

## SHORT STRUCTURAL PAPERS

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## A New Investigation of Ammonium Cadmium Chloride

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**Abstract.**  $\text{NH}_4\text{CdCl}_3$ , orthorhombic,  $Pmnb$ ,  $a = 3.994$  (1),  $b = 9.026$  (3),  $c = 14.938$  (4) Å;  $Z = 4$ ;  $D_m = 2.87$ ,  $D_c = 2.92$  g cm $^{-3}$ ;  $\mu(\text{Mo } K\alpha) = 53.1$  cm $^{-1}$ ;  $F(000) = 440$ ;  $\lambda(\text{Mo } K\alpha_1) = 0.70926$  Å. The structure has been refined by blocked least-squares methods to an  $R$  of 0.038 for 759 observed reflections. Our results confirm the earlier structure but give interatomic distances and angles with greater accuracy. Anisotropic temperature factors were introduced and all hydrogen atoms were located.

**Introduction.** The structure of ammonium cadmium chloride was originally determined by Brasseur & Pauling (1938). The accuracy of their work was limited by the methods available at that time. An accurate knowledge of the geometry of the  $\text{NH}_4\text{CdCl}_3$  molecule was of interest in the framework of our study of thioacetamide complexes, as the present structure also results from the interaction between  $\text{CdCl}_2$  and the hydrolysis product of thioacetamide in an acidic medium. White prismatic crystals were obtained after two weeks of slow evaporation of a mixture of  $\text{CdCl}_2$  in HCl and thioacetamide in ethanol. A single crystal, ground to a sphere of radius 0.24 mm, was used for data collection. Preliminary Weissenberg precession photographs showed systematic absences of  $h0l$  for  $h + l = 2n + 1$  and  $hk0$  for  $k = 2n + 1$ , indicating space group  $Pmnb$  or  $P2_1nb$ .

Intensity data were collected with Mo  $K\alpha_1$  radiation on an automated Enraf–Nonius CAD-3 diffractometer, equipped with a graphite monochromator. The intensity of a standard reflection was measured every 50 reflections; no significant trends were observed. Of 953 independent reflections, 759 were considered observed. The data were corrected for Lorentz and polarization effects and for absorption ( $\mu R = 1.3$ ). As the analysis did not reveal any evidence to rule out the

non-centrosymmetric alternative  $P2_1nb$ , space group  $Pmnb$  was assumed corresponding to the study of Brasseur & Pauling (1938).

With four molecules in the unit cell all the non-hydrogen atoms should lie in the symmetry planes  $x = \frac{1}{4}$  and  $\frac{3}{4}$ . These atoms were located by three-dimensional Patterson and Fourier syntheses. Isotropic and anisotropic least-squares refinement reduced  $R$  to 0.058 and 0.039 respectively. The quantity minimized was  $\sum w(F_o - F_c)^2$  with  $w = 1/\sigma$ . A difference synthesis revealed an ordered, approximately tetrahedral arrangement of H atoms about N(05). The atoms H(06) and H(07) lie in the mirror plane at  $x = \frac{1}{4}$ , as does N(05). The third H atom, H(08), lies in a general position; H(08) and H(08<sup>iii</sup>), related to H(08) by the mirror operation  $\frac{1}{2} - x, y, z$ , complete in this way the coordination of N(05). Subsequent structure factor calculations contained contributions for the scattering of the H atoms, which were assigned the isotropic temperature factor of the N atom. None of the H atom parameters was refined. The final  $R$  was 0.038 and the atomic positions are listed in Table 1.† The atomic

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33634 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates with e.s.d.'s for the non-hydrogen atoms

	$x$	$y$	$z$
Cd(01)	0.2500	0.1656 (1)	0.0565 (1)
Cl(02)	0.2500	0.0249 (2)	-0.1000 (1)
Cl(03)	-0.2500	0.3292 (2)	-0.0043 (1)
Cl(04)	0.2500	0.2827 (2)	0.2091 (1)
N(05)	0.2500	0.4300 (8)	0.8264 (5)
H(06)	0.250	0.509	0.892
H(07)	0.250	0.536	0.784
H(08)	0.417	0.374	0.806

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scattering factor for Cd was taken from Cromer & Mann (1968) and the anomalous dispersion corrections for Cd and Cl were those from *International Tables for X-ray Crystallography* (1974). All calculations were carried out on an IBM 370/158 computer using the XRAY 1976 programs (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976).

**Discussion.** The atomic coordinates of the non-hydrogen atoms are close to those given by Brasseur & Pauling (1938). Each Cd atom is surrounded by six Cl atoms forming a nearly regular octahedron. The octahedra are linked in endless chains running along the *x* axis, with two edges shared by two adjacent octahedra. These chains are condensed in pairs by Cl bridges, see Fig. 1. Interatomic distances and angles within a double chain are given in Table 2. Cl(04) is only bonded to Cd(01) at a distance 2.512 (2) Å which is somewhat smaller than the 2.62 Å found by Brasseur & Pauling (1938); Cl(03) lies at 2.645 (2) Å from Cd(01) and

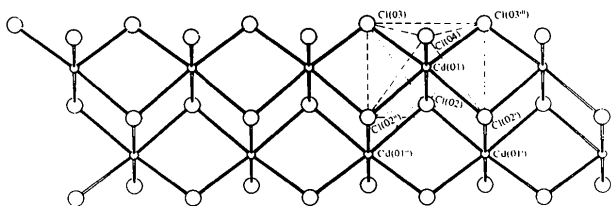


Fig. 1. Clinographic projection of a chain.

Table 2. Interatomic distances (Å) and angles (°)

Cd(01)—Cl(02)	2.660 (2)	Cl(02)—Cd(01 <sup>h</sup> )	2.714 (2)
Cd(01)—Cl(03)	2.645 (2)	Cl(02)—Cd(01 <sup>h</sup> )	2.714 (2)
Cd(01)—Cl(04)	2.512 (2)	Cl(03)—Cd(01 <sup>h</sup> )	2.645 (2)
Cd(01)—Cl(03 <sup>h</sup> )	2.645 (2)	N(05)—H(06)	1.22
Cd(01)—Cl(02 <sup>h</sup> )	2.714 (2)	N(05)—H(07)	1.14
Cd(01)—Cl(02 <sup>h</sup> )	2.714 (2)	N(05)—H(08)	0.89
		N(05)—H(08 <sup>h</sup> )	0.89
Cl(02)—Cd(01)—Cl(02 <sup>h</sup> )	84.71 (5)	H(06)—N(05)—H(07)	88
Cl(02)—Cd(01)—Cl(03)	87.97 (6)	H(06)—N(05)—H(08)	128
Cl(02)—Cd(01)—Cl(03 <sup>h</sup> )	87.97 (6)	H(06)—N(05)—H(08 <sup>h</sup> )	128
Cl(02)—Cd(01)—Cl(02 <sup>h</sup> )	84.71 (5)	H(07)—N(05)—H(08)	106
Cl(04)—Cd(01)—Cl(03)	94.40 (6)	H(07)—N(05)—H(08 <sup>h</sup> )	106
Cl(04)—Cd(01)—Cl(03 <sup>h</sup> )	94.40 (6)	H(08)—N(05)—H(08 <sup>h</sup> )	97
Cl(04)—Cd(01)—Cl(02 <sup>h</sup> )	92.84 (6)		
Cl(04)—Cd(01)—Cl(02 <sup>h</sup> )	92.84 (6)		
Cl(03)—Cd(01)—Cl(03 <sup>h</sup> )	98.06 (5)		
Cl(03)—Cd(01)—Cl(02 <sup>h</sup> )	83.13 (5)		
Cl(02 <sup>h</sup> )—Cd(01)—Cl(03 <sup>h</sup> )	83.13 (5)		
Cl(02 <sup>h</sup> )—Cd(01)—Cl(02 <sup>h</sup> )	94.75 (5)		

Symmetry code

(i)	$x + \frac{1}{2}, \bar{y}, \bar{z}$	(viii)	$x - \frac{1}{2}, 1 - y, 1 - z$
(ii)	$x - \frac{1}{2}, \bar{y}, \bar{z}$	(ix)	$x + 1, y, 1 + z$
(iii)	$x + 1, y, z$	(x)	$x, y, 1 + z$
(iv)	$x - 1, y, z$	(xi)	$x, \frac{1}{2} + y, \frac{1}{2} - z$
(v)	$x + \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z$	(xii)	$\frac{1}{2} - x, y, z$
(vi)	$x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z$	(xiii)	$1 - x, \frac{1}{2} - y, \frac{1}{2} + z$
(vii)	$x + \frac{1}{2}, 1 - y, 1 - z$	(xiv)	$1 + x, \frac{1}{2} + y, \frac{1}{2} - z$

Cd(01<sup>h</sup>), while Cl(02) is bonded to three Cd atoms at different distances. The linkage between adjacent chains occurs by the bonds Cl(02)—Cd(01<sup>h</sup>) and Cl(02)—Cd(01<sup>h</sup>) with the same distance of 2.714 (2) Å. From this we may conclude that the Cl atoms are not equivalent.

An analysis of the coordination of the ammonium ion is given in Table 3. Each ion is in contact with eight Cl atoms at distances smaller than 3.5 Å. The distances N...Cl(02<sup>x</sup>) and H...Cl(02<sup>x</sup>) are greater than the sum of the corresponding van der Waals radii so that this interaction cannot be considered to be significant. The other N...Cl bonds can be divided into two classes: strong bonds, for which H...Cl ≤ 2.5 Å and the average N—H—Cl angle is 166°; bonds of lower strength, for which 2.5 ≤ H...Cl ≤ 3.0 Å and the

Table 3. N—H...Cl geometry

	N...Cl	N—H	H...Cl	∠H
N(05)—H(06)—Cl(03 <sup>h</sup> )	3.433 (8) Å	1.22 Å	2.22 Å	175°
N(05)—H(08)—Cl(04 <sup>h</sup> )	3.278 (6)	0.89	2.42	162
N(05)—H(08 <sup>h</sup> )—Cl(04 <sup>h</sup> )	3.278 (6)	0.89	2.42	162
N(05)—H(07)—Cl(02 <sup>h</sup> )	3.490 (8)	1.14	2.75	121
N(05)—H(07)—Cl(04 <sup>h</sup> )	3.316 (6)	1.14	2.59	120
N(05)—H(07)—Cl(04 <sup>h</sup> )	3.316 (6)	1.14	2.59	120
N(05)—H(06)—Cl(03 <sup>h</sup> )	3.348 (6)	1.22	3.00	96
N(05)—H(06)—Cl(03 <sup>h</sup> )	3.348 (6)	1.22	3.00	96
N(05)—H(08)—Cl(02 <sup>x</sup> )	3.818 (8)	0.89	3.51	103
N(05)—H(08 <sup>h</sup> )—Cl(02 <sup>x</sup> )	3.818 (8)	0.89	3.51	103

Equivalent positions for *Pmnb*, a non-standard setting of *Pnma* (*D*<sub>2h</sub><sup>16</sup>, No. 62)

$x, y, z$	$\bar{x}, \bar{y}, \bar{z}$
$\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$	$\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$
$\frac{1}{2} + x, \bar{y}, \bar{z}$	$\frac{1}{2} - x, y, z$
$x, \frac{1}{2} - y, \frac{1}{2} + z$	$x, \frac{1}{2} + y, \frac{1}{2} - z$

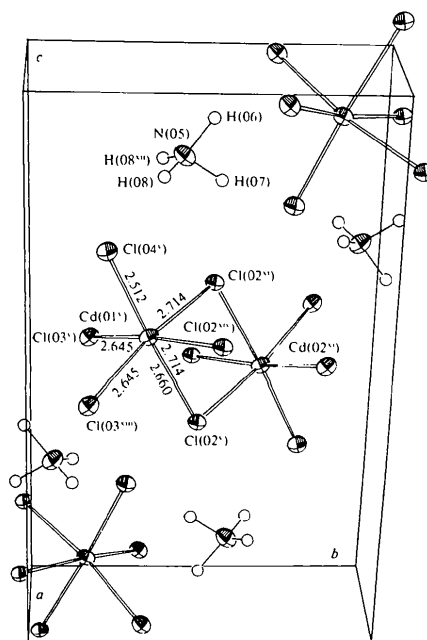


Fig. 2. ORTEP (Johnson, 1965) plot of the unit cell.

average N—H—Cl angle is  $111^\circ$ . It is interesting to note that most of the hydrogen atoms are involved in a strong hydrogen bond. The average N...Cl distance amounts to 3.350 (6) Å, which is in good agreement with that in NH<sub>4</sub>Cl (3.27 Å for the high-temperature form and 3.34 Å for the low-temperature form). In view of the above results, the packing of the double chains is determined by the ammonium ions. Fig. 2 shows the unit cell.

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## Neutron Powder Diffraction Study of Titanium Copper Deuteride TiCuD<sub>0.90</sub>

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**Abstract.** TiCuD<sub>0.90</sub>, tetragonal, *P4/nmm*,  $a = 3.020$  (1),  $c = 6.837$  (3) Å (parameters determined by X-ray powder diffraction),  $Z = 2$ . The structure has been refined by the method of total-profile analysis of a neutron diffraction powder pattern. The composition obtained from the refinement corresponds to the formula TiCuD<sub>0.90(1)</sub> (TiCuD<sub>0.96</sub> by thermal analysis). The D atoms are located at the centers of distorted tetrahedra of Ti atoms, with a Ti—D distance of 1.927 (4) Å.

**Introduction.** The title compound was prepared by absorption of D<sub>2</sub> in  $\gamma$ -TiCu. The sample of  $\gamma$ -TiCu was prepared by arc melting (Maeland, 1978) and contained small quantities of the  $\delta$  phase (Karlsson, 1951). Initially,  $\gamma$ -TiCu was exposed to D<sub>2</sub> at a pressure of 177.5 p.s.i. at room temperature (23°C), and then heated to 200°C over a period of 1.5 h, without apparent absorption of D<sub>2</sub>. After 1 h at 200°C, however, absorption started and the D<sub>2</sub> pressure decreased 124 p.s.i. in 0.5 h. The sample was cooled to room temperature over a period of 20 h and then reheated to 200°C to homogenize it. After 2 h at 200°C it was cooled again to room temperature over a

period of 24 h. The D<sub>2</sub> pressure after this treatment was 37 p.s.i. From the pressure change, the volume of the system and the sample weight, a composition corresponding to the formula TiCuD<sub>0.99</sub> was calculated. Thermal analysis of the powdered sample gave TiCuD<sub>0.96</sub>.

X-ray powder patterns were consistent with the symmetry of space group *P4/nmm*. The lattice parameters determined from these patterns by least-squares analysis are in agreement with the results obtained for TiCuH<sub>0.97(3)</sub> (Maeland, 1978).

Table 1. *Experimental conditions used to measure the powder pattern of TiCuD<sub>0.9</sub>*

Monochromatic beam: reflection 220 of a Cu monochromator  
 Mean neutron wavelength:  $\lambda = 0.925$  (1) Å  
 Horizontal divergences  
 (a) in pile collimator: 20' arc  
 (b) monochromatic beam collimator: 23' arc  
 (c) diffracted beam collimator: 24' arc  
 Monochromator mosaic spread:  $\sim 20'$  arc  
 Sample container: vanadium can of  $\sim 1$  cm diameter  
 $2\theta_{\text{initial}} = 5.0^\circ$ ,  $2\theta_{\text{final}} = 90.0^\circ$ , step =  $0.1^\circ$   
 Number of independent Bragg reflections: 102  
 Number of observations above background: 601

### References

- BRASSEUR, H. & PAULING, L. (1938). *J. Am. Chem. Soc.* **60**, 2886–2890.  
 CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.  
*International Tables for X-ray Crystallography* (1974). Vol. IV, p. 149. Birmingham: Kynoch Press.  
 JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.  
 STEWART, J. M., MACHIN, P. A., DICKINSON, C., AMMON, H. L., HECK, H. & FLACK, H. (1976). The XRAY 76 System. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.