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The Hydrated Proton $H^+(H_2O)_n$. 6.[1a] A Neutron Diffraction Study of the Isolated Group $H_5O_2^+{\cdot}H_2O$ in *o*-Sulfobenzoic Acid Trihydrate[1b]

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A neutron diffraction study of *o*-$C_6H_4(COOH)SO_3H{\cdot}3H_2O$ has been undertaken to gain insight into the arrangement and vibrational behavior of hydrogen atoms within the cationic water structure and the anionic molecule. Three-dimensional single-crystal data were collected yielding 3196 unique reflections. The triclinic cell dimensions are a = 6.963 (3) Å, b = 11.747 (5) Å, c = 7.882 (3) Å, α = 102.61 (2)°, β = 111.88 (2)°, and γ = 103.96 (2)°. In the space group $P\bar{1}$, the unit cell contains two formula units. Full matrix least-squares refinement on F_o^2 including an anisotropic extinction correction led to $R_{F_o^2}$ = 0.083. The arrangement of the three water molecules includes a very short [2.415 (3) Å] and a normal [2.721 (3) Å] hydrogen bond; even in the shorter bridge, the hydrogen atom was found slightly off-center [O–H distances 1.201 (5) and 1.219 (5) Å] with a large vibrational root-mean-square component along the O–O direction. X-ray vs. neutron difference density maps show different electron distributions in these hydrogen bonds. An intramolecular C–H···O interaction was found in the sulfonate anion.

I. Introduction

Structural studies on crystalline hydrates of strong acids have led to the knowledge of different hydrated proton species in the solid state. Although the geometrical arrangement within the cationic water structures may vary considerably, a classification based on the formal description as H_3O^+, $H_5O_2^+$, $H_7O_3^+$, ... yielded characteristic mean O–O distances for these aggregates.[2] The geometries of some $H_5O_2^+$ ions were characterized exactly by means of neutron diffraction studies.[3-8] While most of them are located on crystallographic symmetry elements, which places the (not necessarily truly centered) central hydrogen atom equidistant from the two oxygen atom positions, there are two reports of such ions which have no crystal-imposed symmetry.[4,5] These two ions contain noncentered H atoms in the very short central hydrogen bonds; this is related to their asymmetric environments with respect to the terminal hydrogen bonds. Both $H_5O_2^+$ ions are hydrogen bonded to chains of water molecules extending throughout the structures, but if there is a group of three *isolated* water molecules containing the hydrated proton, usually an aggregate $H_7O_3^+$ is formed.[9-12] This aggregate usually contains two very strong but slightly different hydrogen bonds between the central and the two outer water molecules. A neutron diffraction study of one of these examples shows even the shorter of these two hydrogen bridges to be asymmetric with respect to the position of the bridging hydrogen atom.[13] To compare these $H_7O_3^+$ aggregates, where all water molecules have threefold coordination, with an alternative arrangement of three water molecules, including a fourfold coordination, the trihydrate of *o*-sulfobenzoic acid, $C_6H_4(COOH)SO_3H{\cdot}3H_2O$, was chosen for a neutron diffraction study. The previous x-ray study[14] revealed two rather different O–O distances in the isolated group of water molecules; this group was therefore described as $H_5O_2^+{\cdot}H_2O$, in contrast to the aggregates $H_7O_3^+$ found in ref 9–12.

II. Experimental Section

A. Crystal Preparation. Large crystals up to 6 × 6 × 10 mm were easily grown by slow evaporation of H_2O from a saturated solution of *o*-sulfobenzoic acid, when seeded with a small selected single crystal. The data crystal was cut from a larger crystal and shaped to the final dimensions of approximately 2.5 × 3.0 × 5.5 mm, weighing 67.1 mg. It was fixed in place with epoxy cement and sealed in a lead glass capillary.

B. Unit Cell Parameters. The triclinic unit cell setting of the x-ray work was adopted for this study. The lattice constants were redetermined by a least-squares fit of the angles 2θ, χ, and ϕ of 30 intense reflections; they are a = 6.963 (3) Å, b = 11.747 (5) Å, c = 7.882 (3) Å, α = 102.61 (2)°, β = 111.88 (2)°, and γ = 103.96 (2)°. The Delauney reduced cell may be obtained using the matrix (row by row) 001/111/100. With two formula units per unit cell the density is d_{obsd} = 1.54 (1) g cm^{-3}; d_{calcd} = 1.559 g cm^{-3}.

Table I. Final Agreement Factors R, Scale Factors S, and Anisotropic Extinction Parameters Z_{ij}[a]

	Type I	Type II		Type I	Type II
R[b]	0.086	0.083	Z_{22}	3.0 (5)	0.079 (7)
R_w[c]	0.124	0.123	Z_{33}	12.2 (8)	0.281 (21)
σ_1[d]	0.972	0.961	Z_{12}	0.6 (4)	−0.020 (4)
S	0.868 (4)	0.864 (4)	Z_{13}	−1.7 (4)	−0.029 (7)
Z_{11}	4.1 (6)	0.070 (6)	Z_{23}	−0.4 (4)	−0.025 (7)

[a] As defined and scaled in ref 16. [b] $R = \Sigma||F_o|^2 - |F_c|^2|/\Sigma|F_o|^2$. [c] $R_w = [\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w|F_o|^2$. [d] $\sigma_1 = [\Sigma w{\cdot}(|F_o|^2 - |F_c|^2)/(n-p)]^{1/2}$, where $w^{-1} = \sigma^2(|F_o|^2) = \sigma_c^2(|F_o|^2) + (0.07|F_o|^2)^2$, n = number of parameters, and p = number of variables.

C. Data Collection. An Electronics and Alloys four-circle diffractometer at the CP-5 reactor at Argonne National Laboratory was used to collect full three-dimensional data with a wavelength of 1.142 (1) Å [Be monochromator, θ_m = 30°, (110) reflection]. The fully automated diffractometer operates under remote Sigma 5 computer control. Data were collected by the θ–2θ step scan technique with 0.1° step intervals (40–86 steps) and background counts were taken on each side of the peak. A total of 3196 independent reflections were collected to $(\sin\theta)/\lambda$ = 0.70 Å^{-1}. Two reference reflections were measured after every 50 reflections; the sum of their integrated intensities showed random variations of up to 7% during data collection.

The observed integrated intensity of each reflection was corrected for absorption and placed on an absolute scale by calibration with a standard NaCl crystal. The absorption coefficient μ was determined experimentally with a large flat crystal covering the entire aperture of the primary beam. The observed value of μ = 1.83 cm^{-1} agrees well with the calculated value of 1.82 cm^{-1}, using a scattering cross section of 37 barns for H. Minimum and maximum transmission factors in data reduction were 0.55 and 0.67, respectively.

D. Location of Hydrogen Atoms and Refinement. The x-ray heavy-atom parameters were used to phase an initial difference Fourier summation. All 12 hydrogen atoms were found as the highest (negative) peaks of the map. Full-matrix least-squares refinement began with positional and assigned isotropic thermal parameters for all atoms and was continued by varying positional and anisotropic thermal parameters, the scale factor S, and finally an isotropic secondary extinction parameter (g),[15,16] which led to $R_{F_o^2}$ = 0.094. Careful examination of the data showed that intense reflections with low l index were calculated too strong; those with high l index, too small. An anisotropic extinction correction was then introduced.[16] Application of type I and type II corrections led to slightly different results as summarized in Table I with somewhat better agreement in the type II approximation. Therefore the extinction seems to be dominated by particle size. According to an R-factor test[17] this hypothesis is highly significant at the 99.5% confidence level. In both

Table II. Atomic Parameters ($\times 10^4$) of $o\text{-}C_6H_4(COOH)SO_3H \cdot 3H_2O^a$

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S	3873 (5)	2923 (3)	4 405 (4)	296 (15)	268 (14)	204 (13)	121 (12)	118 (12)	90 (11)
O(21)	6256 (3)	3476 (2)	5 681 (3)	315 (8)	276 (8)	369 (9)	71 (7)	142 (7)	85 (7)
O(22)	3388 (4)	2749 (2)	2 381 (3)	642 (13)	395 (9)	274 (8)	220 (9)	249 (9)	158 (7)
O(23)	2633 (3)	3608 (2)	5 035 (3)	423 (10)	399 (9)	285 (8)	261 (8)	162 (7)	138 (7)
O(71)	5926 (5)	1705 (2)	9 542 (3)	830 (18)	566 (13)	295 (11)	434 (13)	89 (11)	154 (10)
O(72)	4604 (4)	3107 (2)	8 579 (3)	647 (14)	363 (9)	266 (8)	248 (10)	106 (9)	95 (7)
O(W1)	1884 (4)	4454 (2)	11 165 (3)	543 (12)	356 (10)	305 (9)	155 (9)	144 (9)	113 (8)
O(W2)	1656 (4)	4414 (2)	8 019 (3)	450 (11)	439 (11)	301 (9)	202 (9)	176 (8)	95 (8)
O(W3)	1676 (3)	6449 (2)	6 905 (3)	345 (10)	577 (12)	286 (9)	190 (9)	144 (8)	175 (9)
C(1)	3539 (2)	1112 (1)	6 218 (2)	274 (7)	270 (6)	261 (6)	116 (5)	107 (5)	106 (5)
C(2)	2994 (2)	1392 (1)	4 491 (2)	258 (6)	242 (6)	222 (6)	77 (5)	81 (5)	64 (5)
C(3)	1783 (3)	429 (1)	2 700 (2)	361 (8)	313 (7)	256 (7)	59 (6)	74 (6)	28 (6)
C(4)	1067 (3)	−805 (1)	2 601 (3)	405 (9)	284 (8)	410 (9)	47 (7)	101 (8)	6 (7)
C(5)	1611 (3)	−1088 (1)	4 292 (3)	369 (8)	247 (7)	555 (11)	78 (6)	163 (8)	110 (7)
C(6)	2858 (3)	−136 (1)	6 086 (3)	384 (8)	296 (8)	429 (9)	132 (6)	167 (7)	183 (7)
C(7)	4737 (3)	2086 (1)	8 203 (2)	405 (8)	338 (7)	234 (6)	164 (6)	124 (6)	126 (6)
H(1)	6647 (9)	2374 (4)	10 829 (6)	855 (30)	679 (24)	332 (17)	375 (23)	140 (19)	184 (18)
H(3)	1445 (8)	658 (4)	1 394 (5)	743 (27)	609 (23)	307 (17)	119 (20)	89 (17)	91 (16)
H(4)	120 (9)	−1541 (4)	1 202 (7)	783 (30)	430 (20)	584 (26)	53 (20)	87 (23)	−76 (19)
H(5)	1083 (9)	−2050 (4)	4 221 (9)	831 (30)	309 (16)	972 (37)	117 (18)	338 (28)	214 (21)
H(6)	3291 (8)	−356 (4)	7 420 (7)	865 (30)	549 (22)	621 (25)	281 (22)	328 (24)	370 (20)
H(11)	2648 (7)	5250 (3)	12 251 (6)	619 (21)	445 (19)	432 (18)	215 (16)	205 (16)	135 (16)
H(12)	2493 (7)	3833 (3)	11 616 (5)	705 (24)	436 (17)	420 (18)	230 (17)	194 (18)	188 (15)
H(13)	1882 (6)	4493 (3)	9 655 (6)	528 (20)	398 (17)	573 (22)	190 (15)	154 (18)	133 (16)
H(21)	2568 (7)	4041 (4)	7 622 (7)	566 (22)	519 (21)	698 (27)	195 (18)	333 (21)	29 (19)
H(22)	1750 (7)	5186 (4)	7 708 (6)	683 (24)	613 (23)	501 (20)	343 (20)	322 (19)	259 (18)
H(31)	2341 (7)	6464 (4)	6 042 (6)	578 (21)	684 (24)	542 (21)	229 (19)	363 (19)	268 (19)
H(32)	202 (6)	6438 (4)	6 244 (5)	438 (19)	650 (22)	438 (18)	245 (16)	173 (16)	229 (17)

[a] U_{ij} values (Å^2) correspond to the expression $\exp[-8\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{12}hka^*b^* + \ldots)]$.

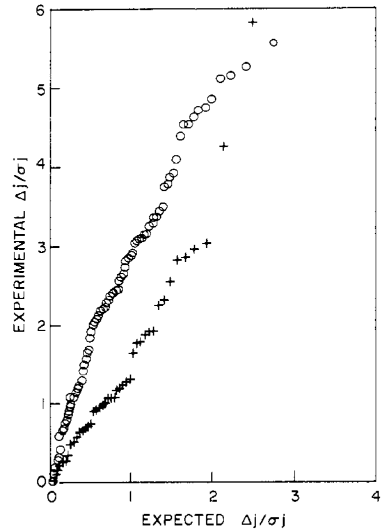

Figure 1. Half-normal probability plots, comparing x-ray and neutron heavy-atom parameters of $o\text{-}C_6H_4(COOH)SO_3H \cdot 3H_2O$: positional parameters, crosses; thermal parameters, circles.

approximations the parameter Z_{33} is about 3 times the values of Z_{11} and Z_{22}.

The results of the refinements are given in Table II, which contains parameters derived by the type II anisotropic extinction model.[18] Observed and calculated structure factors are listed in Table III. The neutron scattering lengths used (in units of 10^{-12} cm) of S, O, C, and H were 0.285, 0.575, 0.663, and −0.372, respectively.[19]

III. Comparison of X-Ray and Neutron Parameters

Agreement between derived parameters of the x-ray and neutron study was tested by means of half-normal probability plots (Figure 1).[19,20] For positional parameters of the heavy atoms (crosses in Figure 1) the slope of the plot is essentially linear, but larger than unity, indicating an underestimation of the standard deviations from the least-squares inverse matrix by at least a factor of 1.6. Two differences exceed $3\bar{\sigma}$ where $\bar{\sigma}$ is the pooled standard deviation of these parameters.

Table IV. Geometry of the Hydrogen Bonds

O–···O′[a]	d(O–O′), Å	d(O–H), Å	d(H···O′), Å	∠OHO′, deg
O(W1)–H(11)···O(21$^{\mathrm{I}}$)	2.685	0.980	1.713	170.6
O(W1)–H(12)···O(22$^{\mathrm{II}}$)	2.671	0.994	1.678	176.8
O(W1)–H(13)–O(W2)	2.414	1.201	1.219	172.5
O(W2)–H(21)···O(23)	2.724	0.956	2.012	129.7
O(W2)–H(21)···O(72)	2.812	0.956	2.025	138.3
O(W2)–H(22)···O(W3)	2.721	0.984	1.742	173.7
O(W3)–H(31)···O(21$^{\mathrm{III}}$)	2.906	0.956	1.950	178.9
O(W3)–H(32)···O(23$^{\mathrm{IV}}$)	2.790	0.958	1.832	179.2
O(71$^{\mathrm{I}}$)–H(1$^{\mathrm{I}}$)···O(W3)	2.728	0.990	1.747	170.7

[a] Roman numeral superscripts refer to the following positions: I = $1-x$, $1-y$, $2-z$; II = x, y, $1+z$; III = $1-x$, $1-y$, $1-z$; IV = $-x$, $1-y$, $1-z$.

Thermal parameters give a nonlinear arrangement of the plotted points (circles in Figure 1). The slope is steeper as for positional parameters. This corresponds to the fact that thermal parameters are often found in poorer agreement than positional parameters.

IV. Discussion

A. The Aggregate $H_5O_2^+ \cdot H_2O$. The water oxygen atoms are arranged in discrete groups, connected with hydrogen bonds within the group but separated from water oxygen atoms of other groups with distances longer than 3.2 Å, i.e., the sum of their van der Waals radii. One such group is shown in Figure 2 with atomic distances and angles around the oxygen atoms. With one rather short [2.414 (3) Å] and one normal [2.721 (3) Å] hydrogen bond between the water oxygen atoms, $H_5O_2^+ \cdot H_2O$ is the appropriate formulation for this group. Hydrogen bonds between the water molecules and to the sulfonate anion are listed in Table IV.

The shortest hydrogen bonds of the structure are around O(W1); at the same time the position of H(13) in the very short hydrogen bond to O(W2) of 2.414 (3) Å length is found nearer O(W1) with O–H distances 1.201 (5) and 1.219 (5) Å, respectively. This difference is not significant in view of the stated standard deviations, especially when an additional underestimation of standard deviations (part 3) is taken into

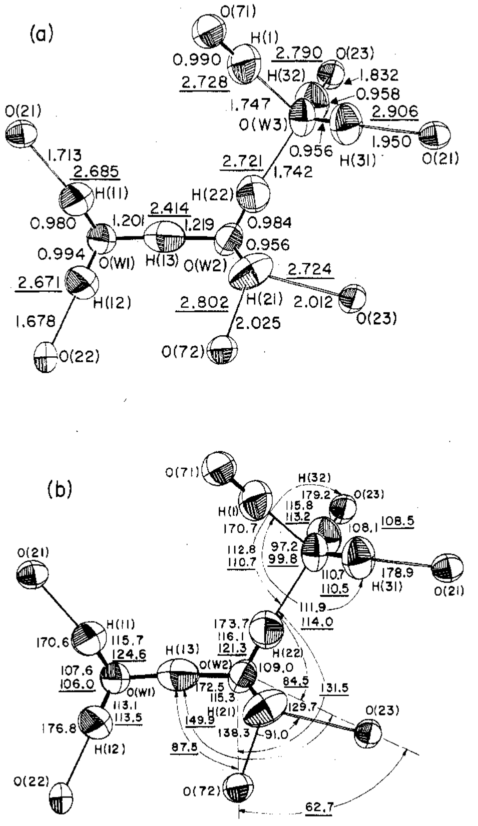

Figure 2. The $H_5O_2^+ \cdot H_2O$ group and its hydrogen-bonded neighbor atoms: (a) distances (Å) O–H ($\sigma = 0.005$ Å) and O–O (underlined, $\sigma = 0.003$ Å); (b) angles (deg) H–O–H ($\sigma = 0.3°$) and O–O–O (underlined, $\sigma = 0.1°$).

account. Therefore, a centered model cannot be ruled out with certainty. The length of the hydrogen bond O(W2)–H(22)···O(W3) indicates that the third water molecule is not part of the cation; the value of 2.721 (3) Å is still somewhat longer than expected for a hydrogen bond originating at $H_5O_2^+$ (mean value 2.70 Å)[2] and is nearer to values found between neutral water molecules (e.g., ice: 2.75 Å) than to the values around O(W1). The hydrogen atom H(21) is engaged in a quite interesting bifurcated hydrogen bond to the sulfonyl oxygen O(23) and carboxyl oxygen O(72) of the same anion. Both acceptor oxygen atoms have the same distance to the hydrogen atom, although the O–O distances differ considerably. The difference in distance is reflected in different angles O(W2)–H(21)···O. The well-known correlation of O–O vs. O–H distances, which gives longer O–H values for stronger (shorter) hydrogen bonds, classifies this bifurcated hydrogen bond as a weaker interaction in view of the rather small O–H value of 0.956 (3) Å, although the hydrogen atom should share in the positive charge of the cation and therefore make up strong interactions. The thermal ellipsoid of H(21) has a rather large component parallel to the O(72)–O(23) direction. This may by an indication of two separate potential minima in both branches of the bifurcated hydrogen bond. As there are observations of considerable correlation of the H–O–H angle in $H_5O_2^+$ with the corresponding O–O–O value,[8] it is reasonable to assume a bending motion of the O(W2)–H(21) bond bringing this H atom from one minimum to the other without influencing the other hydrogen atom positions around O(W2). No disordered model for H(21) was considered.

The neutral water molecule is surrounded by four oxygen atoms forming a nearly regular tetrahedron with distances from the central oxygen atom between 2.721 (3) and 2.906 (3) Å and angles ranging from 99.8 (1) to 114.0 (1)° with a mean value 109.4° (see Figure 2b). As all four hydrogen bonds are almost linear at the hydrogen atom positions, the angles between the four hydrogen atoms at the oxygen site reflect this regularity with values between 97.1 (2) and 115.6 (3)° (mean value 109.4°) although there are of course two pairs of short and long distances near 0.956 (5) and 1.743 (5) Å, respectively.

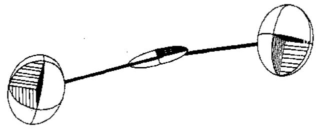

Figure 3. Difference ellipsoid of atom H(13), seen in the plane of the three atoms. For the infinitely small rms value nearly perpendicular to this plane, see text.

The hydrogen bonds to O(W3) from the cationic O(W2) and from the neutral carboxylic O(71) appear to be almost identical. Therefore a comparison with the water structure in $HCl \cdot 3H_2O$[22] and $HBr \cdot 3H_2O$[23] seems appropriate, where in both cases a water molecule accepts hydrogen bonds from two $H_5O_2^+$ groups. These two water molecules have much more asymmetric surroundings of the four neighboring atoms with distorted tetrahedral angles between 98 and 123°, where the extremes are between halide ions, the smallest value being in the chloro compound and the largest in the bromo compound. In these cases rather bent hydrogen bonds are to be expected (which cannot be deduced from x-ray studies), whereas in the present study the angles O–O(W)–O and H–O(W)–H have the same values and the hydrogen bonds are almost linear.

B. Thermal Motion in $H_5O_2^+$. The four outer hydrogen atoms show their largest vibrational root-mean-square components nearly perpendicular to the O–H bond direction. The direction of this component is almost parallel for all three atoms of the group O(W1), H(11), and H(12) (see Figure 2). As atom H(21) is situated in the bifurcated hydrogen bond to O(72) and O(23), which influences the apparent thermal motion (see last section), no similar pattern holds for the atoms around O(W2). The bridging hydrogen atom H(13) in $H_5O_2^+$ has its largest vibrational freedom nearly along the direction O(W1)–O(W2). The "net" motion of this hydrogen atom relative to the oxygen atoms is illustrated in Figure 3, where the difference tensor $\beta_H^{ij} - \langle \beta_O^{ij} \rangle$ is being shown; $\langle \beta_O^{ij} \rangle$ is the averaged value of the atoms O(W1) and O(W2). To achieve a positive definite tensor, the value of β_H^{22} had to be increased by only 0.5σ.

The rms components of this difference tensor are 0.190, 0.053, and 0.001 Å, which clearly shows the large anisotropy along the O–O direction. Similar values in the corresponding O–O directions were found in high-precision neutron diffraction studies of $H_5O_2^+$ cations in picrylsulfonic acid tetrahydrate (0.172 Å),[5] in *trans*-dichlorobis(ethylenediamine)cobalt(III)chloride hydrochloride dihydrate (0.22 Å),[7] and in the two $D_5O_2^+$ cations in 5-sulfosalicylic acid dideuterate (0.22 and 0.16 Å)[8]; this freedom has been related with a broad, flat anharmonic potential well.[24,25] The difference ellipsoid of H(22) in the hydrogen bond O(W2)–O(W3) has its smallest component in the bond direction. This is not unexpected when compared to the situation in 5-sulfosalicylic trihydrate (orthorhombic modification),[13] where a separate group of three water molecules form an aggregate $H_7O_3^+$ with slightly different O–O distances (2.442 vs. 2.516 Å); even with this small difference the largest and the smallest rms components of the two bridging H atoms are in the bond direction.

C. The *o*-Sulfobenzoic Acid Anion. The anion is shown in Figure 4 with bond lengths and bond angles. Bond lengths corrected for thermal motion are given in brackets; these were calculated assuming a rigid-body librational motion.[26] With

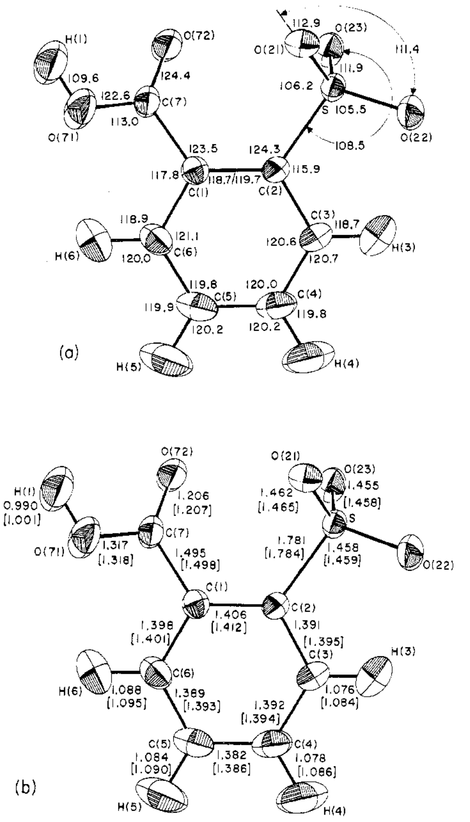

Figure 4. The *o*-sulfobenzoic acid anion showing bond angles (a) and bond lengths (b); values in brackets corrected for thermal motion. Standard deviations of lengths 0.003 Å, 0.005 to H; of angles 0.2–0.4°.

a small and isotropic translational part (rms amplitudes between 0.15 and 0.17 Å) and the largest libration (rms amplitude 4.6° vs. 3.3 and 3.2°) around an axis approximately in the molecular plane passing through the center of the benzene ring and between the carboxyl and sulfonyl group, the agreement between observed and calculated U_{ij} values is fairly good (rms discrepancy 0.0060). As there was no corresponding treatment of the x-ray values, the following comparison will be made with uncorrected values. The average bond length in the benzene ring is increased to 1.393 Å (x-ray value 1.387 Å), mainly due to the highly significant increase of the value C(4)–C(5). This value is by far the shortest in the x-ray structure determination (1.364 (2) Å), a feature also found in the molecular structure of the monoammonium salt of *o*-sulfobenzoic acid. The newly determined value of 1.382 (3) Å is still the smallest within the benzene ring, but with much smaller deviation from the mean value (0.011 vs. 0.023 Å). Other distances between nonhydrogen atoms agree within 2σ. The C–H distances average to 1.082 (3) Å (corrected 1.089 Å); the hydrogen atoms H(4)–H(6) are found in the best plane through the benzene carbon atoms with deviations up to 0.019 (7) Å. The equation of this plane is $6.9452X - 3.6368Y - 2.8075Z = 0.3139$. Atoms S and C(7) are out of this plane 0.076 (5) and −0.086 (3) Å in different directions, due to repulsive forces between carboxyl and sulfonyl groups, as discussed in the x-ray work; this also causes the bond C(1)–C(2) to be the longest in the benzene ring [1.406 (3) Å].

An interesting feature is the displacement of 0.060 (6) Å of atom H(3) out of the benzene ring plane, which is highly significant. At the same time, angles around C(3) are distorted from the expected 120° value. Both facts may be explained by the formation of intramolecular C–H···O hydrogen-bonding interaction with O(22). The H(3)···O(22) distance is 2.291 (4) Å, shortened 0.026 Å compared to the distance from an idealized hydrogen position in the benzene ring plane with 120° angles around C(3) and 1.08 Å from C(3). The very short distance C(13)···O(22) of 2.790 (3) Å results from the nearly staggered arrangement around the C(2)–S bond with a torsional angle of 11.7°; nevertheless the angle C(2)–S–O(22) is the smallest of all three CSO angles, partly due to the repulsion between O(72) and O(21)/O(23). The angle C(3)–H(3)···O(22) is 106.2 (4)°. Although the angles around C(6) are similarly distorted as around C(3), no hydrogen interaction H(6) (not significantly out of plane) to O(71) is considered, as the H–O distance exceeds 2.4 Å.

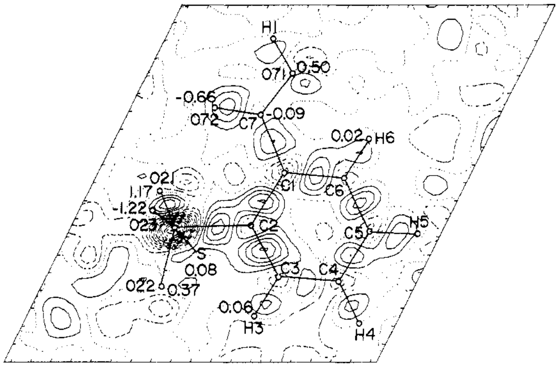

Figure 5. $(F_\mathrm{x} - F_\mathrm{n})$ difference map in the plane of the benzene ring; contour intervals approximately 0.1 e Å^{-1}, zero contour dotted, negative contours dashed. Distances to the plane over 0.02 Å are given.

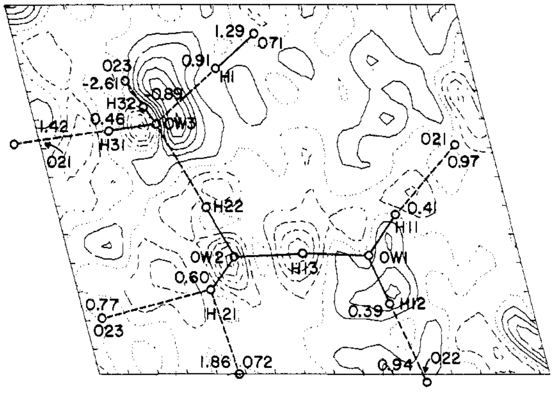

Figure 6. $(F_\mathrm{x} - F_\mathrm{n})$ difference map in the plane of the three water oxygen atoms. For details see Figure 5.

D. X-Ray vs. Neutron Difference Density Calculations. X-ray and neutron diffraction data were combined to study the residual electron density distribution within the acid anion and in hydrogen bonds of the water structure. Quantities $(F_\mathrm{x} - F_\mathrm{n})$ were used as coefficients in Fourier summations where F_x is the observed x-ray structure factor and F_n is the calculated value using positional and thermal parameters from the neutron study with spherical free-atom x-ray scattering factors for S, C, O,[27] and H.[28]

Valence electron density is found in all bonds of the acid anion [except for C(7)–O(71)], as shown in Figure 5. The C–H bonds also show this valence electron density, but with no pronounced negative regions on the other side of the hydrogen nuclear positions, as found in similar studies.[8] Nevertheless, there is a gradient of electron density at the H sites with the nuclear positions near the zero contour due to the polarization of the C–H bonds.

A difference map in the plane of the three water oxygen atoms is given in Figure 6. The main feature is the pronounced negative region in the very short hydrogen bond O(W1)–H(13)–O(W2), which is centered between the two oxygen atoms, with slightly positive peaks near these atoms. This appearance is in contrast to that of the other hydrogen bond seen in the plane, O(W2)–H(21)···O(W3). Here the electron distribution is much more asymmetric with higher electron density near the hydrogen-bond acceptor atom O-(W3). Similar electron density distributions as in the bond O(W2)···O(W3) were observed in short *and* long hydrogen bonds of the water structure in picrylsulfonic acid tetrahydrate.[5]

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Supplementary Material Available: Table III, listing structure factor amplitudes (9 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) This is also considered as part 12 of the series "Crystal Structures of Acid Hydrates and Oxonium Salts". For the preceding paper of both series, see ref 8. (b) Work performed under the auspices of the U.S. Energy Research and Development Administration. (c) Lehrstuhl für Strukturchemie und Anorganische Chemie der Universität Düsseldorf, D-4000 Düsseldorf, West Germany.
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Triboluminescence and Pressure Dependence of the Photoluminescence of Tetrahedral Manganese(II) Complexes

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The triboluminescence of the tetrahedral manganese(II) complexes $Mn(Ph_3PO)_2Cl_2$, $Mn(Ph_3PO)_2Br_2$, $(MePh_3P)_2MnCl_4$, and $(Et_4N)_2MnBr_4$ is a superposition of the $^4T_1 \rightarrow {}^6A_1$ manganese-centered phosphorescence and a weak $^3\Pi_u \rightarrow {}^3\Pi_g$ emission from adsorbed molecular nitrogen. The triboluminescence and atmospheric pressure photoluminescence spectra are superimposable. The energy of the manganese-centered photoluminescence decreases linearly with pressure up to the maximum studied pressure of 42 kbars. The emitting manganese centers in the triboluminescence experiment are at atmospheric pressure. The applicability of previously proposed mechanisms to the manganese complexes is discussed in terms of the spectroscopic results.

Spectroscopic studies of triboluminescence (TL), the emission of light caused by the application of mechanical stress to crystals, have shown that the most common origins of the emission are crystal fluorescence,[1,2] crystal phosphorescence,[2,3] and emission from the second positive group of adsorbed nitrogen.[4,5] The oldest known triboluminescent substance is sugar[6] whose TL originates from adsorbed nitrogen.[5]

The first assignment of the TL of a transition metal complex was made by Cotton and Goodgame[7,8] for several tetrahedral manganese(II) complexes on the basis of the visual similarity of the colors of the photoluminescence and TL. These complexes are ideal candidates for spectroscopic study because the metal-centered transitions respond primarily to the ligands and less strongly to the intermolecular interactions which are important in the delocalized transitions of the π systems of aromatic organic molecules. We report here the TL spectra, the atmospheric pressure photoluminescence spectra, and the pressure dependence of the photoluminescence spectra of a series of tetrahedral manganese(II) complexes. Proposed TL excitation mechanisms are discussed in terms of the spectroscopic results.

Experimental Section

The TL was excited in all of the spectroscopic studies by grinding samples of approximately 0.5 g at room temperature in a Pyrex vial with a stainless steel rod. The TL could also be excited with grinding implements of other material such as wood, Teflon, or glass.

The TL spectra were measured with a Bausch and Lomb 1.0-m monochromator modified as shown in Figure 1 and EMI 9558 photomultipliers in Products for Research refrigerated housings. The TL emission from the sample mounted in a block was passed through