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The Crystal and Molecular Structures of Iminodiacetic Acid Hydrochloride, $C_4H_7NO_4.HCl$, and Iminodiacetic Acid Hydrobromide, $C_4H_7NO_4.HBr$

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The crystal and molecular structures of iminodiacetic acid hydrochloride, $C_4H_7NO_4.HCl$, and iminodiacetic acid hydrobromide, $C_4H_7NO_4.HBr$, have been determined by a symbolic addition method with three-dimensional single crystal X-ray data obtained on a diffractometer. The compounds are isostructural, crystallizing in the orthorhombic space group *Pmmn* with $Z=2$. The unit-cell dimensions are $a=12{\cdot}4101$, $b=5{\cdot}7349$, $c=5{\cdot}1280$ Å and $a=12{\cdot}8150$, $b=5{\cdot}8705$, $c=5{\cdot}0870$ Å for the chloride and bromide respectively. Positively charged iminodiacetic acid ions are connected by hydrogen bonds *via* the halide ions and zigzag layers are formed. These layers are stacked in the **c** direction and the forces between the layers are of van der Waals type.

Introduction

In a research program at this Institute dealing with rare earth carboxylates the crystal and molecular structures of the neodymium iminodiacetate compounds $Nd_2(C_4H_5NO_4)_3.2HCl.7H_2O$ (Albertsson & Oskarsson, 1968) and $Nd(C_4H_5NO_4)Cl.3H_2O$ (Oskarsson, 1971) have been determined. In order to investigate how the geometry of the organic molecule is affected by different crystallographic surroundings, a systematic study of the compounds $C_4H_7NO_4.HX$, where X = F, Cl, Br or I, has been commenced. A comparison of these structures should also give some information concerning hydrogen bonds with halide ions as acceptors. The infrared spectrum of the chloride has been reported (Novak, Cotrait & Joussot-Dubien, 1965), but no experimental data have been published for the other compounds.

In this paper the crystal structures of the chloride and bromide are described. They are referred to below as IDAC and IDAB, respectively.

Crystal data

IDAC, $C_4H_7NO_4.HCl$, F.W. 169·57. Orthorhombic, *Pmmn*, $a=12{\cdot}4101$ (22);* $b=5{\cdot}7349$ (16); $c=5{\cdot}1280$ (11) Å; $V=365{\cdot}00$ (2) Å^3; $Z=2$; $\mu(\text{Cu } K\alpha)=43{\cdot}2$ cm^{-1}; $D_m=1{\cdot}5$; $D_x=1{\cdot}54$ g cm^{-3}.

IDAB, $C_4H_7NO_4$ HBr, F.W. 214·04. Orthorhombic, *Pmmn*, $a=12{\cdot}8150$ (20); $b=5{\cdot}8705$ (7); $c=5{\cdot}0870$ (7) Å; $V=382{\cdot}70$ (1) Å^3; $Z=2$; $\mu(\text{Cu } K\alpha)=76{\cdot}7$ cm^{-1}; $D_m=1{\cdot}8$; $D_x=1{\cdot}86$ g cm^{-3}.

Experimental

Crystals of IDAC and IDAB were obtained by evaporation of solutions of iminodiacetic acid in hydrochloric and hydrobromic acid, respectively. IDAB is stable in air at room temperature but IDAC decomposes slowly (approximately within two months). The compositions of the compounds were checked by elemental analysis. The density, D_m, was determined by the displacement method with benzene.

Weissenberg photographs showed that IDAC and IDAB are isostructural and crystallize in the orthorhombic system. The only systematically absent reflexions, *hk*0 with $h+k\neq 2n$, indicate the space group to be either *Pmmn* or $Pm2_1n$. The cell dimensions were improved by a least-squares treatment of powder spectra obtained with Cu $K\alpha_1$ radiation ($\lambda=1{\cdot}54051$ Å) in a Guinier–Hägg focusing camera. Aluminum ($a=4{\cdot}04962$ Å) was used as an internal standard.

A single crystal of IDAC with dimensions $0{\cdot}12\times0{\cdot}13\times0{\cdot}12$ mm was used for data collection on an automatic single-crystal diffractometer of type CAD-4 (manufactured by Enraf–Nonius, Delft, Holland). Intensities were measured at a take-off angle of 5° with Cu $K\alpha$ radiation. A graphite monochromator was used. The ω–2θ scan technique was employed, with a scan interval $\Delta\omega=1{\cdot}00+0{\cdot}15\tan\theta$. The background was measured for $\frac{1}{4}$ of the scan time at each end of the interval. All 404 independent reflexions in the range $5°<\theta<70°$ were measured with repeated scans. Owing to a failure of the ratemeter, 42 reflexions were excluded in the refinement because they did not obey the condition $(I_1-I_2)^2\leq 8(I_1+I_2)$ in three attempts, where I_1 and I_2 are the intensities in two successive scans of a reflexion. Another 18 reflexions with $I<3\sigma_c(I)$ were judged to be insignificantly different from the background and were excluded. The values of $\sigma_c(I)$ are based on counting statistics. The reflexions 311 and 400 were selected as standards, and the intensity of one of them was recorded every hour. The fluctuation in the intensities of the standard reflexions was 6% and could be described as a function of the exposure time by a polynomial of the 4th degree. This polynomial was used for scaling the data set. The values of I and $\sigma_c(I)$ were

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* Numbers in parentheses represent estimated standard deviations in the last significant digits.

corrected for Lorentz, polarization and absorption effects. The expression $p=(1+\cos^2 2\theta_M \cos^2 2\theta)/(1+\cos^2 2\theta_M)$ with $\theta_M=13{\cdot}3°$ was used in the correction of the polarization effects. The transmission factor, vealuated by numerical integration, varied from 0·607 to 0·667.

A single crystal of IDAB with dimensions $0{\cdot}10\times 0{\cdot}10\times 0{\cdot}22$ mm was used for the data collection on the diffractometer with the same experimental conditions. Of the 432 independent reflexions, 20 were excluded because they did not obey the condition $(I_1-I_2)^2\le 8(I_1+I_2)$ in three successive attempts and seven were considered insignificantly different from the background $[I<3\sigma_c(I)]$. The fluctuation of the intensities of the standard reflections was less than 2%. The transmission factor varied from 0·374 to 0·578.

Structure determination and refinement

The structure of IDAC was solved by symbolic addition (Karle & Karle, 1963; Karle & Karle, 1966). Since $|E|$ statistics indicate a centre of symmetry the space group *Pmmn* was chosen.

Full-matrix least-squares refinement minimizing $\sum w(|F_o|-|F_c|)^2$ was performed with weights $w=1/(\sigma_c^2+a|F_o|^2+b)$. In the last cycles of refinement $a=0{\cdot}005$ and $b=2{\cdot}5$ were used. The convergency was followed by the agreement indices R and R_w defined by $R=\sum||F_o|-|F_c||/\sum|F_o|$ and $R_w=[\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}$. A refinement of the scale factor and the positional parameters for the non-hydrogen atoms with anisotropic thermal parameters converged to $R=0{\cdot}093$ and $R_w=0{\cdot}102$. Two hydrogen atoms were then located in a difference electron density map, which was calculated with data with $\sin\theta/\lambda<0{\cdot}5$. The third independent hydrogen atom could not be located. The region between the chloride ion and the carboxyl group, the only chemically reasonable one, showed negative electron density.

After a preliminary extinction correction (Zachariasen, 1963) a difference map revealed two peaks in the expected region, 0·20 and 0·15 e Å^{-3}, respectively. The remaining hydrogen atom was placed at the position of the strongest peak. However, this hydrogen atom might be disordered as will be discussed later. In the final refinement including an isotropic extinction coefficient (Zachariasen, 1967) the temperature factors of the hydrogen atoms were judged to be too small and were given an arbitrary value of 3·0 Å^2. Refinement converged to $R=0{\cdot}040$ and $R_w=0{\cdot}048$. The extinction parameter $g=1{\cdot}22\ (9)\times 10^4$ corresponds to a mosaic spread of 4·75″ or a domain size of $1{\cdot}89\times 10^{-4}$ cm. In the last cycle of refinement the shifts in the parameters were less than 1% of the estimated standard deviations and the refinement was considered complete. The average values of $w(|F_o|-|F_c|)^2$ were nearly constant in different $|F_o|$ intervals. The value of S, defined by $S=[\sum w(|F_o|-|F_c|)^2/(m-n)]^{1/2}$, where m is the number of observations and n the number of parameters varied, was 1·04. Thus the errors appear to be correctly estimated.

The positional and thermal parameters for IDAC, except those for H(3), were used as preliminary parameters for IDAB. A difference map, obtained from data with $\sin\theta/\lambda<0{\cdot}45$, had the same features as IDAC, and H(3) was placed at the position of the strongest peak. In the last cycle of refinement the shifts in the parameters were less than 1% of the standard deviations. The extinction parameter $g=0{\cdot}48\ (3)\times 10^4$ corresponds to a mosaic spread of 12·1″ or a domain size of $0{\cdot}74\times 10^{-4}$ cm. Weights used in the last cycles of refinement were $w=1/(\sigma_c^2+0{\cdot}00025|F_o|^2+4{\cdot}0)$. This gave $R=0{\cdot}029$, $R_w=0{\cdot}035$, $S=1{\cdot}06$ and a smooth weigthing scheme.

The final difference syntheses were featureless for both structures. The resulting positional and thermal parameters are given in Tables 1 and 2, with the lengths of the principal axes of the thermal motion ellipsoids. Observed and calculated structure factors are compared in Table 3. The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). Selected interatomic distances and angles are given in Table 4.

Table 1. *Positional parameters with estimated standard deviations*

	x	y	z
IDAC			
Cl	$\frac{1}{4}$	$\frac{3}{4}$	0·52896 (28)
N	$\frac{1}{4}$	$\frac{1}{4}$	0·27521 (72)
O(1)	0·43617 (21)	$\frac{1}{4}$	0·53231 (44)
O(2)	0·53711 (20)	$\frac{1}{4}$	0·17030 (50)
C(1)	0·44513 (26)	$\frac{1}{4}$	0·30088 (65)
C(2)	0·35043 (26)	$\frac{1}{4}$	0·11770 (67)
H(1)	$\frac{1}{4}$	0·1118 (77)	0·3880 (79)
H(2)	0·3526 (23)	0·1072 (64)	0·0033 (56)
H(3)	0·5922 (37)	$\frac{1}{4}$	0·2752 (93)
IDAB			
	x	y	z
Br	$\frac{1}{4}$	$\frac{3}{4}$	0·55169 (14)
N	$\frac{1}{4}$	$\frac{1}{4}$	0·26010 (92)
O(1)	0·43068 (27)	$\frac{1}{4}$	0·51992 (56)
O(2)	0·52796 (26)	$\frac{1}{4}$	0·15383 (66)
C(1)	0·43918 (31)	$\frac{1}{4}$	0·28547 (77)
C(2)	0·34698 (33)	$\frac{1}{4}$	0·10217 (76)
H(1)	$\frac{1}{4}$	0·1190 (101)	0·3781 (109)
H(2)	0·3540 (35)	0·1134 (82)	0·0078 (74)
H(3)	0·5761 (50)	$\frac{1}{4}$	0·2318 (131)

Five cycles of refinement in the non-centrosymmetric space group $Pm2_1n$ (a different setting of $Pmn2_1$), with the y parameters of the heavy atoms (except X^-) shifted slightly (and randomly) from 0·25 and 0·75, resulted in an increase in R, R_w and the standard deviations. As the heavy atoms of the organic molecule were found to be situated within 3σ from the planes $y=\frac{1}{4}$ and $y=\frac{3}{4}$ in the non-centrosymmetric structure, it was concluded that a centrosymmetric model well describes the structures of IDAC and IDAB.

All computations were made on the UNIVAC1 108 computer in Lund, Sweden, and programs used are listed in Table 5.

Description of the structure

The structure is built up of halide ions and positively charged iminodiacetic acid ions, $[C_4H_8NO_4]^+$, with the symmetry *mm*. The atoms of this ion are designated in

Fig. 1. The superscripts (i) to (vi) are used to indicate the following equivalent sites in the structure:

(i)	$x,\ y,\ 1+z$	(ii)	$1-x,\ 1-y,\ 1-z$
(iii)	$\frac{1}{2}-x,\ y,\ z$	(iv)	$x,\ \frac{1}{2}-y,\ z$
(v)	$x,\ 1+y,\ z$	(vi)	$x-\frac{1}{2},\ 1-y,\ 1-z$

Table 2. *Thermal parameters* $\beta_{ij}\times 10^5$ *with estimated standard deviations, and root-mean-square components* R_i *along the principal axes of the ellipsoids of thermal vibration*

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

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	R_1	R_2	R_3
IDAC									
Cl	385 (8)	2309 (45)	5384 (77)	0	0	0	0·1734 (19)	0·1962 (19)	0·2678 (19)
N	446 (24)	2631 (137)	2241 (144)	0	0	0	0·1728 (56)	0·1865 (51)	0·2094 (54)
O(1)	563 (16)	3968 (108)	2657 (102)	0	19 (32)	0	0·1880 (36)	0·2096 (30)	0·2571 (35)
O(2)	431 (15)	3922 (107)	3477 (107)	0	176 (33)	0	0·1774 (34)	0·2202 (35)	0·2556 (35)
C(1)	512 (22)	2199 (109)	3105 (133)	0	155 (42)	0	0·1887 (44)	0·1914 (47)	0·2138 (43)
C(2)	481 (24)	3865 (146)	2890 (136)	0	213 (43)	0	0·1764 (48)	0·2119 (46)	0·2538 (48)
IDAB									
Br	391 (5)	1986 (24)	4982 (43)	0	0	0	0·1790 (12)	0·1848 (11)	0·2538 (11)
N	354 (27)	2033 (132)	2225 (163)	0	0	0	0·1687 (62)	0·1707 (57)	0·1859 (58)
O(1)	484 (20)	4348 (141)	2367 (117)	0	−34 (39)	0	0·1752 (40)	0·2000 (41)	0·2739 (45)
O(2)	351 (18)	4005 (125)	3284 (130)	0	91 (39)	0	0·1670 (42)	0·2087 (39)	0·2625 (39)
C(1)	416 (24)	2038 (107)	2677 (154)	0	77 (49)	0	0·1748 (52)	0·1872 (46)	0·1915 (50)
C(2)	427 (27)	3236 (153)	1990 (133)	0	149 (48)	0	0·1523 (52)	0·1937 (56)	0·2335 (54)

Table 3. *Observed and calculated structure factors*

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

IDAB

```
K=  0 L=  0
 2  267  267
 4  607  666
 8  276  270
10  452  471
12  258  256
14  143  145

K=  0 L=  1
 0  583  552
 1   56   49
 2  470  460
 3   71   77
 4  501  493
 5  178  174
 6  692  693
 7   10   12
 8  191  189
 9  114  116
10  238  241
11   62   60
13  100   96
14  109  108
15   11   12

K=  0 L=  2
 0  373  345
 1  329  325
 2  336  324
 3  291  287
 4  139  140
 6  255  253
 7  255  255
 8  159  161
 9   98   99
10  152  148
11  193  198
12  155  154
13   66   61
14   55   57

K=  0 L=  3
 0  382  369
 1  282  277
 2   12    8
 3  205  198
 4  191  185
 5  394  407
 6  120  122
 7  198  202
 8   86   88
 9  138  136
10   92  104
11  131  135
12   65   69
13   91   89

K=  0 L=  4
 0   95   93
 1  250  263
 2   40   42
 3   83   79
 4   50   55
 5  224  230
 6  172  181
 7   83   82
 8   25   21
 9  136  135
10   38   41
11  126  123

K=  0 L=  5
 0  111  109
 1   94   88
 2   42   32
 3   89   86
 4   38   34
 5   58   55
 6   11   16
 7  104   99
 8   52   42
 9   22   24
```

```
K=  0 L=  6
 0   23   18
 1   33   32
 2   81   74
 4   14    5

K=  1 L=  0
 1  178  164
 3  747  746
 5  449  425
 7  302  293
 9  398  398
11   18   11
13  258  257

K=  1 L=  1
 0  781  795
 1  522  520
 2   28   30
 3  776  740
 4  332  312
 5   56   68
 6  153  142
 7  404  399
 8  118  114
 9  317  319
10  191  194
11  217  219
12   72   68
13  169  168
14   70   67
15  113  112

K=  1 L=  2
 0   15    7
 1  332  323
 2  384  380
 3  525  506
 4  218  225
 5  308  297
 6  329  320
 7  312  307
 8  136  142
 9  218  222
11  151  163
12  103  101
13  115  116
14   71   69

K=  1 L=  3
 0  180  193
 1  155  153
 2  261  271
 3  193  179
 4  161  156
 5  199  200
 6   43   40
 7   57   58
 8  197  200
 9  173  176
10  116  117
11   18   17
12   94   91
13   84   88

K=  1 L=  4
 1   11    7
 2  157  165
 3  112  118
 4  199  209
 5  118  121
 6   98  102
 7   44   49
 8  161  164
 9   32   34
10   63   62
11    9   11

K=  1 L=  5
 1   80   74
 2  171  166
 3   63   65
```

```
 4  102   94
 5   44   35
 6  116  109
 7   19   23
 8   88   84
 9   13    8

K=  1 L=  6
 0   94   86
 1   12    9
 2   51   46
 3   11    4

K=  2 L=  0
 0 1261 1356
 2  228  225
 4  561  550
 6  494  479
 8  243  236
10  397  397
12  225  224
14  129  131

K=  2 L=  1
 0  492  476
 1   12    9
 3   87   89
 4  384  374
 5  138  142
 6  553  537
 7   25   29
 8  180  183
 9   99  100
10  214  217
11   46   45
12  189  190
13   87   84
14  100   98

K=  2 L=  2
 0  266  257
 1  276  274
 2  274  271
 3  251  253
 4  159  155
 5   31   35
 6  225  223
 7  218  219
 8  145  148
 9   90   96
10  124  126
11  167  170
12  135  135
13   62   59
14   54   55

K=  2 L=  3
 0  313  307
 1  247  247
 2   35   38
 3  180  180
 4  153  152
 5  332  345
 6   98  103
 7  175  180
 8   85   87
10   85   93
11  120  122
12   57   62

K=  2 L=  4
 1  214  226
 2   39   40
 3   77   77
 4   53   58
 5  196  199
 6  153  156
 7   75   77
 9  122  119
10   34   36
11  115  109
```

```
K=  2 L=  5
 0   91   96
 1   79   78
 3   77   77
 4   35   30
 5   52   47
 6    6   12
 7   89   86
 8   40   35

K=  3 L=  0
 1  247  247
 3  482  484
 5  304  302
 7  250  249
 9  299  300
11   35   40
13  201  195

K=  3 L=  1
 0  420  412
 1  352  347
 2   40   42
 3  492  489
 4  193  191
 6  111  109
 7  303  299
 8   76   80
 9  239  240
10  143  143
11  173  174
12   55   56
13  139  135

K=  3 L=  2
 0   43   48
 1  274  267
 2  236  240
 3  329  324
 4  158  165
 5  226  227
 6  221  223
 7  221  226
 8  107  108
 9  170  174
11  134  137
12   82   78
13   91   89

K=  3 L=  3
 0  133  145
 2  191  199
 3  124  128
 4  120  123
 5  156  158
 6   43   45
 8  153  155
 9  123  122
10   90   90
12   77   73

K=  3 L=  4
 0   90   89
 1   23   12
 2  131  134
 3   75   75
 4  152  155
 5   87   85
 6   85   84
 7   27   32
 8  130  128
 9   25   27
10   51   50

K=  3 L=  5
 0   67   66
 1   61   58
 2  128  124
 3   41   46
 4   81   79
 5   31   24
 6   90   88
```

```
K=  4 L=  0
 0  603  633
 2  206  208
 4  335  338
 6  306  307
 8  175  176
10  264  262
12  161  157

K=  4 L=  1
 0  298  298
 1   29   31
 2  256  257
 3   78   81
 5   73   76
 6  314  317
 7   38   39
 8  144  147
 9   61   63
10  152  153
11   24   24
12  134  130

K=  4 L=  2
 0  156  157
 1  171  174
 2  188  188
 3  158  160
 4  129  128
 6  143  143
 7  137  141
 8  119  117
 9   77   79
10   83   84
11  114  109

K=  4 L=  3
 0  169  173
 1  164  170
 2   61   58
 3  125  131
 4   96   97
 5  221  224
 6   66   67
 7  124  127
 9   89   90
10   62   62

K=  4 L=  4
 0   57   51
 1  149  151
 2   32   29
 3   65   65
 4   44   47
 5  130  134
 6  101   99
 7   62   60
 8   11    3

K=  4 L=  5
 0   57   62
 1   54   54
 2   20   15
 3   56   56

K=  5 L=  0
 1  168  168
 3  265  269
 5  185  184
 7  169  166
 9  172  168
11   44   41

K=  5 L=  1
 0  188  194
 1  217  215
 2   43   45
 3  252  254
 4   95  100
 5  121  121
 6   74   75
 7  177  175
```

```
 8   65   46
 9  151  148
10   91   88

K=  5 L=  2
 0   59   67
 1  165  166
 2  118  127
 3  171  171
 4  104  109
 5  157  157
 6  127  131
 7  132  134
 8   70   68
 9  108  105
10   53   55

K=  5 L=  3
 0   85   92
 1   74   75
 2  123  122
 3   73   72
 4   73   78
 5   96   97
 6   36   38
 7   41   41
 8   95   95

K=  5 L=  4
 0   56   50
 1   16    9
 2   90   87
 3   40   39
 4   96   93

K=  6 L=  0
 0  291  296
 2  149  144
 4  181  177
 6  170  167
 8  110  107

K=  6 L=  1
 0  158  156
 1    7   18
 2  153  145
 3   49   52
 4  150  148
 5   29   30
 6  168  163
 7   29   29
 8   98   92

K=  6 L=  2
 0   85   84
 1   88   91
 2  114  109
 3   85   88
 4   77   75
 5   39   36
 6   72   70

K=  6 L=  3
 0   73   72
 1   93   94
 2   67   65
 3   74   75
 4   55   52

K=  7 L=  0
 1   92   86
 3  135  130

K=  7 L=  1
 0   87   88
 1  115  110
 2   29   28
```

IDAC

```
K=  0 L=  0
 2  [illegible]   37
 4  332  317
 8  [illegible]  [illegible]
10  347  [illegible]
12   56   55
14  [illegible]  [illegible]

K=  0 L=  1
 0  334  [illegible]
 1  151  [illegible]
 2  147  [illegible]
 3  [illegible]  [illegible]
 4  315  296
 5  [illegible]  [illegible]
 6  [illegible]  [illegible]
 7  [illegible]  [illegible]
 8  [illegible]   17
10  [illegible]  [illegible]
11  [illegible]  [illegible]
12  [illegible]  [illegible]
13  [illegible]   25
14  [illegible]   42

K=  0 L=  2
 0  [illegible]  111
 1  [illegible]  [illegible]
 2  [illegible]  [illegible]
 3  [illegible]  [illegible]
 4  [illegible]  [illegible]
 5  [illegible]  [illegible]
 6  [illegible]  [illegible]
 7  [illegible]  [illegible]
 8  [illegible]   51
 9  [illegible]  [illegible]
10  [illegible]   43
11  [illegible]   77
12   65  [illegible]
13   11    5
14  [illegible]  [illegible]

K=  0 L=  3
 0  [illegible]  [illegible]
 1  [illegible]  [illegible]
 2  [illegible]  [illegible]
 3  [illegible]   26
 4  [illegible]  [illegible]
 5  [illegible]  [illegible]
 6  [illegible]   54
 7  [illegible]   56
 8  [illegible]  [illegible]
 9  [illegible]  [illegible]
10  [illegible]  [illegible]
11  [illegible]   52
12  [illegible]  [illegible]
13  [illegible]   17

K=  0 L=  4
 0   77   75
 1  [illegible]  [illegible]
 2   34  [illegible]
 3  [illegible]  [illegible]
 4   77   79
 5  [illegible]  [illegible]
 6  [illegible]  [illegible]
 7   32   34
 9   65  [illegible]
10  [illegible]  [illegible]
11  [illegible]   55

K=  0 L=  5
 0   95  [illegible]
```

```
 1  [illegible]   34
 5  [illegible]    6
 7  [illegible]    5

K=  0 L=  6
 0   33   35
 2  [illegible]   35
 3  [illegible]    5
 4   17  [illegible]

K=  1 L=  0
 1  [illegible]  [illegible]
 3  [illegible]  [illegible]
 5  [illegible]  [illegible]
 7   91  [illegible]
 9  135  [illegible]
11  [illegible]   71
13  [illegible]  126

K=  1 L=  1
 0  [illegible]  [illegible]
 1  [illegible]  [illegible]
 2  [illegible]  [illegible]
 3  [illegible]  [illegible]
 4  [illegible]  [illegible]
 5  [illegible]  [illegible]
 6   55  [illegible]
 7  [illegible]  [illegible]
 8   17  [illegible]
 9  [illegible]  [illegible]
10  [illegible]  [illegible]
11  [illegible]   71
12  [illegible]  [illegible]
13  [illegible]  [illegible]
14  [illegible]  [illegible]

K=  1 L=  2
 0  [illegible]  [illegible]
 1  [illegible]  [illegible]
 2  [illegible]  [illegible]
 3  [illegible]  354
 4  [illegible]  [illegible]
 5  [illegible]  [illegible]
 6  [illegible]  [illegible]
 7  [illegible]  [illegible]
 8   52  [illegible]
 9  [illegible]  [illegible]
10  [illegible]   24
11  [illegible]   73
12  [illegible]   41
13  [illegible]  [illegible]
14   25   22

K=  1 L=  3
 0  [illegible]  [illegible]
 1   93   97
 2  [illegible]  [illegible]
 3  [illegible]  [illegible]
 4  [illegible]   24
 5  [illegible]  [illegible]
 6  [illegible]   73
 7  [illegible]   85
 9  [illegible]  [illegible]
11  [illegible]    9
12  [illegible]   26
13   51   52

K=  1 L=  4
 0  [illegible]  [illegible]
 1   31  [illegible]
 2   42   41
 3   79  [illegible]
```

```
 4   57   53
 5   79   79
 6  [illegible]  [illegible]
 7   45   46
 8  [illegible]  [illegible]
 9   38   38
11   21   18

K=  1 L=  5
 0   43   43
 1   40   38
 2   95   94
 3   74   75
 4   39   35
 5   35   37
 6   34   32
 7   54  [illegible]
 8   55  [illegible]

K=  1 L=  6
 0   46  [illegible]

K=  2 L=  0
 0  [illegible]  [illegible]
 2  [illegible]  [illegible]
 4  [illegible]  276
 6  [illegible]  251
 8  [illegible]  [illegible]
10  271  276
12   57  [illegible]
14  [illegible]   62

K=  2 L=  1
 0  [illegible]  [illegible]
 1  [illegible]  [illegible]
 2  [illegible]  [illegible]
 3  [illegible]  [illegible]
 5   76   78
 6  [illegible]  [illegible]
 7  [illegible]  [illegible]
 8   27   26
 9   15    7
10  [illegible]  [illegible]
11   55  [illegible]
12  [illegible]  [illegible]
13   25   24
14   34   37

K=  2 L=  2
 1  [illegible]   86
 2  [illegible]  118
 3   67  [illegible]
 4  [illegible]   30
 5  [illegible]  115
 6   96   97
 7  [illegible]  [illegible]
 8   47   47
10   32   33
11  [illegible]   65
12   74   74

K=  2 L=  3
 0  [illegible]  219
 2   17   15
 3   27   29
 4   66   65
 5  [illegible]  158
 6   45   43
 7   48   49
 8   22   19
10   74   76
11   45   45
```

```
12   22   19

K=  2 L=  4
 0   59  [illegible]
 1  [illegible]  [illegible]
 2   34   37
 4   73  [illegible]
 5  [illegible]  [illegible]
 6  [illegible]  [illegible]
 7  [illegible]   25
 9   54   51
10   27   27

K=  2 L=  5
 0   85  [illegible]
 1   35   32
 2  [illegible]  [illegible]
 3  [illegible]  [illegible]
 7  [illegible]  [illegible]

K=  3 L=  0
 1  [illegible]  [illegible]
 3  223  222
 5  [illegible]   82
 7   83   83
 9  [illegible]  [illegible]
11   37  [illegible]
13  [illegible]  [illegible]

K=  3 L=  1
 0  [illegible]  [illegible]
 1  112  112
 2  [illegible]  [illegible]
 3  272  [illegible]
 4  [illegible]   87
 5  [illegible]   47
 6   33   34
 7  152  154
 9  [illegible]  [illegible]
10  [illegible]  [illegible]
11   53  [illegible]
12   13  [illegible]
13  [illegible]  [illegible]

K=  3 L=  2
 0   82  [illegible]
 1  123  125
 2  [illegible]  [illegible]
 3  [illegible]  [illegible]
 4   47   54
 6   75   78
 7  [illegible]  [illegible]
 8  [illegible]  [illegible]
 9  [illegible]  [illegible]
11  [illegible]  [illegible]
12   29   28

K=  3 L=  3
 0   35   28
 1   58   62
 3  [illegible]   68
 4   13   14
 5  133  137
 6  [illegible]   45
 7  [illegible]  [illegible]
 8  [illegible]  [illegible]
 9  [illegible]  [illegible]
10  [illegible]    3
11    7   12

K=  3 L=  4
 0   19   17
```

```
 1   26   27
 2   37   34
 3   49   52
 5   57   54
 7   34   32
 8   50   49
 9   29   30

K=  3 L=  5
 0   23   23
 1   32   29
 2   69   67
 3   55   54
 4   32   29
 5   22   22
 6   29   26

K=  4 L=  0
 0  [illegible]  [illegible]
 4  149  149
 6  142  145
10  170  166
12   38   38

K=  4 L=  1
 0  136  [illegible]
 1   35   33
 2   70  [illegible]
 4  [illegible]  [illegible]
 5   25   27
 6  153  151
 7   15   15
10   62   64
11   36   35
12   53   54

K=  4 L=  2
 0   35   33
 1   44   45
 2   76   77
 3  [illegible]   44
 4  [illegible]   34
 5  [illegible]   51
 6  [illegible]  [illegible]
 7   49   52
 8   44   42
11   42   36

K=  4 L=  3
 0  [illegible]  [illegible]
 1   50   51
 2   20   16
 3   21   23
 4   45   41
 5  [illegible]  [illegible]
 6   29   28
 7   33   33
 8   29   31
 9   14   17
10   50   46

K=  4 L=  4
 0   41   41
 1   65   65
 2   28   28
 3   23  [illegible]
 4   55   52
 5   93   89
 6   75   72
 7   11   10
```

```
K=  4 L=  5
 0   62   60
 2   15   14

K=  5 L=  0
 1   26   23
 3  111  113
 7   61   59
 9   56   57

K=  5 L=  1
 0  [illegible]  123
 1   71   70
 2   17   14
 3  122  121
 6   73   75
 7  [illegible]   82
 9   59   58
10   61   56

K=  5 L=  2
 1   76   73
 2   35   38
 3   95   92
 4   32   34
 7   71   68
 8   16   15
 9   53   51

K=  5 L=  3
 0  [illegible]    8
 1   43   44
 2   41   40
 3   34   36
 5   82   77
 7   15   14

K=  5 L=  4
 2   25   24
 3   28   29
 4   20   19

K=  6 L=  0
 0  172  170
 2   26   24
 4   73   73
 6   72   75

K=  6 L=  1
 0   46   67
 1   16   15
 4   62   60
 6   73   74

K=  6 L=  2
 0   20   21
 1   21   19
 2   47   46
 3   22   23
 4   21   21
 5   21   20
 6   27   28

K=  6 L=  3
 0   41   40
 2   20   20
```

Table 4. *Selected interatomic distances* (Å) *and angles* (°) *with estimated standard deviations in IDAC and IDAB*

(*a*) Interlayer distances

	IDAC	IDAB
$H(2^{i})\cdots O(2^{ii})$	2·620 (37)	2·741 (51)
$H(2^{i})\cdots O(1)$	2·753 (29)	2·787 (39)
$O(1)\cdots O(2^{i})$	3·5032 (36)	3·4573 (47)

(*b*) The iminodiacetic acid ion

Distance	IDAC	IDAB
N——C(2)	1·4852 (36)	1·4798 (46)
C(1)——C(2)	1·5045 (47)	1·5051 (57)
C(1)——O(1)	1·1920 (39)	1·1976 (49)
C(1)——O(2)	1·3234 (38)	1·3202 (50)
N——H(1)	0·981 (43)	0·976 (58)
C(2)——H(2)	1·008 (34)	0·939 (46)
O(2)——H(3)	0·870 (49)	0·734 (64)

Angle	IDAC	IDAB
$C(2)-N—C(2^{iii})$	114·1 (4)	114·2 (4)
N—C(2)–C(1)	108·4 (3)	108·8 (3)
C(2)–C(3)–O(2)	111·0 (3)	111·2 (3)
C(2)–C(1)–O(1)	123·3 (3)	123·1 (4)
O(2)–C(1)–O(1)	125·7 (3)	125·7 (4)
C(2)–N—H(1)	109 (1)	110 (2)
$H(1)-N—H(1^{iv})$	108 (5)	104 (7)
N—C(2)–H(2)	110 (2)	111 (3)
C(1)–C(2)–H(2)	110 (2)	104 (3)
$H(2)-C(2)-H(2^{iv})$	98 (2)	104 (3)
C(1)–O(2)–H(3)	111 (3)	118 (5)

Table 4 (*cont.*)

(*c*) The hydrogen bonds

	IDAC	IDAB
$N\cdots\cdots X$	3·1489 (18)	3·2888 (22)
$N\cdots\cdots H(1^{iv})$	0·981 (43)	0·976 (58)
$X\cdots\cdots H(1^{iv})$	2·197 (44)	2·339 (59)
$\angle N—H(1^{iv})\cdots X$	163 (3)	164 (5)
$O(2^{ii})\cdots X$	3·0591 (28)	3·2157 (34)
$O(2^{ii})—H(3^{ii})$	0·870 (49)	0·734 (64)
$X\cdots\cdots H(3^{ii})$	2·201 (49)	2·486 (65)
$\angle O(2^{ii})—H(3^{ii})\cdots X$	169 (4)	174 (7)
$\angle H(1^{iv})\cdots X\cdots\cdots H(1^{v})$	142 (2)	136 (3)
$\angle H(3^{ii})\cdots X\cdots\cdots H(3^{vi})$	126 (2)	127 (3)
$\angle H(1^{iv})\cdots X\cdots\cdots H(3^{ii})$	99 (1)	100 (1)

where x, y, z are the atomic coordinates given in Table 1. The content of one unit cell is shown in Fig. 2. The non-hydrogen atoms of the two iminodiacetic acid ions in the unit cell are located in the mirror planes at $y=\frac{1}{4}$ and $y=\frac{3}{4}$. These ions are connected by hydrogen bonds *via* the halide ions and zigzag shaped infinite layers perpendicular to **c** are formed. All hydrogen atoms capable of hydrogen bonding are thereby used, and the interaction between the layers must be predominantly of van der Waals type.

The lattice parameter c is 0·041 (1) Å smaller in IDAB than in IDAC. This is the result of a more efficient packing of the layers in IDAB. The shortest interlayer contact in IDAC, 2·62 (4) Å, is between $H(2^{i})$ and $O(2^{ii})$, and it indicates van der Waals contact between these atoms. This contact prevents the non-hydrogen atoms in different organic ions from getting closer than 3·503 (4) Å [$O(1)-O(2^{i})$]. In IDAB the distance $H(2^{i})-O(2^{ii})$ has increased to 2·74 (5) Å and it is possible for O(1) and $O(2^{i})$ to get as close as 3·475 (5) Å.

The interatomic distances and angles within the organic ion are not significantly different in IDAC and IDAB (Table 5), and the dimensions agree well with those found in similar compounds (Bauer, 1938; Albertsson, 1972). The angle C–N–C (114·2°) is significantly different from the 'expected' tetrahedral value and the same situation is found in dimethylammonium chloride (Lindgren & Olovsson, 1968). The dimensions of the carboxyl group indicate one double bond, C(1)–O(1), and one single bond, C(1)–O(2). The location of the hydrogen atom H(3) close to O(2) thus seems to be reasonable. The deviations from 120° of the angles around C(1) supports this view. A discussion of the conformation of the iminodiacetic acid molecule in different crystallographic surroundings will be postponed to a later publication.

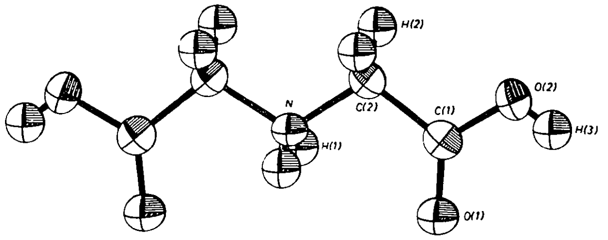

Fig. 1. Designation of the atoms in the positively charged iminodiacetic acid ion. Figs. 1, and 2 were drawn by the program *ORTEP*.

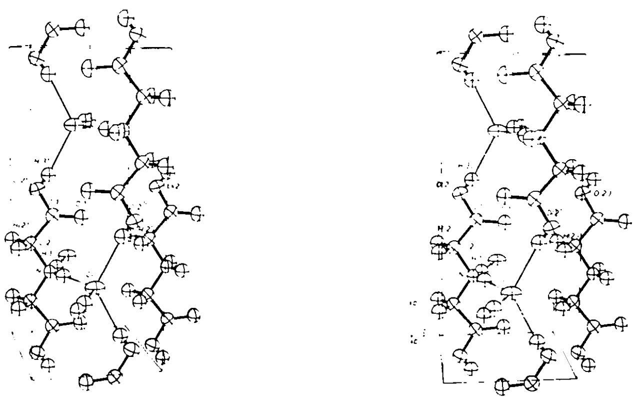

Fig. 2. A stereoscopic pair of drawings showing the content of one unit cell.

Table 5. *Computer programs*

Program	Subject	Authors
CELSIUS	Refinement of unit-cell dimensions.	J. Tegenfeldt.
DATAPC	Corrections for Lorentz, polarization and absorption effects and calculations of extinction components.	P.-G. Jönsson and R. Liminga. It is a modified version of *DATAPH*, written by P. Coppens, L. Leiserowitz & D. Rabinovich.
GAASA	Symbolic addition.	O. Lindgren, O. Lindqvist & J. Nyborg.
DRF	Fourier calculations.	A. Zalkin, modified by R. Liminga & J. O. Lundgren.
LINUS	Full-matrix least-squares refinement with option for refinement of the extinction parameters.	W. R. Busing, K. O. Martin & H. A. Levy. Extended by P. Coppens & W. Hamilton.
WAL	Weighting-scheme analysis.	P.-G. Jönsson.
ORFFE	A crystallographic function and error program.	W. R. Busing, K. O. Martin & H. A. Levy.
ORTEP	A thermal-ellipsoid plot program.	C. K. Johnson.
LALS	Full-matrix least-squares refinement.	P. Gantzel, R. Sparks & K. Trueblood. Modified by A. Zalkin and by R. Liminga, J. O. Lundgren & C. I. Brändén.
DATAP2	Absorption correction.	P. Coppens, L. Leiserowitz & D. Rabinovich. Revised by O. Olofsson & M. Elfström.
EXTDATA	Extinction correction.	B. G. Brandt.
SACTA	Printing of structure factor tables.	J. Albertsson.

From a geometrical point of view, a hydrogen bond is said to exist if a hydrogen atom–heavy atom distance is 0·2 Å or more shorter than the sum of the van der Waals radii (Hamilton & Ibers, 1968). According to this criterion the halide ion is hydrogen bonded to two nitrogen atoms and two oxygen atoms in an approximately tetrahedral arrangement. The deviation from linearity of the hydrogen bonds is in the range 6–17°.

The difficulties in determining the position of H(3) might be due to a disordered arrangement of this atom. The difference map revealed another possible position (0·55,$\frac{1}{4}$,0·83) with a distance of 1·7 Å to O(2^{ii}) and 2·1 Å to O(1). An attempt to refine half a hydrogen in each of the two positions gave in IDAC the result that the half hydrogen atom at (0·55,$\frac{1}{4}$,0·83) was moved to (0·54,$\frac{1}{4}$,0·99), where the distance to O(2^{ii}) and O(1) are 0·9 and 2·7 Å, respectively. The difference electron density map might indicate a weak interaction between the layers, but the refined position contradicts such a conclusion.

Due to the size of the halide ions one would expect stronger hydrogen bonds in IDAC compared with IDAB. The differences $d_{\mathrm{N-Br}}-d_{\mathrm{N-Cl}}$ and $d_{\mathrm{O-Br}}-d_{\mathrm{O-Cl}}$ are 0·140 (3) and 0·157 (4) Å, respectively, which might indicate that the hydrogen bond O–H...X is more affected by the size of the halide ion than the N–H$^+$...X bond. The average difference 0·149 (4) Å, is the same as the difference in the ionic radii of Cl$^-$ and Br$^-$, 0·15 Å (Shannon & Prewitt, 1969). Similar behaviour is found in L-cystine hydrochloride (Steinrauf, Peterson & Jensen, 1958) and L-cystine hydrobromide (Peterson, Steinrauf & Jensen, 1960).

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