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The Crystal Structure of Tetrammineammonium Iodide

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The crystal structure of $NH_4I \cdot 4NH_3$ has been determined from single crystal X-ray data obtained at −140°C. No phase changes were observed between this temperature and the melting point. There are two formula units in the tetragonal cell of the dimensions: a = 8.94 Å, c = 6.55 Å. The space group is $P4/n$. The four ammonia molecules are hydrogen-bonded to ammonium into tetrahedral tetrammine-ammonium groups. The different groups are relatively isolated from each other and are distributed in such a way that an almost close-packed arrangement of twelve nitrogen neighbors is formed around iodine.

In an earlier report on the structures of the triammines of the ammonium halides [1] a general introduction was given to the system NH_4X—NH_3 (X = F, Cl, Br, I). The tetrammine of ammonium iodide has been reported in several earlier works; the corresponding bromide compound so far only by Watt and McBride [2]. For references to earlier works see this article. The present investigation involves the determination of the crystal structure of $NH_4I \cdot 4NH_3$ from single crystal X-ray diffraction data obtained at —140°C. Some preliminary data have been published earlier [3].

EXPERIMENTAL

The crystals were grown from solutions of ammonia and ammonium iodide sealed in glass capillaries. The samples were prepared in the way described earlier [1]. The sample used for the X-ray work had the ratio 4.0 moles ammonia per mole of ammonium iodide. The melting point of this sample was −6°C (earlier reported value −5.1°C).

The single crystals were grown in the usual way by blowing a cooled stream of gas parallel to the capillary; all crystals prepared preferably oriented their a axes along the axis of the capillary. Equi-inclination Weissenberg photographs were taken around the a axis, layers 0−6, at −140°C by the use of Cu-K-radiation. The experimental set-up was the same as that used earlier [1]. Exposures taken at −25°C indicated no changes in structure.

The relative intensities were estimated visually by the use of multiple-film technique (5 films) and comparison with an intensity scale. The data were corrected for the Lorentz and polarization effects.

UNIT CELL AND SPACE GROUP

The data showed the diffraction symmetry of the tetragonal Laue group $4/m$. Systematic absences were: $(hk0)$ for $h + k$ odd. All reflections (hkl) with $h + k + l$ odd were in general considerably weaker than those with $h + k + l$ even. The systematic absences suggest the space group $P4/n$ (C_{4h}^3) and the refinements indicated no deviation from this choice.

The unit-cell dimensions were first approximately determined from rotation and Weissenberg photographs and then somewhat more accurately by the single crystal method described by Weisz, Cochran and Cole [4] ("the Θ-method"). The practical procedure was described earlier [1]. The following values were obtained: $a = 8.94 \pm 0.01$ Å, $c = 6.55 \pm 0.01$ Å. ($t = -140$°C, λCu-$K\alpha_1 = 1.54051$ Å, λCu-$K\alpha_2 = 1.54433$ Å). The approximate density was obtained from the volume and weight of a homogeneous crystal in a cylindrical capillary (the weight was known from the preparation): $d_{obs} = 1.5$ g/cm^3. With two molecules per unit cell a value of 1.35 is calculated.

The general equivalent positions in $P4/n$ are (origin at $\bar{4}$, *cf. International Tables* [5]): (x,y,z); $(\bar{x},\bar{y},z)$; $(\frac{1}{2}+x,\frac{1}{2}+y,\bar{z})$; $(\frac{1}{2}-x,\frac{1}{2}-y,\bar{z})$; $(\bar{y},x,\bar{z})$; $(y,\bar{x},\bar{z})$; $(\frac{1}{2}-y,\frac{1}{2}+x,z)$; $(\frac{1}{2}+y,\frac{1}{2}-x,z)$.

DETERMINATION OF THE ATOMIC COORDINATES

The intensities of the reflections indicated that, among the twofold positions, only those of the form $(0,\frac{1}{2},z)$; $(\frac{1}{2},0,\bar{z})$ were possible for iodine. The z coordinate could be estimated to be about 0.24. This z coordinate was refined in two cycles of least-squares refinement and a three-dimensional F_o-F_c synthesis, based on iodine only, was calculated. From these difference maps,

Table 1. Atomic parameters and standard deviations.

Nitrogen (N_0) in ammonium:	$x = 0$
	$y = 0$
	$z = \frac{1}{2}$
	$B = 2.75$ Å^2
Nitrogen (N_1) in ammonia:	$x = 0.246(4) \pm 0.002(8)$
	$y = 0.132(6) \pm 0.002(8)$
	$z = 0.259(5) \pm 0.002(1)$
	$B = 4.23$ Å^2
Iodine:	$x = 0$
	$y = \frac{1}{2}$
	$z = 0.2414(9) \pm 0.0001(8)$
	$B = 1.20$ Å^2

Table 2. Observed and calculated structure factors. All F values have been multiplied by 1.25.

k	l	$\|F_o\|$	$\|F_c\|$	k	l	$\|F_o\|$	$\|F_c\|$	k	l	$\|F_o\|$	$\|F_c\|$	k	l	$\|F_o\|$	$\|F_c\|$
	$h = 0$			7	4	<10	11	3	6	55	56	8	3	43	46
0	1	16	13	7	5	41	41	−3	6	50	47	8	4	< 8	10
0	2	119	145	7	6	12	13	3	7	13	13	8	5	33	37
0	3	20	18	8	0	81	69	−3	7	18	15	−8	5	41	38
0	4	104	105	8	1	< 5	<1	4	1	85	85	9	0	42	48
0	5	<10	9	8	2	62	58	−4	1	72	77	9	1	< 9	5
0	6	65	58	8	3	10	9	4	2	11	9	9	2	43	49
0	7	16	17	8	4	49	51	−4	2	< 5	10	9	3	< 8	5
1	1	71	101	8	5	< 8	8	4	3	80	71	9	4	33	38
1	2	14	13	9	1	51	49	−4	3	64	66	−9	4	38	37
1	3	79	82	9	2	<10	5	4	4	16	15				
1	4	22	18	9	3	36	44	−4	4	18	15		$h = 2$		
1	5	66	59	9	4	< 8	9	4	5	63	53	2	0	106	126
1	6	23	18	10	0	37	42	−4	5	58	51	2	1	12	6
1	7	54	41	10	1	< 6	<1	4	6	15	16	2	2	83	90
2	0	73	101	10	2	30	37	−4	6	18	16	2	3	19	20
2	1	12	6	10	3	< 7	8	4	7	42	38	2	4	81	78
2	2	56	69	11	1	31	39	−4	7	44	37	2	5	14	12
2	3	27	25	11	2	< 5	4	5	0	62	57	2	6	48	48
2	4	72	70					5	1	12	12	2	7	19	18
2	5	17	15		$h = 1$			−5	1	15	10	3	1	58	66
2	6	50	45	1	0	80	107	5	2	71	66	−3	1	80	100
2	7	22	20	1	1	23	21	−5	2	82	96	3	2	13	12
3	1	109	118	1	2	98	116	5	3	9	9	−3	2	13	9
3	2	9	8	1	3	< 6	6	−5	3	< 7	4	3	3	57	60
3	3	86	91	1	4	73	70	5	4	50	47	−3	3	78	81
3	4	13	14	1	5	21	21	−5	4	69	64	3	4	20	18
3	5	65	63	1	6	56	55	5	5	15	19	−3	4	18	14
3	6	15	15	1	7	14	15	−5	5	15	15	3	5	57	49
3	7	55	42	2	1	87	102	5	6	41	42	−3	5	71	58
4	0	96	105	−2	1	119	153	−5	6	59	49	3	6	20	18
4	1	< 7	4	2	2	11	11	5	7	16	14	−3	6	14	16
4	2	80	79	−2	2	8	7	−5	7	14	12	3	7	41	36
4	3	19	18	2	3	80	82	6	1	91	84	−3	7	50	40
4	4	77	70	−2	3	104	110	−6	1	59	70	4	0	99	110
4	5	12	12	2	4	17	17	6	2	< 9	6	−4	0	93	113
4	6	51	45	−2	4	13	12	−6	2	< 7	7	4	1	< 6	4
4	7	19	17	2	5	61	59	6	3	76	70	−4	1	< 5	4
5	1	85	90	−2	5	81	71	−6	3	66	60	4	2	81	84
5	2	12	7	2	6	11	17	6	4	<10	10	−4	2	85	86
5	3	84	74	−2	6	11	14	−6	4	<10	12	4	3	16	16
5	4	14	12	2	7	43	41	6	5	50	52	−4	3	17	15
5	5	60	54	−2	7	51	46	−6	5	47	47	4	4	72	72
5	6	16	14	3	0	107	124	6	6	< 8	12	−4	4	73	73
5	7	46	38	−3	0	43	66	−6	6	12	13	4	5	9	11
6	0	81	73	3	1	20	14	7	0	72	63	−4	5	13	11
6	1	< 7	<1	−3	1	16	17	7	1	< 9	7	4	6	46	46
6	2	70	59	3	2	117	124	7	2	71	65	−4	6	54	46
6	3	14	14	−3	2	72	81	7	3	<10	6	4	7	18	16
6	4	60	55	3	3	< 7	4	7	4	41	48	−4	7	20	16
6	5	14	11	−3	3	< 6	9	7	5	12	13	5	1	80	83
6	6	39	37	3	4	83	76	7	6	42	39	−5	1	51	63
7	1	62	57	−3	4	64	55	−7	6	42	38	5	2	< 8	7
7	2	<10	7	3	5	17	17	8	1	57	52	−5	2	9	9
7	3	53	51	−3	5	24	21	8	2	<10	6	5	3	72	69

Table 2 (cont.)

k	l	$\|F_o\|$	$\|F_c\|$	k	l	$\|F_o\|$	$\|F_c\|$	k	l	$\|F_o\|$	$\|F_c\|$	k	l	$\|F_o\|$	$\|F_c\|$
−5	3	63	56	4	3	76	74	9	4	30	34	9	2	< 7	5
5	4	14	12	−4	3	77	76	−9	4	42	39	9	3	31	38
−5	4	14	14	4	4	< 8	12	10	1	34	41	10	0	32	42
5	5	49	52	−4	4	12	12	10	2	< 6	4	10	1	<3	<1
−5	5	52	45	4	5	64	55	10	3	30	36	10	2	31	37
5	6	15	14	−4	5	64	56	11	0	25	35				
−5	6	18	15	4	6	14	14							$h = 5$	
6	0	76	76	−4	6	12	13			$h = 4$		5	0	57	61
−6	0	71	73	4	7	47	38	4	0	57	64	5	1	< 8	7
6	1	< 7	<1	−4	7	49	38	4	1	< 2	<1	5	2	64	64
−6	1	< 5	<1	5	0	73	73	4	2	54	51	5	3	< 9	6
6	2	65	61	−5	0	57	69	4	3	19	17	5	4	49	47
−6	2	55	59	5	1	< 7	9	4	4	55	51	5	5	17	14
6	3	16	13	−5	1	8	9	4	5	14	13	5	6	47	39
−6	3	< 9	13	5	2	81	77	4	6	33	36	6	1	58	60
6	4	61	56	−5	2	69	73	5	1	70	71	−6	1	45	50
−6	4	62	55	5	3	< 8	6	−5	1	67	73	6	2	< 9	5
6	5	10	11	−5	3	10	7	5	2	< 8	7	−6	2	<10	6
−6	5	10	11	5	4	62	54	−5	2	< 8	6	6	3	56	53
6	6	42	38	−5	4	59	52	5	3	62	61	−6	3	44	45
−6	6	44	37	5	5	13	15	−5	3	65	62	6	4	< 8	9
7	1	63	61	−5	5	16	16	5	4	< 8	11	−6	4	14	11
7	2	< 9	6	5	6	46	44	−5	4	< 9	11	6	5	43	41
7	3	56	53	−5	6	47	43	5	5	48	47	−6	5	46	37
7	4	9	10	6	1	53	54	−5	5	58	47	7	0	38	45
7	5	42	42	−6	1	60	68	5	6	11	13	7	1	< 9	6
−7	5	57	47	6	2	< 8	8	−5	6	14	13	7	2	43	47
7	6	14	12	−6	2	< 9	6	6	0	71	74	7	3	< 8	6
−7	6	9	11	6	3	51	49	−6	0	75	75	7	4	35	37
8	0	54	53	−6	3	60	58	6	1	< 6	<1	−7	4	52	42
8	1	< 4	<1	6	4	9	13	−6	1	< 7	<1	7	5	14	12
8	2	46	45	−6	4	<10	11	6	2	64	61	−7	5	12	11
8	3	9	11	6	5	39	40	−6	2	65	62	8	1	40	47
8	4	39	42	−6	5	55	45	6	3	10	11	8	2	< 8	5
9	1	47	52	6	6	16	14	−6	3	<10	10	8	3	41	42
9	2	< 8	4	−6	6	15	12	6	4	54	55	9	0	41	44
9	3	43	46	7	0	63	61	−6	4	67	55	9	1	< 7	4
10	0	40	46	7	1	< 8	6	6	5	< 7	9	9	2	42	45
10	1	< 3	<1	7	2	66	63	−6	5	9	9	9	3	< 5	4
10	2	37	40	7	3	< 8	5	6	6	43	37	10	1	27	35
10	3	< 5	7	7	4	47	47	−6	6	46	37				
11	1	25	34	7	5	8	12	7	1	55	53			$h = 6$	
		$h = 3$		−7	5	15	14	7	2	< 8	6	6	0	50	54
3	0	73	83	8	1	58	57	7	3	46	48	6	1	< 3	<1
3	1	13	13	8	2	< 8	5	7	4	< 8	10	6	2	46	46
3	2	82	89	8	3	46	50	7	5	38	38	6	3	<10	10
3	3	< 7	7	8	4	< 7	8	−7	5	40	37	6	4	44	43
3	4	62	60	−8	4	10	9	8	0	53	53	7	1	54	53
3	5	17	18	8	5	38	39	8	1	< 3	<1	7	2	<10	4
3	6	49	48	−8	5	41	37	8	2	40	45	7	3	45	46
3	7	15	13	9	0	35	41	8	3	< 7	9	8	0	40	44
4	1	82	91	9	1	< 8	5	8	4	37	42	8	1	< 5	<1
−4	1	86	94	9	2	36	43	−8	4	44	41	8	2	38	39
4	2	7	7	9	3	< 7	5	9	1	36	42	9	1	35	38
−4	2	< 6	7												

the nitrogen atoms (N_0) in ammonium could be located in the twofold positions $(0,0,\frac{1}{2})$ and $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$. Finally the nitrogen atoms (N_1) belonging to the four ammonia molecules were found to occupy together the general 8-fold positions written down earlier.

The coordinates and isotropic temperature factors for iodine and nitrogen and an over-all scale factor were finally refined by least-squares methods on the IBM 650 computer. R_3 (see below) was the quantity actually minimized; the weighting factor w and some other details of the program have been described earlier [6]. The scattering factors used in these calculations were those of Berghuis *et al.*[7] for neutral N; for I^- they were estimated from the values for neutral I published by Thomas and Umeda [8]. The shifts in the coordinates in the final cycle were less than 0.00002. The results, together with the standard deviations after 12 cycles of refinement, are given in Table 1. The "unreliability factors" at this point were:

$$R_1 = \Sigma||F_o|-|F_c|| \,/\, \Sigma|F_o| = 0.105.$$
$$R_2 = [\Sigma(|F_o|-|F_c|)^2/\Sigma|F_o|^2]^{\frac{1}{2}} = 0.137$$
$$R_3 = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}} = 0.140$$

The observed and calculated structure factors are compared in Table 2. Notice that the positions of iodine and nitrogen N_0 (but not nitrogen N_1) are consistent with the space group $P4/nmm$. The deviation of the diffraction symmetry from $4/mmm$ is therefore expected to be quite small (but is nevertheless obviously real) which is noticeable in Table 2.

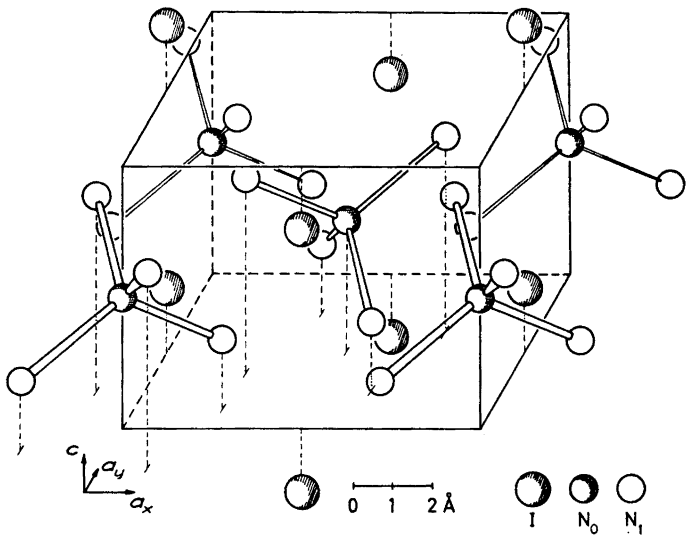

Fig. 1. The crystal structure of $NH_4I \cdot 4NH_3$. N_0 is nitrogen in ammonium, N_1 belongs to ammonia. The hydrogen bonds within the discrete tetrammineammonium tetrahedra are indicated.

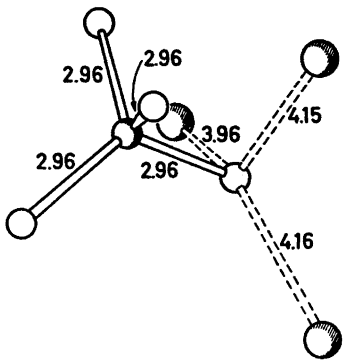

Fig. 2. Bond distances in the tetrammine-ammonium group and the distances between ammonia and its three iodine neighbors.

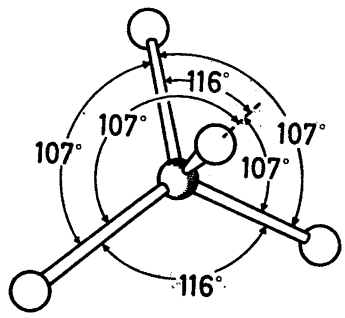

Fig. 3. Bond angles in the tetrammine-ammonium group. The corresponding distances are shown in Fig. 2.

DISCUSSION OF THE STRUCTURE

The structure is shown in Fig. 1. The ammonium ion is tetrahedrally surrounded by the four ammonia molecules, all at 2.96 Å from N_0, see Fig. 2

Table 3. Distances and angles with their standard deviations (compare with Figs. 2—5).

1. Around ammonium

Bond	Distance (Å)	Bonds	Angle (°)
N_0-N_1	2.95(6) ± 0.02(2)	$N_1-N_0-N_1'$	106.5 ± 0.3
N_0-N_1'	—»—	$N_1-N_0-N_1''$	106.5 ± 0.3
N_0-N_1''	—»—	$N_1-N_0-N_1'''$	115.6 ± 0.7
N_0-N_1'''	—»—	$N_1'-N_0-N_1''$	115.6 ± 0.7
		$N_1'-N_0-N_1'''$	106.5 ± 0.3
		$N_1''-N_0-N_1'''$	106.5 ± 0.3

2. Around ammonia

Bond	Distance (Å)	Bonds	Angle (°)
N_1-N_0	2.95(6) ± 0.02(2)	N_0-N_1-I	86.2
N_1-I	3.95(6)	N_0-N_1-I'	82.7
N_1-I'	4.15(1)	N_0-N_1-I''	135.4
N_1-I''	4.16(1)	$I-N_1-I'$	124.4
N_1-other N	>3.6	$I-N_1-I''$	121.1
N_1-other I	>6.1	$I'-N_1-I''$	104.0

3. Around iodine

Four distances $I-N_1$ equal to	3.95(6) Å
» » » » »	4.15(1) Å
» » » » »	4.16(1) Å
Other distances $I-N_1$:	>6.1 Å

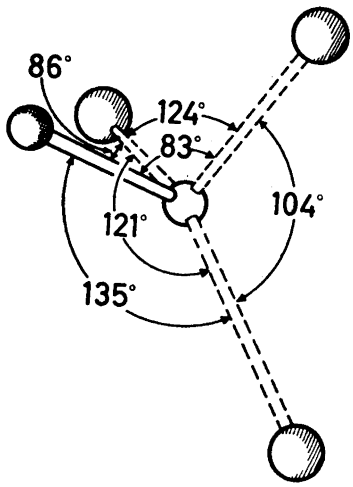

Fig. 4. Angles between the N—N_0 and N—I lines of ammonia. The corresponding distances are shown in Fig. 2.

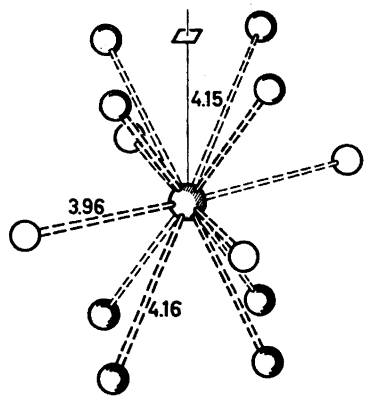

Fig. 5. Distances to the neighbors of iodine. The twelve nitrogen atoms (N_1) form an almost cubic close-packed arrangement around iodine.

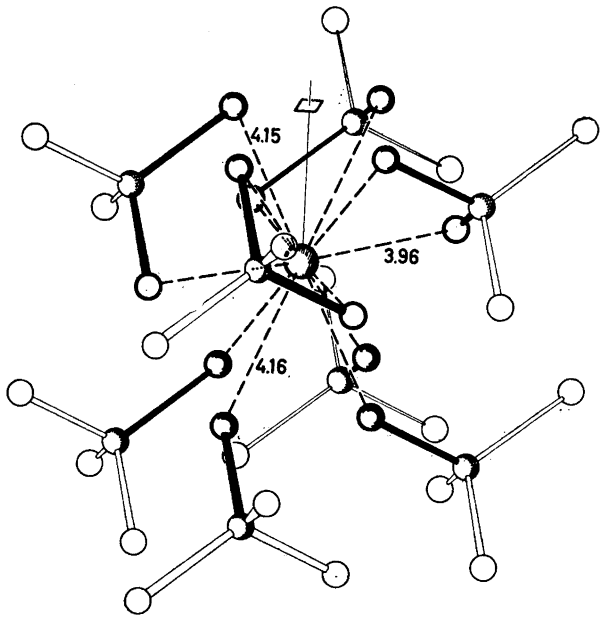

Fig. 6. The distribution of the tetrammineammonium groups around iodine. The twelve closest neighbors (shown separately in Fig. 5) are heavily drawn.

and Table 3. The bond angles are shown in Fig. 3. The central atoms (N_0) are located at $\bar{4}$ and form a *C*-centered arrangement. The hydrogen atoms of ammonium are obviously involved in hydrogen bonds to the ammonia neighbors. The distance $N_0 - - - N_1$, 2.96 Å, is within the usual range for hydrogen bonds of this kind [9]. Compare also with the corresponding distances in $NH_4Cl \cdot 3NH_3$ (2.90, 2.93, and 2.99 Å), $NH_4Br \cdot 3NH_3$ (2.82, 2.92, and 2.95 Å) and $NH_4I \cdot 3NH_3$ (2.66, 2.99, and 3.06 Å) [1].

As the free electron pair of ammonia is obviously involved in the hydrogen bond to ammonium, it seems unlikely that bonding between the different ammonia molecules will occur. All such distances are larger than 3.6 Å. The distances to the iodine neighbors are listed in Table 3. The interaction between ammonia and its neighbors is obviously weak and makes it probable that the threefold axis is oriented along the hydrogen bond to the central ammonium ion. The relatively favorable arrangement of three negatively charged iodine atoms around ammonia (see Figs. 2 and 4) may suggest that the possible rotation around the threefold axis is somewhat restricted and that the molecule is preferably oriented towards these iodide ions. The situation is very similar to that in $NH_4Cl \cdot 3NH_3$, $NH_4Br \cdot 3NH_3$ and $NH_4I \cdot 3NH_3$ [1].

Iodine is located on a fourfold axis and surrounded by twelve nitrogen atoms (N_1) in an almost cubic close-packed arrangement (see Fig. 5). The distribution of the tetrahedral tetrammineammonium groups around iodine is shown in Fig. 6. Compare the distances iodine-ammonia in this compound (3.96, 4.15, and 4.16 Å, *cf.* Table 3) with the corresponding distances in $NH_4I \cdot 3NH_3$ (mean value 3.9 Å)[1]. The iodine atoms form an almost body-centered arrangement (if the *z* coordinate were 1/4 instead of 0.2415, the body-centering would be perfect). This is of course the reason why reflections (*hkl*), with $h+k+l$ odd, are in general considerably weaker than those with $h+k+l$ even.

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REFERENCES

1. Olovsson, I. *Acta Chem. Scand.* **14** (1960) 1453.
2. Watt, G. W. and McBride, W. R. *J. Am. Chem. Soc.* **77** (1955) 1317.
3. Olovsson, I. *Acta Chem. Scand.* **11** (1957) 1273.
4. Weisz, O., Cochran, W. and Cole, W. F. *Acta Cryst.* **1** (1948) 83.
5. *International Tables for X-ray Crystallography, Vol. 1,* Kynoch Press, Birmingham 1952.

6. Olovsson, I and Templeton, D. H. *Acta Cryst* **12** (1959) 827.
7. Berghuis, J., Haanappel, IJ. M., Potters, M., Loopstra, B. O., MacGillavry, C. H. and Veenendaal, A. L. *Acta Cryst.* **8** (1955) 478.
8. Thomas, L. H. and Umeda, K. *J. Chem. Phys.* **26** (1957) 293.
9. Pimentel, G. C. and McClellan, A. L. *The Hydrogen Bond*, Freeman and Co., San Francisco and London 1960.

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