900°, making refractive index determinations impossible.

Acknowledgment.—The author is glad to acknowledge the enthusiastic counsel of Dr. Harold C. Hodge throughout the course of the work.

Summary

1. The mean refractive indices of powdered enamel and dentine samples, with differing and known density limits, were determined by the Becke line procedure.

2. The refractive indices of dried enamel lie between 1.612 and 1.630 and are proportional to the density.

3. The refractive indices of dried dentine lie between 1.555 and 1.580 and are roughly proportional to the density when the fractions are dried under the same conditions for both determinations. Vacuum drying brought about a marked lowering of refractive index.

4. Secondary cementum exhibited a refractive index of 1.560–1.570 which was little affected by vacuum drying.

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The Crystal Structure of Ammonium Cadmium Chloride, NH_4CdCl_3

BY HENRI BRASSEUR[1] AND LINUS PAULING

In crystalline cadmium chloride, $CdCl_2$, there are octahedral groups $CdCl_6$ condensed into layers, each chlorine atom being adjacent to three cadmium atoms.[2] Tetrahedral coördination is shown by cadmium[3] with cyanide groups in $K_2Cd(CN)_4$, and with sulfur, selenium and tellurium atoms in the sphalerite and wurtzite type crystals CdS, CdSe and CdTe, and might well occur with chlorine also. There are accordingly two types of reasonable structures for complexes with the composition $(CdCl_3)_x$, the first involving octahedra with shared corners, as for example in the cubic crystal $KMgF_3$, and the second involving rings or chains of tetrahedra, as in the metasilicates. We have determined completely the structure of the orthorhombic crystal NH_4CdCl_3, and have found it to be based on octahedral coördination about the cadmium atoms, the $CdCl_6$ octahedra being polymerized into infinite double rutile strings which extend parallel to the *c*-axis of the crystal.

Experimental Methods and Results

The crystals of NH_4CdCl_3 used in this investigation were obtained by evaporation of an aqueous solution containing equimolar amounts of NH_4Cl and $CdCl_2$. The transparent white needles used for the x-ray photographs were about 0.1 sq. mm. in cross section and 3 to 10 mm. in length. In addition to single crystals many twins were obtained; the nature of the twinning was not studied.

Crystallographic study[4] has shown the crystals to be orthorhombic, with axial ratios 0.6059:1:0.7992 and density 2.93. X-ray photographs prepared with 15° oscillation about the directions [100], [010], and [001], with use of CuKα radiation filtered through nickel, gave the following dimensions for the unit cell

$$a_0 = 8.96 \pm 0.02 \text{ Å}.$$
$$b_0 = 14.87 \pm 0.03 \text{ Å}.$$
$$c_0 = 3.97 \pm 0.01 \text{ Å}.$$

These lead to the axial ratios 0.603:1:0.267, in good agreement with the crystallographic values, after dividing the crystallographic *c*-axis by three. All indices used in this paper refer to the X-ray axes a_0, b_0, c_0 given above.

The observed reflections show the lattice to be simple. The absence of prism reflections $\{h0l\}$ with h odd and $\{0kl\}$ with $k + l$ odd provides strong evidence that the space group is $D_{2h}^{16}-Pnam$ or its subgroup $C_{2v}^{9}-Pna$. In the absence of any observed deviation from holohedral habit of the crystals, we have assumed the space group to be D_{2h}^{16}; this assumption is given later justification by the derivation of a satisfactory atomic arrangement based on the holohedral space group.

The Atomic Arrangement

The sets of equivalent positions provided by $D_{2h}^{16}-Pnam$ are

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[1] Fellow of the Belgian-American Educational Foundation.

[2] L. Pauling, *Proc. Natl. Acad. Sci.*, **15**, 709 (1929); L. Pauling and J. L. Hoard, *Z. Krist.*, **74**, 546 (1930).

[3] R. G. Dickinson, THIS JOURNAL, **44**, 774 (1922).

[4] H. Traube, *Z. Krist.*, **29**, 602 (1898); A. Johnsen, *N. Jahrb. Mineral.*, **2**, 115 (1903).

4a: $000,\ 0\tfrac{1}{2}0,\ \tfrac{1}{2}0\tfrac{1}{2},\ \tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2}$
4b: $00\tfrac{1}{2},\ 0\tfrac{1}{2}\tfrac{1}{2},\ \tfrac{1}{2}00,\ \tfrac{1}{2}\tfrac{1}{2}0$
4c: $xy\,1/4,\ \tfrac{1}{2}+x\ \tfrac{1}{2}-y\ 1/4,\ \tfrac{1}{2}-x\ \tfrac{1}{2}+y\ 3/4,\ \overline{xy}\ 3/4$
8d: $xyz,\ \tfrac{1}{2}+x\ \tfrac{1}{2}-y\ z,\ \tfrac{1}{2}-x\ \tfrac{1}{2}+y\ \tfrac{1}{2}+z,\ \overline{xy}\ \tfrac{1}{2}+z,\ \overline{xyz},\ \tfrac{1}{2}-x\ \tfrac{1}{2}+y\ \bar{z},\ \tfrac{1}{2}+x,\ \tfrac{1}{2}-y\ \tfrac{1}{2}-z,\ xy\ \tfrac{1}{2}-z$

The unit cell contains 4 NH_4CdCl_3, the number of molecules calculated from the cell dimensions and density being 3.99. The possibility that 8 Cl occupy the positions 8d is ruled out by the small value 3.97 Å. of c_0, since the distance $c_0/2 = 1.99$ Å. between non-bonded chlorine atoms is very much less than that found in any crystal. It was noted, moreover, that the intensities of the X-ray reflections indicate strongly that all of the atoms are in planes $c_0/2$ apart. An arrangement of this type leads to the same structure factor for all the reflections ($hk0$), ($hk2$), ($hk4$), etc., and also for all the reflections ($hk1$), ($hk3$), etc.; and it was observed that on oscillation photographs the intensities of the reflections with $l = 2$ and $l = 4$ reproduce those with $l = 0$, but somewhat diminished because of the larger scattering angles, and that similarly the intensities of the reflections with $l = 3$ reproduce those with $l = 1$.

This observation requires that all of the atoms occupy the positions 4c, forming layers at $z = {}^1/_4$ and $z = {}^3/_4$. (Layers at $z = 0$ and $z = {}^1/_2$ are ruled out by the fact that positions 4a and 4b could accommodate only two of the five atoms in the molecule.)

There are ten parameters to be evaluated in the determination of the atomic arrangement: x_{NH_4}, y_{NH_4}, x_{Cd}, y_{Cd}, x_{I}, y_{I}, x_{II}, y_{II}, x_{III} and y_{III} (the subscripts I, II and III referring to the three non-equivalent sets of chlorine atoms). As the first step in this process sections of the three-dimensional Patterson-Fourier diagram[5] were made for the levels $z = 0$ and $z = {}^1/_2$, as recommended by Harker,[6] with use of the general equation

$$P(x,y,z) = \Sigma_h \Sigma_k \Sigma_l \mid F_{hkl} \mid^2 \cos 2\pi(hx + ky + lz) \quad (1)$$

The calculations could be based on the observed values of intensities of planes ($hk0$) and ($hk1$) alone, because of the intensity regularities, mentioned above, which result from the special values ${}^1/_4$ and ${}^3/_4$ for the z coördinates of all the atoms. The function f^2/Z^2 (f being the atomic scattering power and Z the atomic number) in its dependence on $\sin \theta/\lambda$ has nearly the same values for the atoms Cd, Cl, and N. An averaged function for these atoms was plotted, and summed over l for series of reflections (hkl), with l either even or odd, in order to obtain the factors with which the intensities for reflections ($hk0$) and ($hk1$) were multiplied to give the sums over l in Equation 1. The remaining double summations for $z = 0$ and $z = {}^1/_2$ were then carried out with the aid of the Beevers–Lipson strips,[7] all of the data of Table I being used. The values of $\mid F \mid$ given in the table were obtained from visually estimated intensity values by correction for the Lorentz and polarization factors, the temperature factor being ignored. Contour diagrams representing the results of the calculations are shown as Figs. 1 and 2.

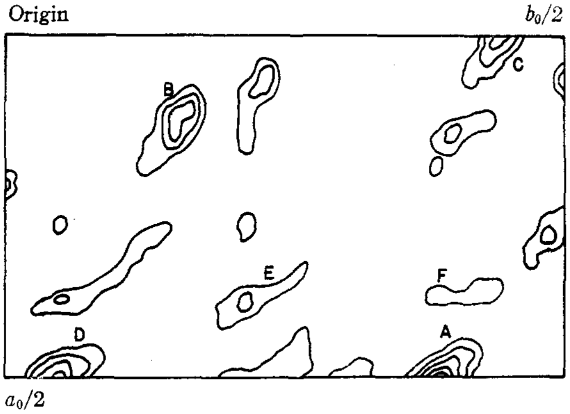

Fig. 1.—Patterson-Harker diagram for the section $z = 0$. The peaks represent the following principal interatomic distances: A, Cd–Cd; B, Cd–Cl_I, Cd–Cl_{III}; C, Cd–Cl_{II} (occurring twice); D, Cd–Cl_{II}, Cd–Cl_I; E, Cd–Cl_I; F, Cd–Cl_{III}.

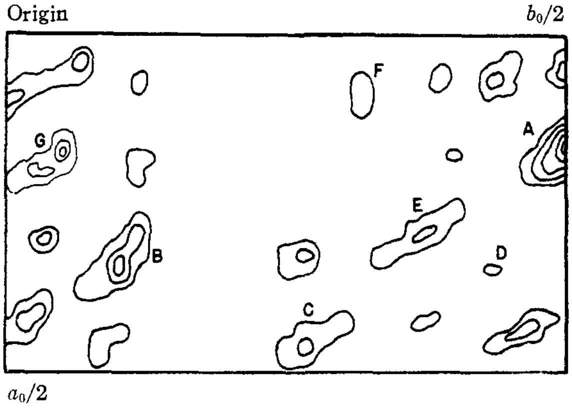

Fig. 2.—Patterson-Harker diagram for the section $z = {}^1/_2$. The peaks represent the following principal interatomic distances: A, Cd–Cd; B, Cd–Cd; C, Cd–Cl_I; Cd–Cl_{II}; E, Cd–Cl_{III}; F, Cd–Cl_I; G, Cd–Cl_{II}; Cd–Cl_{III}.

Peaks in the Patterson-Fourier diagrams represent interatomic distance vectors between pairs of atoms extending from the origin, weighted by the

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(5) A. L. Patterson, *Z. Krist.*, **90**, 517 (1935).

(6) D. Harker, *J. Chem. Phys.*, **4**, 381 (1936).

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TABLE I

Reflections $hk0$, $h+k$ even. Structure factor: $4\,\Sigma_i f_i \cos hx_i \cos ky_i$

$hk0$	$\frac{1}{4} F_{\text{calcd.}}$	$\frac{1}{4}\lvert F\rvert_{\text{obsd.}}$	$hk0$	$\frac{1}{4} F_{\text{calcd.}}$	$\frac{1}{4}\lvert F\rvert_{\text{obsd.}}$	$hk0$	$\frac{1}{4} F_{\text{calcd.}}$	$\frac{1}{4}\lvert F\rvert_{\text{obsd.}}$	$hk0$	$\frac{1}{4} F_{\text{calcd.}}$	$\frac{1}{4}\lvert F\rvert_{\text{obsd.}}$	$hk0$	$\frac{1}{4} F_{\text{calcd.}}$	$\frac{1}{4}\lvert F\rvert_{\text{obsd.}}$
020	36.9	24.4	190	−11.0	13.1	370	−24.3	30.4	570	−8.4	5.1	7·11·0	−14.5	7.4
040	18.8	15.1	11·1·0	−10.8	7.4	390	46.9	46.1	590	−18.7	18.6	7·13·0	−6.9	....
060	−11.6	14.8	11·3·0	−10.5	....	3·11·0	32.4	39.6	5·11·0	−2.9	2.6	820	−10.1	4.0
080	−21.8	22.1	11·5·0	−6.3	....	3·13·0	13.0	21.8	5·13·0	−12.1	....	840	−8.1	7.7
0·10·0	−4.2	....	11·7·0	−8.7	....	3·15·0	−8.5	7.4	5·15·0	−4.1	6.5	860	−2.0	....
0·12·0	−11.8	8.0	11·9·0	15.0	9.1	3·17·0	−16.3	21.8	620	35.6	33.3	880	7.7	7.7
0·14·0	9.6	8.2	220	−10.2	8.8	420	−21.6	19.5	640	9.2	5.0	8·10·0	7.6	10.5
0·16·0	11.6	14.8	240	−27.2	16.8	440	−10.5	12.2	660	−9.2	15.6	8·12·0	2.9	....
0·18·0	38.2	46.5	260	0.2	....	460	−5.4	....	680	−11.1	14.2	910	−15.1	18.2
200	−23.4	14.0	280	11.8	9.4	480	11.7	14.5	6·10·0	−12.6	16.5	930	−0.7	....
400	−9.8	5.1	2·10·0	13.2	9.4	4·10·0	18.6	13.8	6·12·0	−3.9	....	950	4.0	....
600	37.4	31.8	2·12·0	11.6	13.1	4·12·0	−0.2	....	6·14·0	4.0	....	970	29.9	25.8
800	−15.3	12.2	2·14·0	−19.7	21.1	4·14·0	−4.3	....	710	15.3	12.2	990	23.6	30.9
10·0·0	−13.4	10.5	2·16·0	−8.7	10.5	4·16·0	−20.0	21.8	730	−5.4	....	9·11·0	31.6	41.7
110	23.1	10.0	310	−12.4	12.5	510	14.0	11.1	750	−0.5	....	10·2·0	−16.9	17.9
130	7.1	3.5	330	−19.2	10.4	530	−6.9	....	770	−23.2	25.6	10·4·0	−3.7	....
150	−27.7	17.3	350	13.5	14.8	550	−17.6	26.4	790	−5.4	7.9	10·6·0	1.9	....
170	−17.7	18.4												

Reflections $hk0$, $h+k$ odd. Structure factor: $4\,\Sigma_i f_i \sin hx_i \sin ky_i$

120	24.8	12.9	2·11·0	−15.7	16.8	450	−26.8	32.5	610	−9.8	7.1	7·14·0	−24.5	31.5
140	23.6	16.0	2·13·0	−16.5	20.0	470	−10.3	6.8	630	−1.5	....	810	9.8	5.4
160	36.4	33.4	2·15·0	−20.0	17.6	490	−5.2	....	650	5.0	....	830	5.8	2.8
180	1.5	....	2·17·0	1.6	....	4·11·0	10.8	15.7	670	6.5	8.0	850	27.1	35.6
1·10·0	−3.8	6.8	320	8.1	17.7	4·13·0	8.8	11.9	690	5.8	8.0	870	22.1	23.8
1·12·0	−24.9	24.8	340	8.2	7.4	4·15·0	19.7	18.2	6·11·0	9.3	8.0	890	4.6	....
1·14·0	−22.9	33.8	360	−5.8	2.0	520	23.6	25.7	6·13·0	2.9	10.5	8·11·0	−9.2	6.3
1·16·0	−13.8	3.7	380	10.2	6.3	540	29.6	32.5	6·15·0	−4.9	....	8·13·0	−32.5	40.2
1·18·0	−10.5	2.8	3·10·0	−11.4	....	560	−13.2	12.2	720	6.5	7.8	920	−6.0	....
210	9.8	6.5	3·12·0	−2.1	....	580	−7.3	....	740	16.0	20.2	940	−2.7	....
230	29.9	19.7	3·14·0	−2.8	....	5·10·0	9.0	10.7	760	22.8	19.7	960	4.6	8.3
250	28.5	17.9	3·16·0	1.1	....	5·12·0	10.7	....	780	15.7	18.9	980	10.0	6.6
270	28.8	18.5	410	11.1	3.2	5·14·0	20.5	16.6	7·10·0	−8.6	7.7	9·10·0	−1.4	5.4
290	5.0	....	430	−37.9	45.5	5·16·0	23.4	29.3	7·12·0	−23.2	23.7			

Reflections $hk1$, $h+k$ even. Structure factor: $4\,\Sigma_i f_i \sin hx_i \cos ky_i$

$hk1$			$hk1$			$hk1$			$hk1$			$hk1$		
111	27.1	16.2	2·10·1	−15.0	13.3	441	−11.1	11.9	5·15·1	−7.3	11.6	7·11·1	−12.6	....
131	−3.9	5.4	2·12·1	−3.9	....	461	−5.0	....	601	−3.4	....	801	45.4	46.9
151	−3.2	....	2·14·1	3.8	6.1	481	17.7	16.9	621	8.3	6.0	821	17.9	23.5
171	−38.9	37.7	2·16·1	19.2	20.0	4·10·1	21.4	16.8	641	−10.5	3.4	841	−1.2	1.7
191	−23.2	24.6	311	4.9	1.4	4·12·1	6.2	....	661	−3.1	....	861	−10.4	3.7
1·11·1	−28.3	21.1	331	0.1	....	4·14·1	−7.4	....	681	5.5	7.4	881	−12.5	12.3
1·13·1	−10.9	13.1	351	−8.9	7.4	4·16·1	−29.7	24.6	6·10·1	3.2	....	8·10·1	−4.1	....
1·15·1	0.6	8.2	371	5.6	....	511	−8.8	6.5	6·12·1	7.2	....	8·12·1	−10.0	4.8
1·17·1	9.1	4.0	391	−4.9	....	531	−12.5	15.4	6·14·1	−11.2	7.4	911	6.6	....
201	38.3	22.5	3·11·1	9.0	12.2	551	12.2	14.5	711	16.8	20.7	931	1.4	7.1
221	44.9	23.3	3·13·1	−4.6	....	571	17.6	22.9	731	6.8	....	951	−10.6	9.1
241	12.0	4.3	3·15·1	−4.2	....	591	36.3	37.6	751	−24.4	21.9	971	0.6	....
261	−9.8	10.0	401	−27.9	21.0	5·11·1	27.1	36.8	771	−23.0	26.0	991	3.7	....
281	−11.8	10.5	421	−32.5	29.3	5·13·1	13.8	....	791	−27.6	22.0			

Reflections $hk1$, $h+k$ odd. Structure factor: $4\,\Sigma_i f_i \cos hx_i \sin ky_i$

011	13.4	5.4	1·14·1	−17.6	16.9	3·10·1	14.1	16.8	581	15.3	11.6	781	−1.2	....
031	13.3	7.9	1·16·1	−7.2	....	3·12·1	11.4	7.4	5·10·1	−9.7	....	7·10·1	3.8	....
051	45.6	44.9	211	−27.4	23.9	3·14·1	23.2	21.8	5·12·1	13.4	21.3	7·12·1	−19.5	19.4
071	28.0	29.6	231	−16.8	17.5	3·16·1	27.5	31.2	5·14·1	−14.8	6.5	811	−6.6	....
091	7.6	....	251	−18.9	11.8	411	−2.8	....	611	5.9	7.1	831	−11.4	15.1
0·11·1	−7.1	8.2	271	−4.8	5.7	431	−27.9	27.9	631	20.2	26.4	851	−12.5	8.3
0·13·1	−36.9	41.0	291	8.5	8.3	451	13.9	14.5	651	23.7	32.4	871	−3.9	11.1
0·15·1	7.0	15.7	2·11·1	−4.4	....	471	−3.2	....	671	24.4	26.0	891	−1.2	....
0·17·1	6.3	....	2·13·1	9.1	5.1	491	−1.4	....	691	4.8	....	8·11·1	2.7	11.6
121	2.8	4.0	2·15·1	4.6	6.8	4·11·1	5.6	10.2	6·11·1	−17.1	24.0	921	−18.9	17.8
141	8.5	5.4	2·17·1	15.5	11.7	4·13·1	0.5	....	6·13·1	−20.7	24.8	941	−16.2	10.5
161	20.8	15.2	321	31.2	29.3	4·15·1	14.9	12.5	721	7.2	7.1	961	−25.7	31.6
181	16.9	18.6	341	−37.4	31.8	521	−2.8	4.0	741	7.1	7.4	981	−0.9	....
1·10·1	9.2	16.8	361	17.3	16.9	541	16.8	14.2	761	20.2	19.4	9·10·1	2.8	....
1·12·1	−17.1	23.1	381	−9.3	2.0	561	6.3	3.4						

products of the scattering powers of the atoms. The principal peaks expected are those for Cd–Cd and Cd–Cl. At $z = 0$ the Cd–Cd peak should occur for the two atoms at x_{Cd}, y_{Cd} $^1/_4$ and $^1/_2$ +

$x_{Cd}\ ^1/_2 - y_{Cd}\ ^1/_4$; that is, at the point $^1/_2\ ^1/_2 - 2y_{Cd}$. The most pronounced peak in Fig. 1 is in fact at $^1/_2$, 0.385, corresponding to $y_{Cd} = 0.0575$. The most pronounced peak of Fig. 2, at 0.1667, $^1/_2$, similarly corresponds to $^1/_2 - 2x_{Cd}\ ^1/_2$, and leads to the value $x_{Cd} = 0.1667$. Another Cd–Cd peak, at $2x_{Cd}2y_{Cd}$, also appears on this diagram in the position required by these parameter values.

These values of x_{Cd} and y_{Cd} can be combined with the coördinates of the remaining peaks to obtain values for the coördinates for chlorine atoms. Thus for the level $z = 0$ Cd–Cl or Cd–N peaks are expected at $x_{Cd} - x, y_{Cd} - y$; $^1/_2 + x_{Cd} - x$, $^1/_2 - y_{Cd} - y$; etc. The parameter values obtained in this way are

$$\begin{aligned} x_{I} &= 0.305 & y_{I} &= 0.219 \\ x_{II} &= .164 & y_{II} &= .505 \\ x_{III} &= .025 & y_{III} &= .893 \end{aligned}$$

In addition the ammonium ions can be assigned the parameter values $x_{NH_4} = 0.43$, $y_{NH_4} = 0.82$, inasmuch as these positions are the only ones compatible with a minimum NH_4–Cl distance of about 3.1 Å. These parameter values lead to a structure which is stereochemically satisfactory, as described below.

In order to obtain more accurate values of the parameters a section at $z = {}^1/_4$ of a three-dimensional Bragg–Fourier calculation was carried out, with use as the signs of the F's of those given by the approximate parameter values. The summation over l for the series

$$D(x,y,z) = \Sigma_h \Sigma_k \Sigma_l F_{hkl} \cos 2\pi(hx + ky + lz) \qquad (2)$$

was made in a way similar to that for the Patterson diagrams, namely, by summing the quantity f/Z for series of reflections (hkl) with l even or odd to obtain factors for F_{hk0} and F_{hk1}.

The Bragg–Fourier diagram at $z = {}^1/_4$, shown as Fig. 3, has a very high peak for the cadmium atom, three peaks for the three chlorine atoms, and a small peak for the ammonium ion, in positions corresponding to the following parameter values, which differ by only small amounts from the initial values:

$$\begin{aligned} x_{Cd} &= 0.165 & y_{Cd} &= 0.054 \\ x_{I} &= .284 & y_{I} &= .215 \\ x_{II} &= .167 & y_{II} &= .496 \\ x_{III} &= .026 & y_{III} &= .898 \\ x_{NH_4} &= .43 & y_{NH_4} &= .82 \end{aligned}$$

The agreement between observed and calculated amplitudes of reflection is seen from Table I to be satisfactory. Screening-constant atomic scattering factors[8] were used in the calculation of the F values.

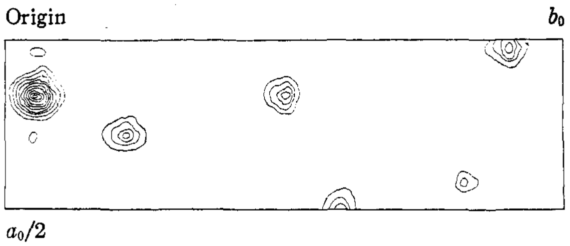

Fig. 3.—Bragg–Fourier diagram for the section $z = {}^1/_4$. The four peaks in the upper part of the diagram represent, from left to right, the atoms Cd, Cl_I, Cl_{II}, and Cl_{III}, and the two peaks below represent Cl_{III} (in part) and NH_4.

Description of the Structure

The structure found for NH_4CdCl_3 is shown in Fig. 4. Each cadmium atom is surrounded by six chlorine atoms, which form a nearly regular octahedron. The Cd–Cl distances have the values 2.60 (2), 2.62, 2.64, and 2.72 (2) Å., the average of these, 2.65 Å., being almost identical with the Cd–Cl distance in $CdCl_2$, 2.66 Å. The variation about the average is probably not real, but the result of small errors in the parameter values. The Cl–Cl distances along octahedral edges have the values 3.53 (2), 3.68 (2), 3.69 (2), 3.73 (2), 3.80 (2), and 3.97 (2) Å. Each octahedron shares two opposed edges with other octahedra to form octahedral strings parallel to the c-axis, as in the rutile structure. These rutile

TABLE II

INTERATOMIC DISTANCES IN NH_4CdCl_3

Atom	Neighbors	Distance Å.	Atom	Neighbors	Distance Å.
Cd	2 Cl_{II}	2.60	Cl_{II}	2 Cd	2.60
	1 Cl_I	2.62		2 NH_4	3.40
	1 Cl_{III}	2.64		1 NH_4	3.47
	2 Cl_{III}	2.72		1 Cl_{III}	3.53
				2 Cl_{II}	3.62
NH_4	4 Cl_I	3.27		2 Cl_I	3.76
	1 Cl_{III}	3.34		2 Cl_{III}	3.80
	2 Cl_{II}	3.40		2 Cl_{II}	3.97
	1 Cl_{II}	3.47		1 Cl_I	4.30
	1 Cl_{III}	3.82		1 Cl_I	4.64
Cl_I	1 Cd	2.62	Cl_{III}	1 Cd	2.64
	4 NH_4	3.27		2 Cd	2.72
	2 Cl_{II}	3.73		1 NH_4	3.34
	2 Cl_{III}	3.76		1 NH_4	3.82
	2 Cl_{III}	3.80		1 Cl_{II}	3.53
	2 Cl_I	3.97		2 Cl_{III}	3.68
	1 Cl_{II}	4.30		2 Cl_{II}	3.69
	2 Cl_I	4.59		2 Cl_I	3.76
	1 Cl_{II}	4.64		2 Cl_I	3.80
				2 Cl_{III}	3.97

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(8) L. Pauling and J. Sherman, *Z. Krist.*, **81**, 1 (1932).

strings are further condensed in pairs, each octahedron sharing two edges with octahedra of the adjacent string. The four shared edges are, as usual for partially ionic crystals, somewhat shorter than the unshared edges.

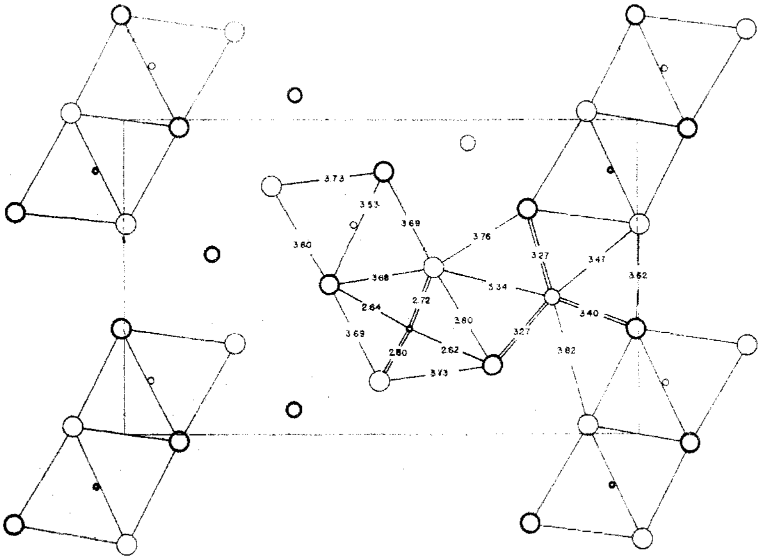

Fig. 4.—The structure of NH_4CdCl_3, projected on the plane (001). Light circles represent atoms at $z = {}^1/_4$ and heavy circles those at $z = {}^3/_4$. Cadmium and chlorine atoms are shown as small and large circles, and ammonium ions as circles of intermediate size.

Each ammonium ion is in contact with nine chlorine atoms, at about 3.27 (2), 3.27 (2), 3.34, 3.40 (2), 3.47, and 3.82 Å. The average of these distances, excluding the largest, is 3.31 Å., which is nearly the same as in NH_4Cl (NH_4–Cl = 3.27 Å. for the high temperature form, with the sodium chloride structure, and 3.34 Å. for the low temperature form, with the cesium chloride structure). The nine chlorine atoms are arranged in the most compact configuration possible for coördination number nine—a triangle of three in the equator, and smaller triangles above and below rotated through 60°. The Cl–Cl distances along the edges of this polyhedron have the values 3.62 (2), 3.69 (2), 3.73 (2), 3.76 (4), 3.80 (2), 4.30 (2), 4.59 (2), and 4.64 (2) Å.

Cleavage along planes of the zone [001] might be expected for the crystal; no cleavage has been reported, however, nor did we observe any in experiments with our small crystals.

The chlorine atoms form bonds to the following numbers:

Cl_I: 1 with Cd, 4 with NH_4
Cl_{II}: 2 with Cd, 3 with NH_4
Cl_{III}: 3 with Cd, 2 with NH_4

These have the total strengths 7/9, 1, and 11/9, respectively; there is, accordingly, some discrepancy with the electrostatic valence rule.[9] It is interesting that the substance crystallizes with this structure rather than a structure such as that of $KMgF_3$, in which the halogen atoms are equivalent, each being common to two octahedra.

The arrangement of the chlorine atoms is compact; as shown in Table II, each chlorine atom has eleven or twelve chlorine atoms as neighbors, at distances between 3.53 and 4.64 Å.

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Summary

A complete structure determination has been made of the orthorhombic crystal NH_4CdCl_3. The unit of structure has the dimensions $a_0 = 8.96 \pm 0.02$ Å., $b_0 = 14.87 \pm 0.03$ Å., $c_0 = 3.97 \pm 0.01$ Å., and contains 4 NH_4CdCl_3. The atomic positions are $xy\,1/4$, $\frac{1}{2} + x\ \frac{1}{2} - y\ 1/4$, $\frac{1}{2} - x\ \frac{1}{2} + y\ 3/4$, $\bar{x}\bar{y}\ 3/4$ of the space group $D_{2h}^{16} - Pnam$, with the following parameter values x, y: Cd, 0.165, 0.054; Cl_I, 0.284, 0.215; Cl_{II}, 0.167, 0.496; Cl_{III}, 0.026, 0.898; NH_4, 0.43, 0.82.

The $CdCl_3$ complexes occur in the crystal as infinite polymers, in the form of double rutile strings of $CdCl_6$ octahedra parallel to the c-axis. These complexes are held together by ammonium ions, each of which has nine chlorine atoms coördinated about it. Interatomic distances in the crystal (Table II) are closely related to those in $CdCl_2$ and NH_4Cl.

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[9] L. Pauling, THIS JOURNAL, 51, 1010 (1929).