{K}_2\text{S}_2\text{O}_5 \cdot 4\text{KHSO}_3$ . Maylor, Gill & Goodall (1972) described the preparation of three compounds:  $\text{NR}_3\text{HSO}_3$ , with  $R = \text{ethyl, } n\text{-butyl and } n\text{-amyl}$ . The existence of  $\text{NH}_4\text{HSO}_3$  has also been reported (Hisatune & Heicklen, 1975). The conclusion that these compounds really contained the  $\text{HSO}_3^-$  ion was based on evidence from IR and Raman spectroscopy. The existence of  $\text{CsHSO}_3$  and  $\text{RbHSO}_3$  was disputed by Schmidt & Wirwoll (1960) who argued that the failure of  $\text{CsHSO}_3$  and  $\text{RbHSO}_3$  to react with

$\text{S}_2\text{Cl}_2$  in anhydrous tetrahydrofuran forming  $\text{HCl}$  and  $\text{M}_2\text{S}_4\text{O}_6$  ( $2\text{MHSO}_3 + \text{S}_2\text{Cl}_2 \rightarrow 2\text{HCl} + \text{M}_2\text{S}_4\text{O}_6$ ) showed that these salts did not contain hydrogensulfite ions but were pyrosulfites. However, a recent spectroscopic investigation (Meyer, Peter & Shaskey-Rosenlund, 1979) provides ample evidence for the existence of the  $\text{HSO}_3^-$  ion.

The structure of the  $\text{HSO}_3^-$  ion has also been a matter of discussion. The proton may be connected either to an O atom,  $\text{HO-SO}_2^-$ , or to the S atom,  $\text{HSO}_3^-$ . IR and Raman studies of solid salts and solutions have indicated the form  $\text{HSO}_3^-$  rather than  $\text{HO-SO}_2^-$  (Simon & Schmidt, 1960; Hisatune & Heicklen, 1975; Meyer *et al.*, 1979). However, some authors believe that the two forms exist in equilibrium in aqueous solution (Simon & Kriegsmann, 1956; Golding, 1960).

The present study of  $\text{CsHSO}_3$  is the first crystallographic structure determination of a compound containing the  $\text{HSO}_3^-$  ion.

### Experimental

Crystals of  $\text{CsHSO}_3$  were prepared by dissolving 2.0 g of dry  $\text{Cs}_2\text{CO}_3$  in 4.0 ml  $\text{H}_2\text{O}$  under  $\text{N}_2$ . The reaction vessel was then held at 313 K, while  $\text{SO}_2(\text{g})$  was passed through the solution to saturation,  $\text{CO}_2(\text{g})$  being evolved. The clear yellow liquid was then cooled slowly under  $\text{SO}_2(\text{g})$ . At 301 K colorless crystals formed; most were irregular in shape, but some were well formed, flat, trigonal pyramids with the corners of the basal plane truncated. Dry crystals are stable in air.

A few crystals were ground in an agate mortar and the IR spectrum (Table 1) was recorded with the Nujol mull technique. The spectrum agrees well with that published by Simon & Schmidt (1960), who assigned

the absorption at  $\sim 2580 \text{ cm}^{-1}$  to an S—H stretching vibration.

A pyramidal crystal of height 0.06 mm and with a truncated basal plane approximately 0.12 mm in cross section was mounted on a glass rod. Data were collected with a four-circle computer-controlled Syntex  $P2_1$  diffractometer. Crystallographic data and information relevant to the data collection are given in Table 2. The cell dimensions were refined from Guinier powder data with  $\text{Pb}(\text{NO}_3)_2$  as internal standard [ $a_{\text{Pb}(\text{NO}_3)_2} = 7.8566 \text{ \AA}$  at 294 K; *International Tables for X-ray Crystallography*, 1962] with *POWDER* (Lindqvist & Wengelin, 1967).

Integrated intensities and  $\sigma(I)$  values were obtained by the Lehmann & Larsen (1974) profile-analysis method (*LELA*; Lindqvist & Ljungström, 1979). The reflections were corrected for Lp effects, and an absorption correction was carried out with *DATAPH* (Coppens, Leiserowitz & Rabinovich, 1965; modified by W. C. Hamilton).

Table 1. Infrared absorption frequencies ( $\text{cm}^{-1}$ ) for  $\text{CsHSO}_3$  in Nujol mull

513	1122
633	1205
1043	2579

Table 2. Experimental data

(a) Physical and crystallographic data

Formula	$\text{CsHSO}_3$	$a_r = 4.6721 (7) \text{ \AA}$
$M_r$	213.97	$\alpha_r = 85.31 (1)^\circ$
Space group	$R3m$	$V_r = 101.01 (2) \text{ \AA}^3$
$\mu$	$9.62 \text{ mm}^{-1}$	$a_h = 6.332 (1) \text{ \AA}$
$d_c$	$3.51 \text{ Mg m}^{-3}$	$c_h = 8.729 (1)$
Crystal habit	Colorless pyramids (truncated)	$Z_r = 1$
		$F(000) = 96$

(b) Data collection

Crystal dimensions (index of limiting crystal planes and distance to common origin)

$h$	$k$	$l$	$d$ (mm)
-1	0	0	0.040
1	0	0	0.060
0	-1	0	0.040
0	1	0	0.060
0	0	-1	0.040
0	0	-1	0.060
1	1	1	0.050

Radiation	Mo $K\alpha$
Monochromator	Graphite crystal
Maximum $2\theta$	$80.0^\circ$
Scan interval ( $\Delta\omega$ )	$1.4 - 1.7^\circ$ ( $\omega-2\theta$ mode)
Standard reflection	52 at intervals of 50 reflections $102\,000 \pm 1300 - 108\,000 \pm 1300$ stable
Recorded reflections	2600 (complete sphere)
Significant reflections	2556 [ $I/\sigma(I) > 3.0$ ]
Independent reflections	506
(Friedel pairs were not averaged)	
Cell refinement	Guinier powder data

## Structure determination

The diffraction pattern showed  $3m$  Laue symmetry. There were no systematic absences and thus the space group could be either  $R3m$  or  $R\bar{3}m$ . Since  $Z = 1$ , it was concluded that the Cs and S atoms are situated on the threefold axis in space group  $R3m$ . The origin was fixed by specifying the Cs coordinates as (0,0,0). A Fourier summation gave the S position on the threefold axis, and the O atoms were located at a threefold position on the mirror planes. Since Cs contributes to all the reflections, it was not possible to determine the position of the H atom. A neutron diffraction study is in progress.

2556 symmetry-related reflections were averaged, giving 506 independent reflections. The individual e.s.d.'s were modified as  $\sigma(F)_{\text{ind}} = [\sigma^2(F)_{\text{count}} + (0.02F)^2]^{1/2}$  and the e.s.d.'s for the averaged structure factors were evaluated as  $\sigma(\bar{F})_{\text{ave}} = (1-n)^{-1} \sum (F_{\text{ind}} - \bar{F})^2 \sigma^{-2}(F)_{\text{ind}} / \sum \sigma^{-2}(F)_{\text{ind}}$  for  $n = 3$  or 6. For reflections of class  $hhh$  (i.e.  $n = 1$ ),  $\sigma(\bar{F})_{\text{ave}}$  was set to  $2\sigma(F)_{\text{ind}}$ .

The final refinement, based on the averaged structure factors, was performed with the full-matrix least-squares program *LINUS* (Coppens & Hamilton, 1970). Atomic coordinates, anisotropic temperature factors and a parameter for secondary extinction were varied and the results are given in Table 3.\*

The scattering factors of Doyle & Turner (1968) were used for  $\text{Cs}^+$ , S and O, and the calculated structure factors were corrected for anomalous dispersion (Cromer, 1965). The configuration given in Table 3 is correct with respect to the right-hand unit cell, since a refinement of the inverted structure raised  $R$  from 0.014 to 0.029. The physical properties of the  $\text{CsHSO}_3$  crystals have not been studied, and the only

\* Lists of structure factors and powder data have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35431 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Atomic parameters

Positional parameters are given as fractions of the lattice translation. The temperature factor is given as  $T = \exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23}) \times 10^4]$ .

	$x$	$y$	$z$			
Cs	0	0	0			
S	0.4461 (3)	0.4461 (3)	0.4461 (3)			
O	0.1461 (4)	0.5293 (7)	0.5293 (7)			
	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Cs	234 (2)	234 (2)	234 (2)	13 (1)	13 (1)	13 (1)
S	189 (3)	189 (3)	189 (3)	-8 (3)	-8 (3)	-8 (3)
O	205 (6)	356 (9)	356 (9)	31 (7)	31 (7)	15 (6)

Extinction parameter:  $g = 0.005 (1) \times 10^4$

$R = \sum |F_o - F_c| / \sum F_o = 0.014$

$R_w = (\sum w|F_o - F_c|^2 / \sum wF_o^2)^{1/2} = 0.019$

feature which may be related to the absolute configuration is that the triangular basal plane of O atoms of the  $\text{HSO}_3^-$  ion is oriented in the same way as the basal plane of the crystal investigated.

### Discussion

Bond distances and angles are given in Table 4. The geometry of the  $\text{HSO}_3^-$  ion is illustrated in Fig. 1.

Although the position of the H atom could not be determined, it may be concluded that the H atom is indeed bonded to S. Structural evidence for such a conclusion is the  $C_{3v}$  symmetry of the  $\text{SO}_3$  group and the short S—O distance. The existence of an S—H bond is further supported by the IR data (Table 1).

The packing of the  $\text{Cs}^+$  and  $\text{HSO}_3^-$  ions may be regarded as that of a distorted  $\text{CsCl}$ -type structure. However, the real O atom coordination of the  $\text{Cs}^+$  ion is more complicated, with six short and three long Cs—O contacts (Table 4).

S—O distances and angles are compared in Table 5 for some representative compounds. An S—O single bond has been estimated to be 1.69 Å (Pauling, 1952), and it is therefore reasonable to assume contributions of  $\pi$ -bond character in all the anions. Cruickshank (1961), Cruickshank & Webster (1968) and Kirkegaard, Larsson & Nyberg (1972) have suggested the formation of two  $\pi$ -bonding orbitals from the S 3d orbitals and the O 2p orbitals in tetrahedrally

Table 5. *Some interatomic distances (Å) and angles (°) for representative compounds containing tetrahedrally coordinated S*

	S—O	O—S—O	O—O	Reference
$\text{Na}_2\text{SO}_3$	1.504 (3)	105.69 (17)	2.397 (6)	Larsson & Kirkegaard (1969)
$\text{Cu}(\text{CH}_3\text{SO}_3)_2 \cdot 4\text{H}_2\text{O}^*$	1.456 (2)	112.1 (1)	2.416	Charbonnier, Faure & Loiseleur (1977)
$\text{CsHSO}_3$	1.454 (2)	113.1 (2)	2.426 (6)	This work
$\text{Na}_2\text{SO}_4^*$	1.476 (1)	109.48	2.410 (2)	Nord (1973)

\* Average values are given.

coordinated S—O ions. This explains the short S—O distance (1.476 Å) in the  $\text{SO}_4^{2-}$  ion. The replacement of one of the O atoms in the sulfate group by an entity unable to participate in  $\pi$  bonding may thus lead to a strengthening of the remaining S—O bonds, since the available 3d orbitals of S will now be shared by only three O atoms. For the  $\text{SO}_3^{2-}$  ion the lone pair on the S atom will cause an increase in energy for the S 3d orbitals, thus decreasing the S—O bond strength. The repulsive forces exerted by the lone pair on the S atom will also tend to decrease the O—S—O angle in the sulfite ion.

This line of reasoning accounts successfully for the bond lengths and angles found in  $\text{CsHSO}_3$ . As predicted, the S—O distance in the  $\text{HSO}_3^-$  ion is shorter than in both the sulfite and the sulfate ions, 1.454 (2) Å compared to 1.504 (3) ( $\text{Na}_2\text{SO}_3$ ) and 1.476 (1) Å ( $\text{Na}_2\text{SO}_4$ ). Furthermore, the S—O distance in  $\text{CsHSO}_3$  is close to the values found for  $\text{CH}_3\text{—SO}_3^-$ . This is to be expected since neither  $\text{CH}_3$  nor H can participate in  $\pi$  bonding and the two entities are chemically similar.

The O—S—O angle in the sulfite group will tend to increase due to repulsion between the O atoms and to decrease due to repulsion between the lone pair on S and the O atoms. In  $\text{Na}_2\text{SO}_3$  this results in an O—S—O angle (105.7°) which is smaller than the tetrahedral angle (109.47°). In  $\text{HSO}_3^-$  the repulsive forces between the O atoms are no longer balanced by the repulsion due to the lone pair, giving an O—S—O angle of 113.1°.

The fact that an O—H bond is normally stronger than an S—H bond would favor the configuration  $\text{HO—SO}_2^-$  rather than  $\text{H—SO}_3^-$ . However, according to Meyer, Peter & Spitzer (1977), the orbital corresponding to the lone pair on the S atom is antibonding. When the proton is accepted this orbital loses its antibonding character and the three S—O bonds are further stabilized, which is evident from a comparison between the S—O lengths in  $\text{SO}_3^{2-}$  and  $\text{HSO}_3^-$ .

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Table 4. *Interatomic distances (Å) and angles (°)*

#### The $\text{HSO}_3^-$ ion

S—O	1.454 (2)	O—S—O	113.13 (20)
O—O	2.426 (6)		

#### The Cs—O coordination polyhedron

Cs—3O'	3.231 (4)	O'—Cs—O'	74.37 (7)
Cs—6O''	3.249 (4)	O'—Cs—O''	92.27 (9)
Cs—3O'''	3.775 (4)	O'—Cs—O'''	140.00 (8)
		O'—Cs—O''	65.69 (7)
		O''—Cs—O''	153.93 (8)
		O''—Cs—O'''	73.87 (6)
		O''—Cs—O'''	116.72 (6)
		O'''—Cs—O'''	43.84 (6)

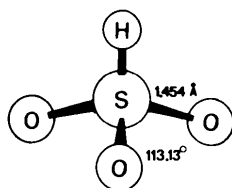


Fig. 1. The  $\text{HSO}_3^-$  ion.

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## The Structure of Diammonium Tricalcium Bis(pyrophosphate) Hexahydrate

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### Abstract

$\text{Ca}_3(\text{NH}_4)_2(\text{P}_2\text{O}_7)_2 \cdot 6\text{H}_2\text{O}$  crystallizes in the monoclinic space group  $P2_1/n$  with  $a = 7.674$  (1),  $b = 11.455$  (2),  $c = 11.014$  (2) Å,  $\beta = 92.44$  (5)° and  $Z = 2$  at room temperature. The structure was refined to  $R = 0.059$ ,  $R_w = 0.057$  for 2179 reflections with  $F_o > 3\sigma(F_o)$ . The structure consists of layers of  $\text{Ca}^{2+}$  and  $[\text{P}_2\text{O}_7]^{4-}$  ions alternating with layers of  $\text{Ca}^{2+}$  and  $[\text{NH}_4]^+$  ions and water molecules. The coordinations of the  $\text{Ca}^{2+}$  ions in the two layers are different.  $[\text{NH}_4]^+$  ions and water molecules are hydrogen bonded to  $[\text{P}_2\text{O}_7]^{4-}$  ions.

(Fleisch & Russel, 1972). Detailed structural analyses of a number of pyrophosphates, particularly those formed at or about the physiological conditions, are necessary for any generalizations on their structural features and related properties. A survey of the known pyrophosphates has shown that the  $[\text{P}_2\text{O}_7]^{4-}$  ion is capable of adopting a wide variety of conformations with different cations (Mandel, 1975). As part of our program to elucidate the crystal chemistry of calcium pyrophosphates, we report the structure of  $\text{Ca}_3(\text{NH}_4)_2(\text{P}_2\text{O}_7)_2 \cdot 6\text{H}_2\text{O}$ .

### Experimental

Suitable crystals of  $\text{Ca}_3(\text{NH}_4)_2(\text{P}_2\text{O}_7)_2 \cdot 6\text{H}_2\text{O}$  were prepared by a slight modification of the procedure given by Brown, Lehr, Smith & Frazier (1963). Freshly precipitated  $\text{Ca}_2\text{P}_2\text{O}_7$  (prepared by mixing  $\text{K}_4\text{P}_2\text{O}_7$  and

### Introduction

Inorganic pyrophosphates are known to play an important role in the mineralization of teeth and bones