

The Crystal and Molecular Structure of Iminodiacetic Acid Hydrofluoride Monohydrate, $C_4H_7NO_4 \cdot HF \cdot H_2O$, at $-100^\circ C$

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The crystal and molecular structure of iminodiacetic acid hydrofluoride monohydrate, $C_4H_7NO_4 \cdot HF \cdot H_2O$, has been determined from X-ray intensities collected at $-100^\circ C$ with a four-circle single-crystal diffractometer. The space group is $P2_1/c$ with $Z=4$, and the unit-cell dimensions are $a=11.8784$ (29), $b=6.4045$ (9), $c=10.0568$ (22) Å, $\beta=110.65$ (2)°. The structure has been refined to $R=0.038$. Positively charged iminodiacetic acid ions are connected by hydrogen bonds, *via* the fluoride ions and the water molecules, forming layers that are stacked in the c direction. The forces between the layers are of van der Waals type.

Introduction

In a systematic study of the geometry of the positively charged iminodiacetic acid ion, $[C_4H_8NO_4]^+$, in the solid state, the crystal structures of $C_4H_7NO_4 \cdot HX$, where $X=Cl, Br$ or I , have been reported (Oskarsson, 1973, 1974). These investigations have now been extended to a fluoride, which crystallizes with one mole of water. Due to the different halide ions, one would expect differences in packing and hydrogen bonding in these compounds which might affect the conformation of the organic ion. A comparison of these structures should also give information concerning hydrogen bonds with halide ions as acceptors.

This communication reports the crystal structure of iminodiacetic acid hydrofluoride monohydrate, denoted as IDAF below.

Crystal data

$C_4H_7NO_4 \cdot HF \cdot H_2O$; F.W. 171.13. Monoclinic, $P2_1/c$, $a=11.8784$ (29),* $b=6.4045$ (9), $c=10.0568$ (22) Å, $\beta=110.65$ (2)°, $V=715.9$ Å³; $Z=4$; $\mu(Cu K\alpha)=14.5$ cm⁻¹; $D_m=1.6$, $D_x=1.59$ g cm⁻³.

Experimental

Crystals of IDAF were obtained by evaporation of an aqueous solution of iminodiacetic acid in hydrofluoric acid. When removed from the mother liquor the crystals decompose within 24 h if stored at room temperature, but at $-100^\circ C$ they are stable for a long time.

Weissenberg photographs showed that IDAF crystallizes in the monoclinic system. The systematically absent reflexions, $0k0$ with $k \neq 2n$, and $h0l$ with $l \neq 2n$,

are consistent with the space group $P2_1/c$. Accurate cell dimensions were determined at $-100^\circ C$ from the θ values of 60 reflexions, measured as described by Danielsson, Grenthe & Oskarsson (1974). The density was determined from the loss of weight in benzene.

A single crystal with dimensions $0.2 \times 0.3 \times 0.08$ mm was used for collecting intensities at $-100^\circ C$ on a computer-controlled four-circle diffractometer of type CAD-4, equipped with a modified commercial low-temperature device (Danielsson, Grenthe & Oskarsson, 1974). The crystal was cooled to $-100^\circ C$ within 30 min of being removed from the mother liquor. Experimental conditions and data reduction are described by Oskarsson (1973), but with one exception. The scan interval, $\Delta\omega$, was extended 25% at both ends for the background measurement. Of the 1425 independent reflexions in the range $5^\circ < \theta < 70^\circ$, 55 could not be measured owing to obscuration by the low-temperature device. Of the observed reflexions, 110 with $I < 3\sigma_c(I)$ were considered not significantly different from the background and were excluded from the refinement. The transmission factors evaluated by numerical integration varied from 0.754 to 0.898.

Structure determination and refinement

The positions of the non-hydrogen atoms were determined by symbolic addition (Karle & Karle, 1963, 1966).

Full-matrix least-squares refinement minimizing $\sum w(|F_o| - |F_c|)^2$ was performed with weights $w = 1/(\sigma_c^2 + a|F_o|^2 + b)$, where a and b were chosen so that the average value of $w(|F_o| - |F_c|)^2$ was almost equal in different $|F_o|$ and $\sin \theta$ intervals. In the last cycles of refinement $a=0.00045$ and $b=1.5$ were used. The convergency was followed by the R and R_w defined by $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$. The refinement of a scale factor and the

* Numbers in parentheses represent e.s.d.'s in the last significant digits.

positional parameters, with the anisotropic thermal parameters, converged to $R=0.079$. All hydrogen atoms were then located in a difference map using the data with $\sin \theta/\lambda \leq 0.5 \text{ \AA}^{-1}$. Further refinement including the hydrogen atoms with isotropic temperature factors resulted in $R=0.038$ and $R_w=0.046$. In the last cycle of refinement, the shifts in the parameters were less than 10% of the estimated standard deviations.

The presence of extinction was investigated by use of an isotropic model (Zachariasen, 1967), but no such effects were observed.

Table 1. Atomic coordinates with *e.s.d.*'s

B denotes the isotropic temperature factor.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)
F	0.24810 (9)	0.04217 (19)	0.20852 (11)	
N	0.7426 (1)	0.2157 (3)	-0.0019 (2)	
O(1)	0.4233 (1)	0.3016 (2)	-0.0982 (2)	
O(2)	0.5490 (1)	0.3840 (2)	-0.2136 (1)	
O(3)	1.0434 (1)	0.0774 (2)	0.2258 (1)	
O(4)	0.9733 (1)	0.2392 (2)	0.0138 (1)	
O(5)	0.2044 (1)	0.3714 (3)	0.0158 (2)	
C(1)	0.5278 (2)	0.3049 (3)	-0.1163 (2)	
C(2)	0.6208 (2)	0.1929 (3)	0.0057 (2)	
C(3)	0.8366 (2)	0.1274 (3)	0.1259 (2)	
C(4)	0.9593 (2)	0.1558 (3)	0.1144 (2)	
H(1)	0.620 (2)	0.253 (3)	0.093 (2)	1.0 (4)
H(2)	0.602 (2)	0.040 (4)	0.002 (2)	2.0 (5)
H(3)	0.833 (2)	0.196 (4)	0.211 (2)	1.2 (4)
H(4)	0.821 (2)	-0.022 (4)	0.133 (2)	1.1 (4)
H(5)	0.746 (2)	0.144 (4)	-0.076 (2)	1.2 (4)
H(6)	0.755 (2)	0.347 (5)	-0.007 (3)	2.7 (6)
H(7)	1.108 (3)	0.083 (5)	0.215 (3)	3.6 (7)
H(8)	0.373 (3)	0.348 (5)	-0.159 (3)	2.9 (6)
H(9)	0.134 (3)	0.354 (5)	0.006 (3)	3.2 (7)
H(10)	0.237 (3)	0.301 (5)	0.086 (3)	3.7 (8)

The scattering factors were taken from *International Tables for X-ray Crystallography* (1962) for the heavy atoms and from Stewart, Davidson & Simpson (1965) for the hydrogen atom. The positional and thermal parameters, with the r.m.s. components, are given in Tables 1 and 2. Observed and calculated structure factors are presented in Table 3. Selected interatomic distances and angles are shown in Table 4.

Description of the structure

The atoms of the organic ion are designated in Fig. 1. The structure is composed of water molecules, fluoride ions and positively charged iminodiacetic acid ions, $[\text{C}_4\text{H}_8\text{NO}_4]^+$. The latter ions are connected by hydrogen bonds $\text{O}-\text{H}\cdots\text{F}\cdots\text{H}-\text{O}$ forming chains running in the direction $[102]$ (Fig. 2). These chains are cross-linked with hydrogen bonds $\text{N}-\text{H}\cdots\text{F}$ forming layers that are stacked in the *c* direction. The water molecule increases the stability within the layers by donating hydrogen bonds to a fluoride ion and to a carboxylic group and by accepting one hydrogen bond from the NH_2 group. The layers have a thickness of $c/2$. The closest contact distances between the layers are $\text{F}-\text{H}(1)$, $\text{F}-\text{H}(3)$ and $\text{O}(1)-\text{H}(2)$, 2.75 (3), 2.67 (3) and 2.46 (3) Å, respectively, indicating van der Waals contacts.

Related interatomic distances and angles are not significantly different in the two halves of the organic ion [Table 4(a)]. They agree well with those found in the chloride, bromide and iodide (Oskarsson, 1973, 1974) except for the angle $\text{C}-\text{N}-\text{C}$, discussed below. Dihedral angles $\text{N}-\text{C}-\text{C}-\text{O}$ are given in Table 4(b). The non-hydrogen atoms form two planes (Table 5)

Table 2. Thermal parameters $\beta_{ij} \times 10^4$ with *e.s.d.*'s, and r.m.s. components R_i (Å) along the principal axes of the ellipsoids of thermal vibration

The expression used is $\exp [-(\beta_{11}h^2 + \dots + 2\beta_{12}hk + \dots)]$.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	R_1	R_2	R_3
F	24 (1)	144 (4)	58 (1)	1 (1)	9 (1)	-13 (2)	0.122	0.156	0.183
N	22 (1)	83 (5)	46 (2)	2 (2)	13 (1)	3 (2)	0.114	0.131	0.145
O(1)	20 (1)	138 (5)	53 (2)	10 (2)	9 (1)	18 (2)	0.108	0.149	0.180
O(2)	34 (1)	146 (5)	52 (2)	6 (2)	17 (1)	19 (2)	0.140	0.144	0.183
O(3)	21 (1)	151 (5)	49 (2)	10 (2)	9 (1)	9 (2)	0.112	0.151	0.180
O(4)	26 (1)	117 (4)	58 (2)	1 (2)	16 (1)	12 (2)	0.124	0.146	0.170
O(5)	27 (1)	119 (5)	79 (2)	-4 (2)	10 (1)	27 (2)	0.129	0.142	0.208
C(1)	27 (1)	84 (5)	53 (2)	0 (2)	13 (1)	-6 (3)	0.129	0.131	0.157
C(2)	24 (1)	119 (6)	56 (2)	0 (2)	17 (1)	10 (3)	0.115	0.148	0.167
C(3)	28 (1)	105 (6)	48 (2)	1 (2)	12 (1)	2 (3)	0.132	0.146	0.150
C(4)	27 (1)	85 (5)	52 (2)	-2 (2)	13 (1)	-15 (2)	0.123	0.129	0.162



Fig. 1. A stereoscopic pair of drawings showing the positively charged iminodiacetic acid ion. Figs. 1, 2 and 4 have been drawn by the program ORTEP.

that are twisted 5° at the nitrogen atom. A detailed discussion of the conformation of the positively charged iminodiacetic acid ion, $[\text{C}_4\text{H}_8\text{NO}_4]^+$, in different crystallographic surroundings is postponed to a subsequent publication.

The fluoride ion is hydrogen-bonded to two carboxylic oxygens, one nitrogen atom and one water-molecule [Table 4(c)]. Since the two fluoride-carboxylic-oxygen distances are very similar, the mean value for this distance [2.505 (3) Å] is compared with the related distances in the chloride and bromide. The differences $d_{\text{O}-\text{Br}}-d_{\text{O}-\text{F}}$ and $d_{\text{O}-\text{Cl}}-d_{\text{O}-\text{F}}$ are 0.711 (5) and 0.554 (5) Å respectively, which are about 0.1 Å larger than the differences in ionic radii for the halide ions

Table 3. Observed and calculated structure factors

The columns are h , $10 \times |F_o|$ and $10 \times |F_c|$.

h	$10 \times F_o $	$10 \times F_c $
1	1.485 (3)	1.485 (3)
2	1.487 (3)	1.487 (3)
3	1.512 (3)	1.512 (3)
4	1.510 (3)	1.510 (3)
5	1.318 (3)	1.318 (3)
6	1.203 (3)	1.203 (3)
7	1.311 (3)	1.311 (3)
8	1.207 (3)	1.207 (3)
9	0.99 (3)	0.99 (3)
10	1.00 (3)	1.00 (3)
11	0.95 (3)	0.95 (3)
12	0.97 (3)	0.97 (3)
13	0.89 (3)	0.89 (3)
14	0.93 (4)	0.93 (4)
15	0.90 (4)	0.90 (4)
16	0.80 (4)	0.80 (4)

Table 4. Selected interatomic distances (Å) and angles ($^\circ$) with *e.s.d.*'s

(a) The iminodiacetic acid ion			
N—C(2)	1.485 (3)	C(2)—N—C(3)	111.4 (2)
N—C(3)	1.487 (3)	N—C(2)—C(1)	110.9 (2)
C(2)—C(1)	1.512 (3)	N—C(3)—C(4)	109.7 (2)
C(3)—C(4)	1.510 (3)	C(2)—C(1)—O(1)	109.5 (2)
C(1)—O(1)	1.318 (3)	C(2)—C(1)—O(2)	123.9 (2)
C(1)—O(2)	1.203 (3)	O(1)—C(1)—O(2)	126.6 (2)
C(4)—O(3)	1.311 (3)	C(3)—C(4)—O(3)	110.7 (2)
C(4)—O(4)	1.207 (3)	C(3)—C(4)—O(4)	122.7 (2)
C(2)—H(1)	0.99 (3)	O(3)—C(4)—O(4)	126.6 (2)
C(2)—H(2)	1.00 (3)	H(1)—C(2)—H(2)	112 (2)
C(3)—H(3)	0.95 (3)	H(3)—C(3)—H(4)	108 (2)
C(3)—H(4)	0.97 (3)	H(5)—N—H(6)	107 (3)
N—H(5)	0.89 (3)	C(1)—O(1)—H(8)	114 (3)
N—H(6)	0.93 (4)	C(4)—O(3)—H(7)	108 (2)
O(3)—H(7)	0.90 (4)		
O(1)—H(8)	0.80 (4)		

(b) Dihedral angles

N—C(2)—C(1)—O(1)	6.9
N—C(2)—C(1)—O(2)	6.7
N—C(3)—C(4)—O(3)	0.5
N—C(3)—C(4)—O(4)	0.0

(c) The hydrogen bonds

O(1)···F	2.502 (2)
O(1)—H(8)	0.80 (4)
F·····H(8)	1.70 (4)
O(1)—H(8)···F	176 (4)
N···F	2.688 (3)
N—H(5)	0.89 (3)
F···H(5)	1.81 (3)
N—H(5)···F	169 (3)
N·····O(5)	2.737 (3)
H—(N6)	0.93 (4)
H(6)···O(5)	1.81 (4)
N—H(6)···O(5)	173 (3)
O(3)···F	2.508 (2)
O(3)—H(7)	0.90 (4)
F·····H(7)	1.63 (4)
O(3)—H(7)···F	163 (4)
O(5)···F	2.777 (2)
O(5)—H(10)	0.80 (3)
F·····H(10)	2.04 (3)
O(5)—H(10)···F	152 (3)
O(5)···O(4)	2.858 (2)
O(5)—H(9)	0.81 (3)
O(4)···H(9)	2.07 (3)
O(5)—H(9)···O(4)	164 (3)

(d) The water molecule

O(5)—H(10)	0.80 (3)
O(5)—H(9)	0.81 (3)
H(9)—O(5)—H(10)	102 (3)

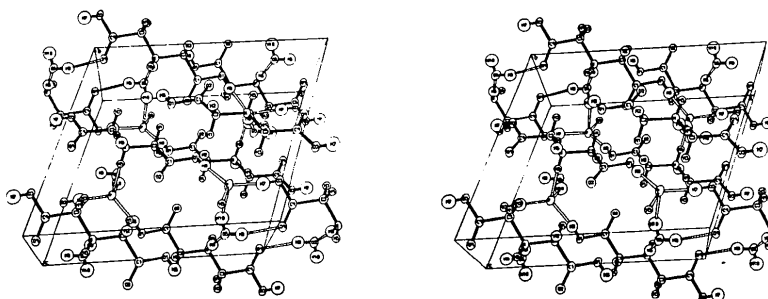


Fig. 2. The structure of IDAF. Unshaded bonds symbolize hydrogen bonds.

Table 5. Deviations (Å) from the least-squares planes through the non-hydrogen atoms of the independent halves of the ion $[\text{C}_4\text{H}_8\text{NO}_4]^+$

Atoms defining plane I are N, C(1), C(2), O(1) and O(2), and atoms defining plane II are N, C(3), C(4), O(3) and O(4). The angle between the planes is 5° .

I		II	
N	0.048	N	-0.003
C(1)	-0.011	C(3)	0.003
C(2)	-0.060	C(4)	0.003
O(1)	0.040	O(3)	-0.003
O(2)	-0.016	O(4)	0.000

involved. Part of this difference might be due to the different temperatures at which the structures have been determined, but it might also reflect the expected tendency for the fluoride ion to form stronger hydrogen bonds than the chloride and bromide. The fluoride-carboxylic-oxygen distances are remarkably short. The value 2.7 \AA is given by Hamilton & Ibers (1968) as a characteristic distance for the $\text{OH}\cdots\text{F}$ bond. However, if the fluoride ion acts as a donor, the $\text{O}\cdots\text{HF}$ may be as short as 2.38 \AA (Altenburg & Mootz, 1971).

It is also of interest to compare the hydrogen bonds in IDAF with the situation found in solutions of potassium fluoride in glacial acetic acid (Emsley, 1971).

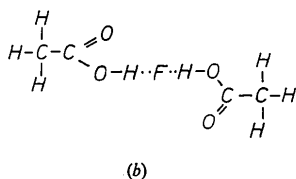
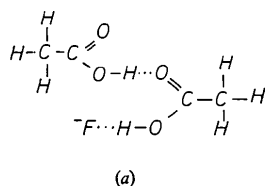


Fig. 3. Possible structures of the acetic acid dimers in solutions of potassium fluoride in glacial acetic acid. (a) The structure proposed by Emsley (1971). (b) The structure proposed by the present author.

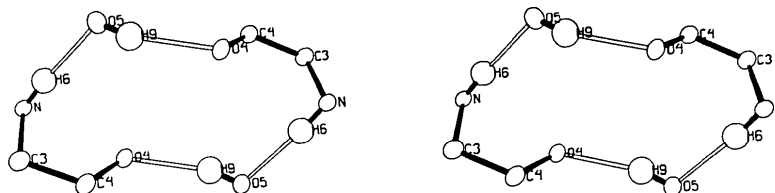


Fig. 4. A stereoscopic view of the 14-membered ring.

From viscosity measurements, Emsley concluded that the solution contains mainly acetic acid dimers, and he proposes the structure given in Fig. 3(a). From IR and thermodynamic data, he calculates an energy for the bond $^-\text{F}\cdots\text{H}-\text{O}$ of 120 kJ mole^{-1} , which is a very strong hydrogen bond. Since the fluoride ion accepts hydrogen bonds from two carboxylic oxygens in IDAF, this possibility cannot be excluded in solution, and the structure proposed in Fig. 3(b) might also be possible for the linear acetic acid dimer.

The C-N-C angle, $111.4 (2)^\circ$, is significantly smaller in IDAF than in the related chloride, bromide and iodide, where it is in the range $114.1\text{--}114.7^\circ$. If the $\text{N}-\text{H}\cdots\text{F}$ bond is stronger than the $\text{N}-\text{H}\cdots\text{X}$ bond, $\text{X}=\text{Cl}, \text{Br}$ or I , the positive net charge on the hydrogen atom with respect to the electrons involved in the N-H bond should be reduced in the fluoride structure compared with the others, resulting in a more pronounced lone-pair character of the electrons in this bond. A simple electrostatic theory then predicts that the other bond angles around the nitrogen should decrease (Gillespie & Nyholm, 1957). Thus the comparatively small value of the C-N-C angle in IDAF may be a consequence of the strength of the $\text{H}\cdots\text{F}$ bond.

The dimensions of the water molecule [Table 4(d)] agree well with those found in other hydrates (Padmanabhan, Srikantha & Ali, 1965; Levy & Peterson, 1957). It takes part in a 14-membered ring composed of $\text{O}(5)-\text{H}(9)-\text{O}(4)-\text{C}(4)-\text{C}(3)-\text{N}-\text{H}(6)$ and a centrosymmetrically related set of atoms (Fig. 4). Similar ring formations having a centre of symmetry were also found in the iodide and in a monoclinic phase of imino-diacetic acid (Boman, Herbertsson & Oskarsson, 1974).

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Hexaaquocobalt(II) Bis(hydrogen-2,2'-dithiobisbenzoate)-hexahydrate-Tetrakis-methanol and its Isostructural Nickel(II) Homologue

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$\text{CoS}_4\text{O}_{24}\text{C}_{32}\text{H}_{58}$, or $\text{Co}(\text{H}_2\text{O})_6(\text{HOOC}-\text{C}_6\text{H}_4-\text{SS}-\text{C}_6\text{H}_4-\text{COO})_2(\text{H}_2\text{O})_6(\text{CH}_3\text{OH})_4$, triclinic, $P\bar{1}$, $a=7.549(1)$, $b=12.988(2)$, $c=13.073(2)$ Å, $\alpha=107.06(1)^\circ$, $\beta=97.19(1)^\circ$, $\gamma=94.30(1)^\circ$, $V=1207.2$ Å³ at 19°C, $D_x=1.400$ g cm⁻³, $D_{\text{obs}}=1.41(2)$ g cm⁻³. The structure consists of one hexaaquocobalt(II) cation at the origin and two $\text{C}_{14}\text{H}_9\text{S}_2\text{O}_7^-$ anions, all linked together in a hydrogen-bonding scheme involving six additional waters and four methanol molecules, two of which are disordered. $\text{NiS}_4\text{O}_{24}\text{C}_{32}\text{H}_{58}$ is isostructural: $a=7.545(1)$, $b=12.946(5)$, $c=13.050(2)$ Å, $\alpha=106.96(2)$, $\beta=97.08(1)$, $\gamma=94.12(3)^\circ$ and $V=1202.1$ Å³.

Introduction

Transition metal ions such as mercury(II) (Challenger, 1959), palladium(II) (Kawanishi, Yokoyama & Tanaka, 1972; Boschi, Crociani, Toniolo & Belluco, 1970) and copper(I) (Ottersen, Warner & Seff, 1973) function as electrophiles in the cleavage of the sulfur-sulfur bond in organic disulfides. Also, transition metal ion-organic disulfide interactions can behave 'non-innocently' in the functioning of metalloenzymes (Hemmerich, 1966). Thus, the study of transition metal ion-organic disulfide complexes is of some importance.

When aqueous methanol solutions of Co(II) or Ni(II) salts and 2,2'-dithiobisbenzoic acid are mixed in the presence of the hindered base 2,6-dimethylpyridine, and the solutions slowly concentrated, pink crystals of the Co(II) title compound or green crystals of the Ni(II) homologue are produced. The compositions of the crystals, and their stability relative to loss of solvent and the accompanying crystal degradation and color change, depend upon the water:methanol ratio of the mother liquor. When this ratio is approximately 3:1, the crystals are the most stable. (Solvent exchange

or loss in flotation liquids prevented an accurate density measurement.) The structure determination was carried out to study the disulfide, *i.e.* the CSSC dihedral angle and the S-S bond length, and to investigate possible interactions between the metal ion and the disulfide anion. Although spectral evidence indicated no direct interactions, it was hoped that a structural investigation might help in explaining the spectral changes which indicated alterations in the Co(II) coordination environment upon loss of solvent.

A computer-controlled Syntex $P\bar{1}$ automated diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($K\alpha_1$, $\lambda=0.70926$ Å; $K\alpha_2$, $\lambda=0.71354$ Å) and a pulse-height analyzer was used to study the Co(II) complex further. A crystal approximately $0.4 \times 0.3 \times 0.1$ mm in size was used. Diffraction intensities were collected by the θ - 2θ scanning mode with scan speed variable from 1° to 24° min⁻¹, depending on the peak intensity of the reflection. Three check reflections re-measured after every 100 during data collection showed no systematic variations, so no decay correction was applied. Standard deviations of the individual reflections were taken as the square root of the total counts with a 2% addition for instrumental instability. Of the 3176 symmetry independent reflections measured, all those for which $2\theta < 45^\circ$, 2512 had intensities greater

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