

vont de 2,53 à 2,94 Å. Leur longueur moyenne (2,68 Å) ne diffère pas de façon significative de la longueur moyenne de leurs homologues dans $\text{Ag}_4\text{P}_2\text{S}_6$ monoclinique (2,63 Å), dans $\text{Ag}_2\text{P}_2\text{S}_6$ (Toffoli, Khodadad & Rodier, 1978b) (2,66 Å) ou dans $\text{Ag}_4\text{P}_2\text{S}_7$ (Toffoli, Khodadad & Rodier, 1977) (2,64 Å).

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Crystal Form and Structure of Ammonium Hexaaquamagnesium Trichloride, $\text{NH}_4[\text{Mg}(\text{H}_2\text{O})_6]\text{Cl}_3$

BY X. SOLANS AND M. FONT-ALTABA

Departamento de Cristalografía y Mineralogía, Universidad de Barcelona, Gran Via 585, Barcelona 7, Spain

M. AGUILÓ

Cristalografía, Facultad de Química, Universidad de Barcelona, P. Imperial Tarraco s/n, Tarragona, Spain

AND J. SOLANS* AND V. DOMENECH

Departamento de Cristalografía y Mineralogía, Universidad de Oviedo, Arias de Velasco s/n, Oviedo, Spain

(Received 28 December 1982; accepted 5 July 1983)

Abstract. $M_r = 256.8$, monoclinic, $C2/c$, $a = 9.320$ (3), $b = 9.582$ (3), $c = 13.327$ (4) Å, $\beta = 90.12$ (4)°, $V = 1190$ (1) Å³, $D_x = 1.43$ Mg m⁻³, $Z = 4$, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu(\text{Mo } K\alpha) = 0.812$ mm⁻¹, $F(000) = 536$, room temperature. The structure was solved by direct methods and refined by full-matrix least squares to an R of 0.075 for all observed reflections. The Mg^{2+} and NH_4^+ ions display an octahedral coordination of water molecules and Cl^- ions, respectively, while the Cl^- ions are coordinated to six water molecules and two NH_4^+ ions. In general, the crystal shows the faces $\{001\}$ and $\{110\}$. A qualitative and quantitative morphological analysis has been carried out. The main periodic bond-chain (PBC) directions are $[001]$, $\frac{1}{2}\langle 110 \rangle$, $[100]$, $[010]$, $\frac{1}{2}\langle 112 \rangle$ and $\frac{1}{2}\langle \bar{1}12 \rangle$. The main F faces are $\{001\}$, $\{110\}$, $\{112\}$, $\{\bar{1}12\}$ from minor to major attachment energy.

Introduction. The crystallization of the β -phase of ammonium pentaborate tetrahydrate by slow evaporation at room temperature (Domenech, 1981) is linked to the presence in the solution of $\text{NH}_4\text{MgCl}_3 \cdot 6\text{H}_2\text{O}$. A structural and morphological study of the title compound has been carried out in order to obtain crystallographic data to determine the possible influence of this compound on the obtention of different phases of ammonium pentaborate tetrahydrate.

Experimental. Colourless hygroscopic crystals were obtained by fractional crystallization and slow evaporation from a solution of NH_3 , H_3BO_3 and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ in water. In the first crystallization crystals of the β -phase of ammonium pentaborate tetrahydrate were separated. In the second, crystals of the title compound were obtained.

Equidimensional crystals, $0.2 \times 0.2 \times 0.2$ mm, Philips PW 1100 diffractometer, $\text{Mo } K\alpha$, graphite

* Present address: Departamento de Cristalografía y Mineralogía, Universidad de Barcelona, Barcelona, Spain.

monochromator, lattice parameters from 20 reflections ($4 \leq \theta \leq 12^\circ$). Comparison between $I(hkl)$ and $I(\bar{h}\bar{k}\bar{l})$ confirmed the crystal system. ω -scan technique, scan width 1° , scan speed 0.3°s^{-1} . Three standard reflections measured every 2 h: no variation of intensity. 939 independent reflections, $\theta \leq 25^\circ$, range of hkl : $-11,11$; $0,11$; $0,15$, respectively, 914 with $I \geq 2.5\sigma(I)$, L_p correction, absorption ignored. Cl and Mg atoms from *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), remaining non-hydrogen atoms from *DIRDIF* (Beurskens, Bosman, Doesburg, Gould, van den Hark & Prick, 1980). Anisotropic full matrix (*SHELX*, Sheldrick, 1976), H (from $\Delta\rho$ synthesis) with overall isotropic temperature factor, final $R = 0.075$, $R_w = 0.078$, $w|F_o| - |F_c|$ minimized, $w = [\sigma^2(F_o) + 0.0433 |F_o|^2]^{-1}$; f , f' and f'' from *International Tables for X-ray Crystallography* (1974), ratio of maximum l.s. shift to error 3.4 in z coordinate of H(O2), maximum and minimum heights in final $\Delta\rho$ map 0.4 and -0.3 e \AA^{-3} , respectively: VAX-750.

The dihedral angle between the crystal faces was measured by optical goniometry. In general, the crystals are equidimensional, and show faces $\{001\}$ and $\{110\}$; faces $\{\bar{1}12\}$ were observed in one crystal (among 54). 20% of crystals are penetration twins; these were studied by automatic diffractometry. The twin law is a twofold axis parallel to the $[001]$ axis. The symmetry of twin crystals is $P112_1$, with the same cell parameters, and their crystal structure shows a disorder in the locations of the water molecules.

Discussion. Final atomic parameters are given in Table 1.*

The structure consists of discrete $\text{Mg}(\text{H}_2\text{O})_6^{2+}$, Cl^- and NH_4^+ ions linked by ionic forces and hydrogen-bond interactions. Each Mg atom is surrounded by six water molecules in an octahedral arrangement. The average Mg—O bond lengths and O—Mg—O angles are $2.053(3) \text{ \AA}$ and $89.7(1)^\circ$, respectively. Each NH_4^+ ion is surrounded by six Cl^- ions in an octahedral arrangement with an average Cl—N distance of $3.34(4) \text{ \AA}$. Finally, each Cl^- ion is hydrogen bonded to six water molecules and two NH_4^+ ions (*cf.* Table 2).

A crystallization unit involving the atoms shown in Fig. 1 was defined in order to determine the PBC's. One-eighth of each N atom and one-quarter of each Cl^- ion is assumed, in order to obtain stoichiometry and non-polarity conditions (Hartman, 1973; Woensdregt, 1980). The main PBC's are listed in Table 3.

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38706 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Figs. 2 and 3 show projections of the structure down the main PBC directions.

In the $[001]$ zone (Fig. 2) there are two $[001]$ PBC's per unit cell. The bonding between these PBC's leads to the (110) , (100) and (010) slices, in which the $[001]$ are connected by the $\frac{1}{2}(a+b)$, a or b translation. In the $\frac{1}{2}[110]$ zone (Fig. 3) there are two non-translation-equivalent $\frac{1}{2}[110]$ PBC's per unit cell. The bonding between them leads to (001) and $(\bar{1}12)$ slices, in which the $\frac{1}{2}[110]$ are connected by a c glide plane or an n glide plane.

Table 1. Final atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters (\AA^2)

$$B_{\text{eq}} = \frac{1}{3}\pi^2 \sum_i U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	B_{eq}
Cl(1)	5000	0	5000	3.5 (1)
Cl(2)	2544 (1)	7384 (2)	7467 (1)	3.3 (1)
Mg	5000	5000	5000	1.9 (1)
N	5000	13 (6)	7500	5.1 (4)
O(1)	4103 (3)	6876 (2)	5381 (2)	3.3 (1)
O(2)	3194 (3)	3990 (2)	5511 (2)	3.4 (1)
O(3)	4084 (3)	5134 (3)	3601 (2)	3.3 (1)

Table 2. Interatomic distances (\AA) and angles ($^\circ$)

Mg—O(1)	2.047 (2)	Cl(2) \cdots O(1)	3.177 (3)
Mg—O(2)	2.059 (2)	Cl(2 vi) \cdots O(2)	3.180 (3)
Mg—O(3)	2.053 (2)	Cl(2 vii) \cdots O(3)	3.186 (3)
Cl(1 iv) \cdots N	3.332 (2)	Cl(2 viii) \cdots O(3)	3.159 (3)
Cl(2 ii) \cdots N	3.404 (3)	O(1)—Mg—O(2)	89.8 (1)
Cl(2 iii) \cdots N	3.284 (3)	O(1)—Mg—O(3)	90.1 (1)
Cl(1 iv) \cdots O(1)	3.149 (2)	O(2)—Mg—O(3)	89.5 (1)
Cl(1 v) \cdots O(2)	3.202 (2)		

Symmetry code

- | | |
|---|--|
| (i) x, y, z | (v) $x - \frac{1}{2}, y + \frac{1}{2}, z$ |
| (ii) $x, y - 1, z$ | (vi) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$ |
| (iii) $x + \frac{1}{2}, y - \frac{1}{2}, z$ | (vii) $x, 1 - y, z - \frac{1}{2}$ |
| (iv) $x, y + 1, z$ | (viii) $\frac{1}{2} - x, \frac{3}{2} - y, 1 - z$ |

Table 3. Main PBC's with interaction ionic energies between crystallization units in kJ mol^{-1} and slice (E_{sl}), attachment (E_{att}) and crystallization (E_{cr}) energies in kJ mol^{-1} for the F faces

(a) Main PBC's				
$\{001\} (1,000)$	\bar{a}	$(4,010)$	\bar{a}	$(1,001)$
$\frac{1}{2}\{110\} (1,000)$	\bar{a}	$(3,000)$		
$\frac{1}{2}\{\bar{1}10\} (1,000)$	\bar{a}	$(3,100)$		
$\{100\} (1,000)$	\bar{b}	$(1,100)$		$E_a = -247$
$\{010\} (1,000)$	\bar{b}	$(1,010)$		$E_b = -83.8$
$\{201\} (1,000)$	\bar{b}	$(4,110)$	\bar{b}	$(1,201)$
$\{021\} (1,000)$	\bar{b}	$(4,020)$	\bar{b}	$(1,021)$
$\{101\} (1,000)$	\bar{a}	$(4,010)$	\bar{b}	$(1,101)$
$\{011\} (1,000)$	\bar{a}	$(4,010)$	\bar{b}	$(1,011)$
(b) Main F slices				
	E_{sl}	E_{att}	E_{att}^*	E_{cr}
001	-1326	-613.7	-648.0	-1274 (21)
110	-1319	-613.7	-681.9	-1273 (21)
112	-1002	-770.2	-872.8	-1271 (21)
100	-692.4	-928.0	-1064	-1274 (21)
010	-690.3	-928.9	-1065	-1274 (21)

* Includes contribution of hydrogen bond.

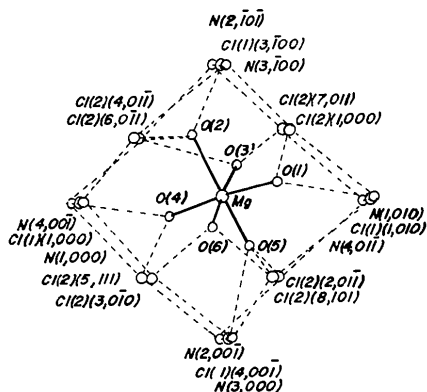


Fig. 1. View of the crystallization unit. (q, n, m, p) indicates the symmetry code; values for q : (1) $x+n, y+m, z+p$; (2) $\frac{1}{2}+x+n, \frac{1}{2}-y+m, \frac{1}{2}+z+p$; (3) $\frac{1}{2}+x+n, \frac{1}{2}+y+m, z+p$; (4) $x+n, -y+m, \frac{1}{2}+z+p$; (5) $-x+n, -y+m, -z+p$; (6) $\frac{1}{2}-x+n, \frac{1}{2}+y+m, \frac{1}{2}-z+p$; (7) $\frac{1}{2}-x+n, \frac{1}{2}-y+m, -z+p$; (8) $-x+n, y+m, \frac{1}{2}-z+p$.

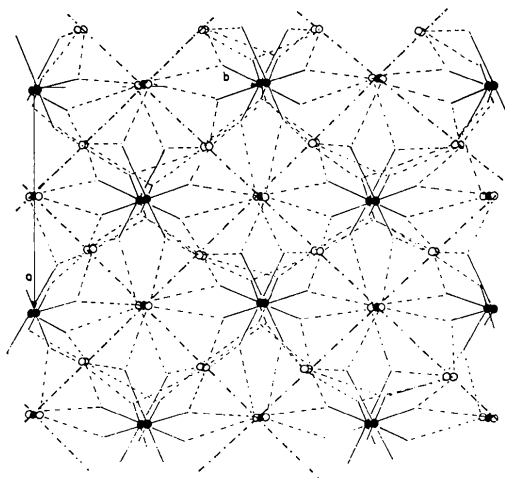


Fig. 2. Projection down the $[001]$ PBC direction.

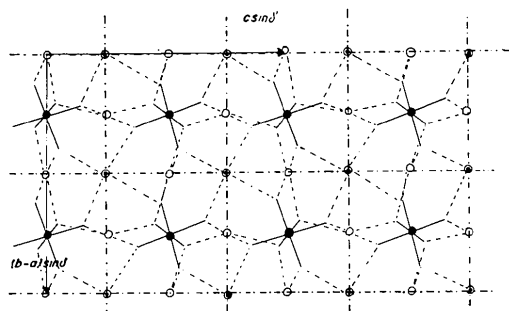


Fig. 3. Projection down the $[110]$ PBC direction; $\delta = [1\bar{1}0] \wedge [110]$; $\delta' = [110] \wedge [001]$.

Slice, attachment and crystallization energies defined by Hartman (1973) were computed assuming Coulomb interactions only. The crystallization unit was considered as pre-formed and +2, -1 and +1 charges were assigned to the positions of Mg, Cl and N atoms, respectively. The computer program used was *MORFE* (Solans, 1982). The slice, attachment and crystallization energies are listed in Table 3. The e.s.d.'s of the crystallization energies were calculated from the e.s.d.'s of the atomic coordinates, in order to determine the influence of the error of the structure determination in the final values. According to these results, $\{001\}$ and $\{110\}$ faces have equal attachment energies. This is due to the assumed distribution of charges, which produces a pseudocubic cell with $a = 6.675(5) \text{ \AA}$.

In order to determine the influence of water molecules, the energies of $\text{OH}\cdots\text{Cl}$ contacts were considered as ion-dipole interactions. The average value of this energy is $-17.1 \text{ kJ mol}^{-1}$. The attachment energy has been corrected according to this value. The results are also listed in Table 3. The application of the Hartman-Perdok theory explains the crystal forms of the title compound. The relationship between the attachment energy of faces $\{110\}$ and $\{001\}$ is very close to the approximate ratios between the surfaces (from 0.7 to 0.9), which were computed from the lengths of the edges.

This work was sponsored by the University of Barcelona.

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