Solid-State Structure, Nuclear Quadrupole Resonance Spectrum, and the Resultant Symmetry Implications for Tetrachloroiodic Acid Tetrahydrate

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Abstract: The crystal structure of tetrachloroiodic acid tetrahydrate, $HICl_4 \cdot 4H_2O$, has been determined at $-25 \pm 3°$ from three-dimensional X-ray diffraction data. The compound crystallizes with two molecules in a monoclinic unit cell of symmetry $P2_1/b$ and lattice constants $a = 8.46 \pm 0.03$, $b = 11.34 \pm 0.03$, $c = 5.31 \pm 0.03$ Å, and $\gamma = 96.1 \pm 0.1°$. The packing of the nearly square-planar ICl_4^- ions is such that the iodine atoms are located at centrosymmetric sites in the unit cell. The ^{35}Cl nuclear quadrupole resonance (nqr) spectrum at 5° consists of four resonances between 21.3 and 22.9 MHz. No phase transitions were evident from the nqr measurements between 15 and $-140°$. The apparent contradiction between the structural and magnetic resonance measurements with regard to the symmetry of the ICl_4^- ion is resolved if a proton disorder or a systematic reduction of symmetry having a negligible effect on the X-ray film data is assumed.

The solid-state structures of hydrated acids have recently been of considerable interest, particularly with the observation of polyaquo ions.[3–9] The principal polyaquo species noted to date has been the diaquo ion $H_5O_2^+$, first confirmed by Williams[3] in the solid state in *trans*-$[Co(en)_2Cl_2^+]Cl^-(H_5O_2^+)Cl^-$. The proton hydrates $H_7O_3^+$ and $H_9O_4^+$ have been found by Lundgren and Olovsson[8] to be constituents of $HBr \cdot 4H_2O$. The cation $H_7O_3^+$ has also been suggested as a possibility for the compound $H_7O_3^+[C_6H_3(COOH)(OH)SO_3^-]$.[9] The main interest in these types of ions has been focused upon the short $O \cdots H \cdots O$ hydrogen bond lengths, which are typically between 2.4 and 2.5 Å in the diaquo species. One notable exception to date has been observed by Williams and Peterson[7] in the neutron diffraction structural determination of $HAuCl_4 \cdot 4H_2O$, in which an $O \cdots H \cdots O$ hydrogen bond distance of 2.57 Å was found for the $H_5O_2^+$ ion. The length of such a hydrogen bond is often used as one criterion for the nature of the potential function (*i.e.*, a single- *vs.* a double-minimum potential well) of the acid proton.[10]

The preparation and solid-state characterization of several tetrachloroiodate ions was first made by Wells, Wheeler, and Penfield.[11] The crystal structure of the potassium salt was first determined by Mooney,[12] in which I–Cl bond distances whose values were approximately equal to the sum of the covalent radii were obtained. That this was in fact the monohydrated species was discovered by Cornwell and Yamasaki.[13] Interatomic distances substantially longer than the sum of the covalent radii were subsequently observed by Elema, de Boer, and Vos[14] in the refinement of the crystal structure of $KICl_4 \cdot H_2O$.

The relationship between the average ^{35}Cl nuclear quadrupole resonance (nqr) frequency and the idealized square-planar geometry of ICl_4^- has been treated by Cornwell and Yamasaki[13] for several alkali tetrachloroiodates. The bond length differences within the tetrachloroiodate ion of 0.2 Å in $KICl_4 \cdot H_2O$ are consistent with the ^{35}Cl nqr study of Cozzini, Verdieck, and Cornwell.[15] The present paper reports the details of the reduced-temperature, single-crystal, X-ray structural determination of the solid hydrated acid $HICl_4 \cdot 4H_2O$ and the relationship of this structure to its polycrystalline nqr spectrum.

Experimental Section

Single-Crystal X-Ray Data. The compound was prepared by the addition of iodine trichloride (Alfa Inorganics) to concentrated HCl followed by cooling in an ice bath to initiate crystallization. A second sample was prepared by passage of chlorine gas through a concentrated HCl solution to which a stoichiometric amount of solid iodine had been added. The passage of chlorine gas was continued until the solution attained constant weight, and the solution was then cooled in an ice bath. Solutions obtained from both preparative methods exhibited severe supercooling; large crystals were grown from seed crystals by a slow reduction of temperature over a 2° range to about 15°. The crystals melt at approximately 19° when in contact with their saturated solution. To obtain suitable crystals for the X-ray investigation, large crystals were cooled to $-70°$ on a cold stage in a nitrogen atmosphere. Crystals of appropriate size were obtained by the fracture of these large crystals and mounted in thin-walled Lindemann-glass capillaries.

The three-dimensional single-crystal X-ray data were collected at $-25 \pm 3°$ with the use of a modification of the low-temperature Weissenberg camera described by Molin-Case.[16] This apparatus utilizes an unshrouded cold gas stream incident directly upon the capillary.

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(1) Based in part on a thesis submitted by R. J. B. in partial fulfillment of the requirements for the Ph.D. degree, University of Wisconsin, 1969.

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After a preliminary X-ray investigation of $HICl_4 \cdot 4H_2O$, a suitable single crystal was found and determined to be of monoclinic point group C_{2h}-$2/m$. A crystal of approximate dimensions 0.3 × 0.2 × 0.2 mm, mounted with the 0.3-mm direction oriented along the Weissenberg spindle axis, was used for the collection of intensity data. Multiple-film, equiinclination Weissenberg data were collected for reciprocal levels $0kl$–$8kl$ with zirconium-filtered Mo K$\bar{\alpha}$ radiation (λ 0.7107 Å). The intensities of the 794 visible independent reflections were visually estimated by comparison with a calibrated filmstrip. Individual judgings of a given reflection were averaged and corrected for Lorentz-polarization effects and spot extension[17] of the nonzero Weissenberg reciprocal layers. No corrections were made for absorption or extinction. The linear absorption coefficient for Mo K$\bar{\alpha}$ radiation of 38.4 cm^{-1} results in an approximate μR_{max} of 0.7; because of the uniform cross section of the crystal, it was estimated that the maximum intensity variation on a given Weissenberg reciprocal layer due to absorption was less than 10%.[18]

Lattice constants were measured from $0kl$ and $hk0$ Weissenberg photographs (taken at −25°), which were calibrated with photographs of a NaCl crystal to minimize thermal variation of the film-holder radius and film. Thermal expansion corrections of the NaCl lattice[19] are less than 2 ppt in the NaCl lattice constant and were included in the uncertainty estimates for determination of the lattice parameters.

Unit Cell and Space Group. The orange-yellow crystals o $HICl_4 \cdot 4H_2O$ are monoclinic with lattice parameters $a = 8.46 \pm 0.03$, $b = 11.34 \pm 0.03$, $c = 5.31 \pm 0.03$ Å, and $\gamma = 96.1 \pm 0.1°$. The volume of the unit cell is 507 Å^3. The calculated density based on two formula units per unit cell is 2.24 g/cm^3. The experimental determination of the crystal density was not made owing to the high solubility and low melting point of the compound. The systematic absences of $\{hk0\}$ for k odd and $\{00l\}$ for l odd uniquely indicate the space group to be $P2_1/b$ (C_{2h}^5 no. 14 with c axis unique). The subsequent structural analysis showed that the crystallographic asymmetric unit contains one iodine, two chlorine, two oxygen, and five hydrogen atoms. The iodine atom occupies the twofold set of special positions (2a) on the centers of symmetry at (0, 0, 0) and (0, $^1/_2$, $^1/_2$). The remaining independent nonhydrogen atoms occupy the fourfold set of general positions (4e) $\pm(x, y, z;\ x, {}^1/_2 + y, {}^1/_2 - z)$.

Determination of the Structure. The crystal structure was determined by the usual combination of Patterson and Fourier methods and refined with the use of full-matrix least squares to the discrepancy factors $R_1 = [\Sigma||F_o| - |F_c||/\Sigma|F_o|] \times 100 = 7.1\%$ and $R_2 = [\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2] \times 100 = 8.4\%$, when anisotropic temperature factors were used for the iodine and chlorine atoms. With atomic thermal motion constrained to be isotropic, final discrepancy factors of $R_1 = 9.6\%$ and $R_2 = 11.1\%$ were obtained. A three-dimensional Fourier difference map based on the final output parameters showed no residual density greater than 1.8 e/Å^3 or less than −3.1 e/Å^3 where the negative peaks were observed in the vicinity of the iodine atoms. No attempt was made to locate the hydrogen atoms. In order to determine the overall correctness of the molecular determination, structure factors for all reflections not utilized in the X-ray analysis were generated to the edge of the reciprocal lattice corresponding to $\theta = 50°$. Each of these reflections was assigned a value equivalent to the minimum observed intensity for the given reciprocal level. A comparison of the derived structure factors for these unobserved but experimentally accessible reflections with the corresponding calculated structure factors revealed no $F_c > 1.7F_{min}$. Because of the observed data-to-parameter ratio of nearly 20 to 1, no further refinement of the structure was performed including these unobserved data.

All three-dimensional Fourier maps were calculated with the Blount program.[20] The full-matrix least-squares refinement cycles were performed with a local version of the Busing–Martin–Levy ORFLS program,[21] where the function minimized was $\Sigma w||F_o| - |F_c||^2$; individual weights were assigned to the observed structure factors according to the relationships $\sigma = F_o/20$ for all $I_o \geq \sqrt{10}I$(min) and $\sigma = (F_o/20)(\sqrt{10}I(\text{min})/I_o)^2$ for $I_o < \sqrt{10}I$(min). The atomic scattering factors for all atoms were those of Hanson, *et al.*[22] Anomalous dispersion corrections to the iodine form factors were used in the structural determination. The Busing–Martin–Levy ORFFE program[23] was used to calculate the bond lengths and bond angles and their standard deviations.

The final atomic positional and thermal parameters with their standard deviations for the anisotropic refinement cycles are listed in Table I,[24] along with the isotropic and anisotropic temperature factors. Interatomic distances and angles calculated from the parameters of Table I are listed in Tables II and III.

Table I. Final Atomic Parameters for $HICl_4 \cdot 4H_2O$ with Standard Deviations[a]

	X	*Y*	*Z*	*B*
I[b]	0.0000 (0)	0.0000 (0)	0.0000 (0)	*c*, *d*
Cl(1)	0.2915 (5)	0.0717 (3)	−0.0282 (7)	*c*, *d*
Cl(2)	−0.0338 (4)	0.1457 (3)	0.3536 (5)	*c*, *d*
O(1)	0.4476 (14)	0.3861 (9)	−0.0069 (23)	*d*
O(2)	0.6626 (16)	0.2249 (10)	−0.0556 (20)	*d*

[a] The standard deviations of the last significant figures are given in parentheses. [b] The iodine atom is located at the special position (0, 0, 0). [c] Anisotropic temperature factors of the form $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$ were used for the iodine and chlorine atoms; the resulting thermal coefficients are

Atom	10^4B_{11}	10^4B_{22}	10^4B_{33}	10^4B_{12}	10^4B_{13}	10^4B_{23}
I	77 (17)	30 (1)	106 (3)	−7 (1)	6 (3)	5 (2)
Cl(1)	100 (18)	62 (2)	273 (15)	−14 (3)	27 (6)	−19 (5)
Cl(2)	112 (18)	44 (2)	150 (9)	−7 (2)	4 (5)	−16 (4)

[d] Isotropic temperature factors of the form $\exp[-B \sin^2 \theta/\lambda^2]$ were used for all atoms for the isotropic refinement. The resulting values are

Atom	*B*	Atom	*B*
I	1.40 (3)	O(1)	3.50 (22)
Cl(1)	2.95 (9)	O(2)	3.65 (28)
Cl(2)	2.13 (7)		

Table II. Interatomic Distances (Å) with Standard Deviations for $HICl_4 \cdot 4H_2O$[a]

Iodine–Chlorine Distances		Chlorine···Oxygen Distances	
I–Cl(1)	2.515 (9)	Cl(1)···O(1)	3.670 (11)
I–Cl(2)	2.538 (9)	Cl(1)···O(2)	3.423 (16)
		Cl(1)···O(1)[c]	3.539 (18)
Chlorine···Chlorine Distances		Cl(1)···O(2)[c]	3.402 (16)
Cl(1)···Cl(2)	3.586 (12)	Cl(1)···O(1)[d]	3.851 (18)
Cl(1)···Cl(2)	3.559 (9)	Cl(1)···O(2)[e]	3.455 (15)
Cl(2)···Cl(2)[b]	3.561 (13)	Cl(2)···O(2)[c]	3.353 (17)
Cl(2)···Cl(1)[b]	4.110 (15)	Cl(2)[b]···O(2)[c]	3.550 (16)
		Cl(2)···O(1)[b]	3.556 (17)
Oxygen···Oxygen Distances		Cl(1)[f]···O(1)[c]	3.365 (17)
O(1)···O(2)	2.723 (18)	Cl(1)[f]···O(2)[c]	3.623 (18)
O(1)···O(2)[c]	2.819 (20)	Cl(1)[f]···O(1)[d]	3.585 (16)
O(1)···O(1)[c]	4.236 (31)		
O(1)[c]···O(1)[d]	2.640 (22)		
O(1)[c]···O(2)	3.270 (22)		
O(2)···O(2)[c]	3.907 (23)		

[a] Positions are indicated by superscripts. Standard deviations of the last significant figures are given in parentheses. [b] $-x, {}^1/_2 - y, {}^1/_2 + z$. [c] $1 - x, {}^1/_2 - y, {}^1/_2 + z$. [d] $x, -{}^1/_2 + y, {}^1/_2 - z$. [e] $1 - x, -y, -z$. [f] $x, y, 1 + z$.

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(24) Calculated and observed structure factors for $HICl_4 \cdot 4H_2O$ will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

Table III. Interatomic Angles (Deg) with Standard Deviations for $HICl_4 \cdot 4H_2O^a$

Cl–I–Cl Angles		O···Cl···O Angles	
Cl(1)–I–Cl(2)	90.43 (16)	O(1)^c···Cl(1)···O(2)^c	46.2 (5)
Cl(1)–I–Cl(2)^h	89.57 (16)	O(1)^c···Cl(1)^b···O(2)^c	45.7 (5)
Cl(1)^b–I^b···Cl(2)	85.55 (15)	O(1)^c···Cl(1)···O(1)^d	41.6 (5)
Cl(2)^b–I^b···Cl(2)	111.30 (16)	O(1)^c···Cl(1)^b···O(1)^d	44.5 (5)
O···O···O Angles		O(1)^c···Cl(1)^b···O(1)^e	100.5 (5)
O(2)^c···O(1)^c···O(1)^d	118.8 (7)	Cl···Cl···O Angles	
O(2)···O(1)^c···O(2)^c	80.8 (4)	O(1)^c···Cl(1)···Cl(2)	90.4 (4)
O(2)···O(1)^c···O(1)^d	117.0 (7)	O(1)^c···Cl(1)^b···Cl(2)^b	154.2 (5)
O(1)···O(2)^c···O(2)^b	116.0 (7)	O(2)^c···Cl(1)···Cl(2)	57.2 (4)
O(1)···O(2)^c···O(2)	44.2 (3)	O(2)^c···Cl(1)^b···Cl(2)^b	108.7 (5)
O(2)···O(2)^c···O(1)^c	55.7 (4)	O(1)^d···Cl(1)···Cl(2)	91.5 (4)
O(2)^b···O(1)^c···O(1)^d	118.3 (7)	O(2)^c···Cl(2)^c···Cl(2)^b	110.9 (4)
O(1)···O(2)^c···O(1)^b	121.2 (6)	O(1)^d···Cl(1)^b···Cl(2)^b	149.9 (5)
O(1)···O(2)^c···O(1)^c	99.7 (6)		
O(1)^c···O(2)^c···O(1)^b	89.5 (5)	O···O···Cl Angles	
O(2)···O(1)^c···O(2)^b	89.6 (5)	O(1)···O(2)^c···Cl(1)	71.6 (5)
O(2)···O(2)^c···O(2)^b	85.6 (5)	O(1)···O(2)^c···Cl(1)^b	157.7 (5)
O(2)···O(2)^c···O(1)^b	119.0 (7)	O(1)···O(2)^c···Cl(2)	108.8 (5)
O(1)^c···O(2)^c···O(2)^b	46.2 (4)	O(1)···O(2)^c···Cl(2)^f	120.8 (5)
O(2)^b···O(2)^c···O(1)^b	43.5 (3)	O(2)···O(1)^c···Cl(1)	60.2 (4)
		O(2)···O(1)^c···Cl(1)^b	153.7 (5)
Cl···O···Cl Angles		O(1)^d···O(1)^c···Cl(1)	75.5 (5)
Cl(1)···O(2)^c···Cl(2)	64.1 (4)	O(1)^d···O(1)^c···Cl(1)^b	72.2 (4)
Cl(1)^b···O(2)^c···Cl(2)	78.5 (4)	O(1)^c···O(2)^c···Cl(1)	69.6 (4)
Cl(2)···O(2)^c···Cl(2)^f	62.0 (4)	O(1)^c···O(2)^c···Cl(2)	112.3 (5)
Cl(1)···O(2)^c···Cl(2)^f	126.1 (5)	O(1)^c···O(2)^c···Cl(2)^f	131.5 (5)
Cl(1)^b···O(2)^c···Cl(2)^f	69.9 (5)	O(1)^c···O(2)^c···Cl(1)^b	62.1 (4)
Cl(1)···O(1)^c···Cl(1)^b	98.2 (5)	O(2)^c···O(1)^c···Cl(1)	64.3 (4)
Cl(1)···O(1)^c···Cl(1)^g	69.2 (5)		
Cl(1)···O(2)^c···Cl(1)^b	100.5 (5)		
Cl(1)^b···O(1)^c···Cl(1)^g	135.5 (5)		

[a] Positions are indicated by superscripts. Standard deviations of the last significant figures are given in parentheses. [b] $x, y, 1 + z$. [c] $1 - x, {}^1/_2 - y, {}^1/_2 + z$. [d] $x, -{}^1/_2 + y, {}^1/_2 - z$. [e] $1 - x, {}^1/_2 - y, {}^3/_2 + z$. [f] $-x, {}^1/_2 - y, {}^1/_2 + z$. [g] $1 - x, -y, -z$. [h] $-x, -y, -z$.

Nqr Data. The temperature dependence of the ^{35}Cl nqr spectrum of $HICl_4 \cdot 4H_2O$ between 15 and −140° was obtained with a locally modified Wilks NQR-1 spectrometer. The low-temperature cell consisted of a dewar containing the rf coil and sample which was cooled by nitrogen gas derived by the boiling of liquid nitrogen. Temperature control was achieved by adjustment of the flow rate, and the apparatus was operated in a steady-state mode. Because of the corrosiveness of the sample, the thermocouple was placed in the exit gas stream and not in the sample. Comparison of runs of the solid acid with runs of a sample of KCl revealed the exit gas stream to be within ±1° at low temperatures and ±2° at higher temperatures of the KCl sample temperature for the flow rates used.

Frequencies were measured by coupling the CW signal from a grid dip meter into the superregenerative oscillator circuit. To reduce the estimated frequency uncertainties (to ±0.05 MHz), a Jerrold Model 900B sweep-signal generator was used for spectral display. The signal obtained from a pickup coil located near the superregenerative oscillator tank circuit was mixed with the sweep-signal generator output in a Hewlett-Packard Model 10534A mixer. The output of this mixer was fed into the detector of the sweep-signal generator, and displayed on an oscilloscope.

The measured frequencies at 278°K are 21.3, 21.9, 22.7, and 22.9 MHz, with an uncertainty of ±0.1 MHz. It is very significant that four resonances are observed over the entire temperature range covered. These have roughly equal intensities, clearly revealing the presence of four inequivalent chlorine atom sites.

Discussion

The X-ray data indicate a structure with two chlorine atom sites, while the nqr data require four sites. Since nqr frequencies are very sensitive to crystal structure distortions, it is appropriate first to discuss the the structure in terms of the symmetry indicated by the X-ray data, and then to consider the slight distortion which might account for the observed nqr splittings without invalidating the interpretation of the X-ray data.

Description of the Structure. The solid state structure of tetrachloroiodic acid tetrahydrate is a stratified configuration which contains alternating layers of tetrachloroiodate ions and a hydrogen-bonded hydrate network as shown in Figure 1. The sheets are formed such that their normals are parallel to the crystallographic *a* axis. The iodine atoms of the ICl_4^- ions occupy the special positions (2a) (0, 0, 0; 0, $^1/_2$, $^1/_2$); the chlorine atoms occupy general positions (4e) in the uniquely determined, centric space group $P2_1/b$ (*c* unique).

Since the iodine atom of the tetrachloroiodate ion is located at a center of symmetry, the ion is strictly planar and it also nearly possesses its idealized square-planar geometry with the two unique iodine–chlorine bond distances being 2.52 and 2.54 Å. The average iodine–chlorine bond distance of 2.53 Å is similar to the average iodine–chlorine bond distances observed in $KICl_4 \cdot H_2O$ (2.51 Å)[14] and $NaICl_4 \cdot 2H_2O$ (2.50 Å).[25]

The tetrachloroiodate ions in $HICl_4 \cdot 4H_2O$ are packed in columns which extend along the crystallographic *c* direction as in $KICl_4 \cdot H_2O$. In the solid acid the shortest iodine–iodine distance within an ICl_4^- column is 5.31 Å, substantially longer than either the corresponding distance in $KICl_4 \cdot H_2O$ (4.28 Å) or the van der Waals diameter of iodine (4.30 Å). The shortest distance between two symmetry-related, nonbonded chlorine atoms of adjacent ICl_4^- ions within a column is 3.75 Å, which is slightly longer than the chlorine van der Waals diameter of 3.60 Å. The nearest chlorine···iodine nonbonding distance within a column is 4.07 Å. The shortest nonbonding chlorine···chlorine distance between two columns is 3.56 Å.

The sheets of water molecules in the acid may be considered to be composed of partially overlapping

(25) R. J. Bateman, manuscript in preparation.

Table IV. Comparison of Interatomic Distances in $HICl_4 \cdot 4H_2O$ and $HAuCl_4 \cdot 4H_2O$

$HICl_4 \cdot 4H_2O^a$	Distance, Å	$HAuCl_4 \cdot 4H_2O^b$	Distance, Å
I–Cl(av)	2.53	Au–Cl(av)	2.284
O(2)···Cl(1)	3.42	O(2)···Cl(1)	3.423
$O(2)^c \cdots Cl(2)$	3.35	O(2)···Cl(2)	3.375
O(1)···O(2)	2.72	O(1)···O(2′)	3.096
$O(1) \cdots O(2)^c$	2.82	O(1)···O(2)	2.743
$O(1)^c \cdots O(1)^d$	2.64	O(1)···O(1)	2.57
$O(1)^c \cdots O(2)$	3.27	O(1)···O(2)	2.743

[a] Superscripts refer to same positions as those in Table II. [b] J. M. Williams and S. W. Peterson, *J. Amer. Chem. Soc.*, **91**, 776 (1969). The prime notation is used here to denote an oxygen atom of a different chain. [c] See footnote *c*, Table II. [d] See footnote *d*, Table II.

chains of hydrogen-bonded water molecules which extend parallel to the crystallographic *c* axis. The outermost oxygen atoms within a chain, labeled O(2), are surrounded by six chlorine atoms at distances of 3.35, 3.40, 3.42, 3.46, 3.55, and 3.62 Å. The absence of short oxygen–chlorine distances may be a result of the reduced effective negative charge on the chlorine atoms compared with simple chloride ions.[14] The mean nearest-neighbor chlorine–oxygen distance of 3.48 Å is similar to the corresponding average distances observed in $KICl_4 \cdot H_2O$ (3.44 Å)[14] and $NaICl_4 \cdot 2H_2O$ (3.44 Å).[25] The remaining oxygen atom of the asymmetric unit has six chlorine atoms in close proximity at distances of 3.36, 3.54, 3.56, 3.58, 3.67, and 3.85 Å.

The three independent oxygen···oxygen distances in each chain are 2.64, 2.82, and 3.27 Å. The shortest oxygen···oxygen distance between adjacent hydrate chains is 2.72 Å, which is typical of a reasonably strong hydrogen bond (*e.g.*, for ice (I) the hydrogen-bonded oxygen–oxygen distance is between 2.73 and 2.76 Å).[26] The short oxygen–oxygen distance of 2.64 Å between the two centrosymmetrically related oxygen atoms within a chain suggests the possible presence of a weakly formed diaquo ion, $H_5O_2^+$. The solid acids in which a well-defined $H_5O_2^+$ has been observed possess O···O distances in the range 2.41–2.57 Å.[3–7] In addition, the proton hydrates $H_7O_3^+$ and $H_9O_4^+$ have been suggested[8] for $HBr \cdot 4H_2O$ with O···O distances in the range 2.46–2.59 Å.

The stoichiometry of $HICl_4 \cdot 4H_2O$ requires that the acid proton occupy one of the centrosymmetric special positions (2b), (2c), or (2d). The positions (2c) and (2d) may be rejected on a chemical basis, whereas (2b) is reasonable and would require that the proton be involved in a symmetrical hydrogen bond between the two adjacent O(1) atoms.

The crystal structure of tetrachloroiodic acid tetrahydrate may be directly compared with that of $HAuCl_4 \cdot 4H_2O$ recently reported by Williams and Peterson.[7] The gold(III) compound exhibits a disorder of the chlorine atoms, but within an ordered domain the two compounds are nearly isostructural. There is a significant difference between the oxygen networks of the two compounds in that the O(1)···O(1′) distance is 0.07 Å longer in the iodine compound, whereas the O(1)···O(2) distance is shorter. Hence, the chain network is better defined in $HAuCl_4 \cdot 4H_2O$ with strong hydrogen bonding within a chain and only very weak hydrogen bonding between chains. The pertinent interatomic distances in the two compounds are compared in Table IV, where the numbering for the atoms in $HAuCl_4 \cdot 4H_2O$ is the same as in Figure 1. The question arises whether a chlorine disorder similar to that observed in $HAuCl_4 \cdot 4H_2O$ may have also been present in $HICl_4 \cdot 4H_2O$ but not detected in the X-ray analysis. Such a chlorine disorder, in which two half-atoms are related by a mirror plane at $z = 0$, would have raised the space groups symmetry of $HICl_4 \cdot 4H_2O$ from $P2_1/b$ to $A2/m$. The systematic absences required for the higher symmetry space group were not observed.

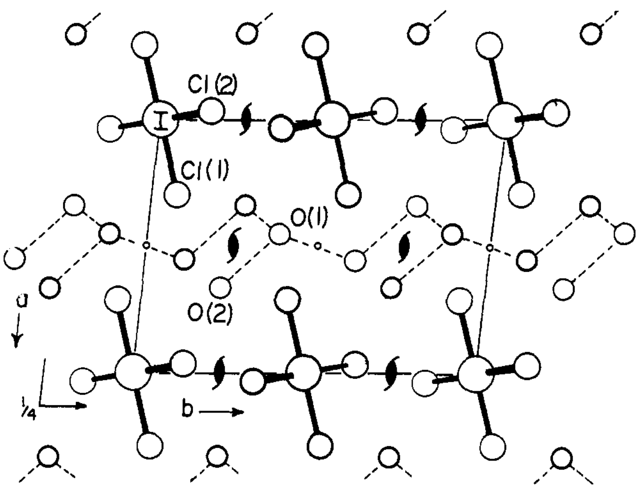

Figure 1. Unit cell of $HICl_4 \cdot 4H_2O$ viewed parallel to the crystallographic *c* axis.

Nqr Results and the Relationships to the Structure. From their nqr study of the chlorine and iodine resonance frequencies in polyhalide ions, Cornwell and Yamasaki[13,27] have described the intraionic bonding in di- and tetrachloroiodides within the framework of a resonance hybrid model, estimated bonding electron populations for both the iodine and chlorine atoms, and obtained approximate molecular orbitals within an LCAO formalism. The average nqr frequency for $HICl_4 \cdot 4H_2O$ (22.2 MHz) is close to that for other tetrachloroiodates (22.4 MHz).

The observed splittings of the ^{35}Cl resonances from their average value in $HICl_4 \cdot 4H_2O$ is almost certainly a result of the crystal-field perturbation of the ion. In addition, no phase transitions were observed throughout the temperature range studied, as shown by the temperature dependence of the ^{35}Cl resonance frequencies depicted in Figure 2.

The four-line ^{35}Cl nqr spectrum requires a noncentrosymmetric ICl_4^- ion. This is inconsistent with the symmetry deduced from the X-ray analysis. A possible explanation of this spectrum is suggested by the occurrence of the relatively long (2.64 Å) O(1)···O(1′) distance. This distance is significantly longer than similar oxygen···oxygen distances observed in solid acids which possess well-defined $H_5O_2^+$ ions.[3–6] On the basis of a broad survey of experimental data, Pimental and McClellan[10] suggest that for hydrogen-bonded oxygen···oxygen distances greater than 2.55 Å,

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(26) Reference 10, p 280.

(27) R. S. Yamasaki and C. D. Cornwell, *J. Chem. Phys.*, **30**, 1265 (1959).

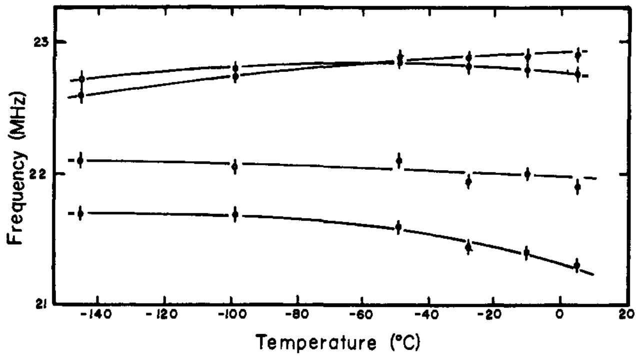

Figure 2. ^{35}Cl nqr frequency as a function of temperature for $HICl_4 \cdot 4H_2O$.

the proton potential function is very likely to be of the double-minimum type. The O···O distance of 2.64 Å for $HICl_4 \cdot 4H_2O$ would strongly indicate that the proton is in a double-minimum potential. Unless the barrier were low ($\ll kT$), this would imply a lowering of the unit cell symmetry from $P2_1/b$ to Pb or $P2_1$, but with the possibility of disorder leading to the higher average symmetry $P2_1/b$. Either of these lower space group symmetries is consistent with the X-ray structural results if it is assumed that the heavy-atom positions are not displaced appreciably from the positions required for space group symmetry $P2_1/b$.

The observed nqr results are consistent with the expected double-minimum potential (*vide supra*), provided the jump rate between the two minima is slow relative to the nqr line width (5 kHz). The proton jump rate would certainly be slow relative to an X-ray or neutron diffraction process. As a consequence, a lower symmetry should be expected in a diffraction experiment if the structure is ordered. The high apparent symmetry could result if the structure is disordered, with each of the atoms affected by the disorder appearing as two half-atoms centrosymmetrically related. For either the ordered or disordered model, the lower symmetry space group required by the nqr measurements is consistent with the X-ray data only if it is assumed that the heavy atom positions are not affected enough to alter the X-ray intensities appreciably. In addition, if a static disorder does exist such that the two half-protons are centrosymmetrically related, then sufficient short-range order must exist about most of the chlorine atoms in the crystal so that the nqr line is not noticeably broadened. This interpretation is consistent with the temperature dependence of the nqr spectrum of $HAuCl_4 \cdot 4H_2O$.[28]

In order to more fully interpret the nqr spectrum and its relationship to the solid-state structure of $HICl_4 \cdot 4H_2O$, it would be desirable to have proton positional parameters determined from diffraction data.

Acknowledgments. This work was accomplished with the financial support of the National Science Foundation and the Wisconsin Alumni Research Foundation. The authors wish to express their appreciation to Professors C. D. Cornwell and L. F. Dahl for many helpful discussions. The computer usage at the University of Wisconsin Computing Center was made available through partial support of NSF and WARF through the University Research Committee.

(28) R. J. Bateman and C. D. Cornwell, manuscript in preparation.