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## The Crystal Structures of Nitrates of Divalent Hexaquocations. II. Hexaquomagnesium Nitrate

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The crystals of hexaquomagnesium nitrate are monoclinic, space group  $P2_1/c$ . The structure, determined from three-dimensional data, consists of hexaquomagnesium cations which are nearly octahedral with Mg-OH<sub>2av</sub> equal to 2.058 Å and of nitrate groups which are not trigonally symmetric with N-O bond lengths 1.20, 1.25, 1.26 Å. The hexaquocations and the nitrate groups are bound together by hydrogen bonds whose lengths are in the range 2.75–2.90 Å. The differences in the crystal structures of the hexaquozinc nitrate, orthorhombic, and of the hexaquomagnesium nitrate, monoclinic, seem to be related to the different disposition of the hydrogen bonds radiating from the hexaquocations towards the nitrate groups.

### Introduction

The hexaquocations of divalent metals are assigned octahedral structures, but small deviations from perfectly cubic symmetry are expected either because of the electronic configuration of the metal cation or because of the strains from the hydrogen bonds in the crystal.

The assessment of the extent of these perturbations is the object of the widely extending structural studies on the compounds of hexaquocations. The hexaquometal (II) nitrates crystallize in several different crystal systems or space groups and it seems to us worth while to endeavour to understand how far this fact is related to the distortions in the octahedral arrangement of the water molecules around the metal. Here are presented the results of the crystal structure determination of the magnesium compound.

### Experimental

#### Preparation

The crystals are obtained by crystallization from aqueous solutions. They are prismatic, highly hygroscopic and, for X-ray work, need to be sealed into capillary tubes.

#### Crystal data

Hexaquomagnesium nitrate, [Mg(OH<sub>2</sub>)<sub>6</sub>](NO<sub>3</sub>)<sub>2</sub>; F.W. 256.432.

For the structure determinations we used the refined crystal data of Mozzi & Bekebrede (1961):

$a = 6.194 \pm 0.002$ ,  $b = 12.707 \pm 0.003$ ,  $c = 6.600 \pm 0.002$  Å  
 $\beta = 92.99 \pm 0.02^\circ$ ,  $V = 518.8$  Å<sup>3</sup>  $Z = 2$

$D_m = 1.636$  g.cm<sup>-3</sup>,  $D_x = 1.641$  g.cm<sup>-3</sup>,  $\mu = 21.45$  cm<sup>-1</sup> (Cu K $\alpha$ )

Space group  $P2_1/c$  ( $C_{2h}^5$ , No.14) from systematic absences.

#### Intensity data

Integrated reflexions  $0kl$ ,  $1kl$ ,  $2kl$ ,  $3kl$ ,  $4kl$ ,  $5kl$ , photographically recorded on a Weissenberg camera, were

Table 1. Fractional atomic coordinates  $\times 10^4$  (with e.s.d.'s).

	x	y	z
Mg	0000	5000	5000
H <sub>2</sub> O(1)	-0358 (11)	3398 (4)	4764 (13)
H <sub>2</sub> O(2)	3022 (10)	4805 (5)	4616 (10)
H <sub>2</sub> O(3)	-1432 (13)	4993 (4)	7750 (10)
N(4)	4668 (12)	2040 (4)	5362 (11)
O(5)	6031 (14)	1301 (4)	5330 (12)
O(6)	2814 (15)	1881 (3)	5685 (17)
O(7)	5339 (14)	2962 (4)	5172 (16)

measured by a microdensitometer. Corrections for absorption and for secondary extinction were applied.

All the calculations were performed on the Olivetti Elea computer 6001/S of the Centro di Calcolo Elettronico of the University of Parma.

### Determination and refinement of the structure

The structure was solved by Fourier methods and the refinement was carried out by differential syntheses. The anisotropic thermal parameters were refined following the method of Nardelli & Fava (1960).

The final results are quoted in Tables 1–5. (Final  $R_{hkl}=0.156$ , observed reflexions only.)

The e.s.d.'s of the fractional coordinates (Table 1) are those obtained from the differential syntheses. For the thermal parameters (Table 2) no significant e.s.d. can be given; the maximum and average shifts of the last cycle are quoted as a rough indication of the fluctuations of the values. On the other hand no definite physical meaning has been attributed to the thermal parameters, which are to be taken as mathematical coefficients comprehensive of several factors, indicating only that the refinement process has converged. One of the factors probably affecting the thermal parameters and the  $R_{hkl}$  value as well could be a certain sort of disorder in the crystal, as suggested by diffuse reflexions on the photographs.

Table 2. Anisotropic thermal parameters\* ( $\text{\AA}^2$ )

	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$
Mg	3.390	2.876	3.551	-0.124	-0.418	0.046
H <sub>2</sub> O(1)	4.669	3.555	6.411	-0.018	-0.738	-0.026
H <sub>2</sub> O(2)	3.909	4.305	5.621	0.226	-1.247	-0.289
H <sub>2</sub> O(3)	5.836	4.385	4.950	-0.007	0.351	-0.151
N(4)	3.487	3.239	4.108	0.259	0.004	0.588
O(5)	5.781	4.966	6.372	1.628	-0.067	0.487
O(6)	4.684	4.504	8.040	0.470	0.554	1.546
O(7)	5.221	4.362	8.709	0.107	0.099	0.455

\* In the last cycle for all the atoms the average shift,  $|\Delta B_{ij}|_{av}$ , and the maximum shift,  $|\Delta B_{ij}|_{max}$ , were:

$$|\Delta B_{ij}|_{av} = 0.051$$

$$|\Delta B_{ij}|_{max} = 0.272$$

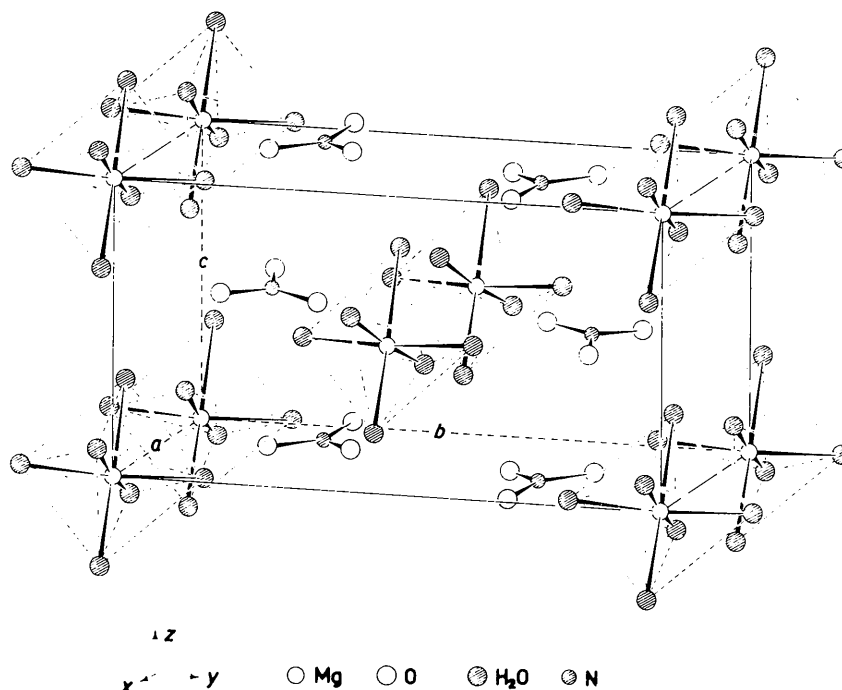


Fig. 1. Clinographic projection of the structure of hexaquomagnesium nitrate.





the coordination around the magnesium cation is substantially octahedral, as was expected for magnesium ion with  $s^2p^6$  configuration.

The average of the distances Mg–OH<sub>2</sub> in the literature is 2.06 Å as compared with (Mg–OH<sub>2</sub>)<sub>av</sub> = 2.058 (4 Å)

in the present compound. The nitrate group (Fig. 3) is not exactly planar (Table 6) and significant departures from trigonal symmetry are observed. The three N–O bond lengths are; 1.20, 1.25, 1.26 Å. This result is in contrast with that obtained for hexaquo zinc nitrate

Table 5. Main interatomic distances and angles (with *e.s.d.*'s)

Asymmetric units			
'	$\bar{x}, \frac{1}{2} + y, \frac{3}{2} - z$		
''	$\bar{1} + x, y, z$		
'''	$1 - x, \frac{1}{2} + y, \frac{3}{2} - z$		
iv	$\bar{1} + x, \frac{1}{2} - y, \frac{1}{2} + z$		
Hexaquomagnesium cation			
Mg–OH <sub>2</sub> (1)	2.053 (5) Å	H <sub>2</sub> O(2)–Mg–OH <sub>2</sub> (3)	91.3 (3)°
Mg–OH <sub>2</sub> (2)	2.063 (6)	H <sub>2</sub> O(1)–Mg–OH <sub>2</sub> (3)	90.7 (3)
Mg–OH <sub>2</sub> (3)	2.061 (7)	H <sub>2</sub> O(1)–Mg–OH <sub>2</sub> (2)	90.4 (3)
Mg–OH <sub>2</sub> <sub>av</sub>	2.058 (4)		
Nitrate anion			
N(4)–O(5)	1.264 (9) Å	O(5)–N(4)–O(6)	121.7 (6)°
N(4)–O(6)	1.196 (12)	O(6)–N(4)–O(7)	120.2 (7)
N(4)–O(7)	1.252 (8)	O(7)–N(4)–O(5)	117.9 (8)
Hydrogen bonds			
H <sub>2</sub> O(1)–O(6)	2.797 (10) Å	O(6)—H <sub>2</sub> O(1)–Mg	126.5 (3)°
H <sub>2</sub> O(1)–O(7'')	2.749 (11)	O(7'')–H <sub>2</sub> O(1)–Mg	107.1 (3)
		O(7'')–H <sub>2</sub> O(1)–O(6)	120.9 (3)
H <sub>2</sub> O(2)–O(7)	2.888 (9)	O(7)—H <sub>2</sub> O(2)–Mg	114.9 (3)
H <sub>2</sub> O(2)–O(5'')	2.905 (9)	O(5'')–H <sub>2</sub> O(2)–Mg	113.6 (3)
		O(5'')–H <sub>2</sub> O(2)–O(7)	131.0 (3)
H <sub>2</sub> O(3)–O(6')	2.765 (9)	O(6')–H <sub>2</sub> O(3)–Mg	118.8 (3)
H <sub>2</sub> O(3)–O(5 <sup>iv</sup> )	2.890 (10)	O(5 <sup>iv</sup> )–H <sub>2</sub> O(3)–Mg	142.5 (3)
		O(5 <sup>iv</sup> )–H <sub>2</sub> O(3)–O(6')	94.9 (3)

Table 6. Analysis of the planarity of the nitrate group

Equation of plane:  $0.14173X' + 0.07964Y' + 0.98669Z' = 4.09505$  with  $Z'$  normal to  $(x, y)$  and  $X = x$ .

Atoms		N(4)	O(5)	O(6)	O(7)
Deviations from plane (Å)	$\left\{ \begin{array}{l} d \\ \sigma_{\perp} \end{array} \right.$	-0.01686	+0.00734	+0.01266	+0.01266
		0.00713	0.00789	0.01125	0.01054

$$\Sigma \left( \frac{d}{\sigma_{\perp}} \right)^2 = 9.17 \quad \chi^2_{95\%} = 3.84$$

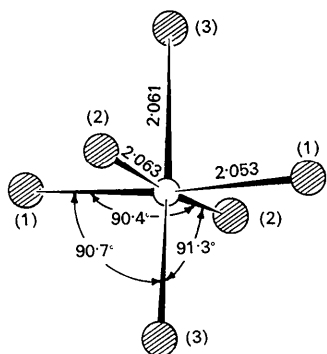


Fig. 2. Hexaquomagnesium cation, [Mg(OH<sub>2</sub>)<sub>6</sub>]<sup>2+</sup>. Bond lengths in Å.

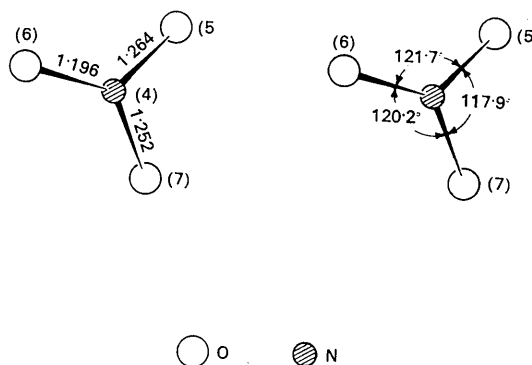


Fig. 3. Nitrate anion, NO<sub>3</sub><sup>-</sup>. Bond lengths in Å.

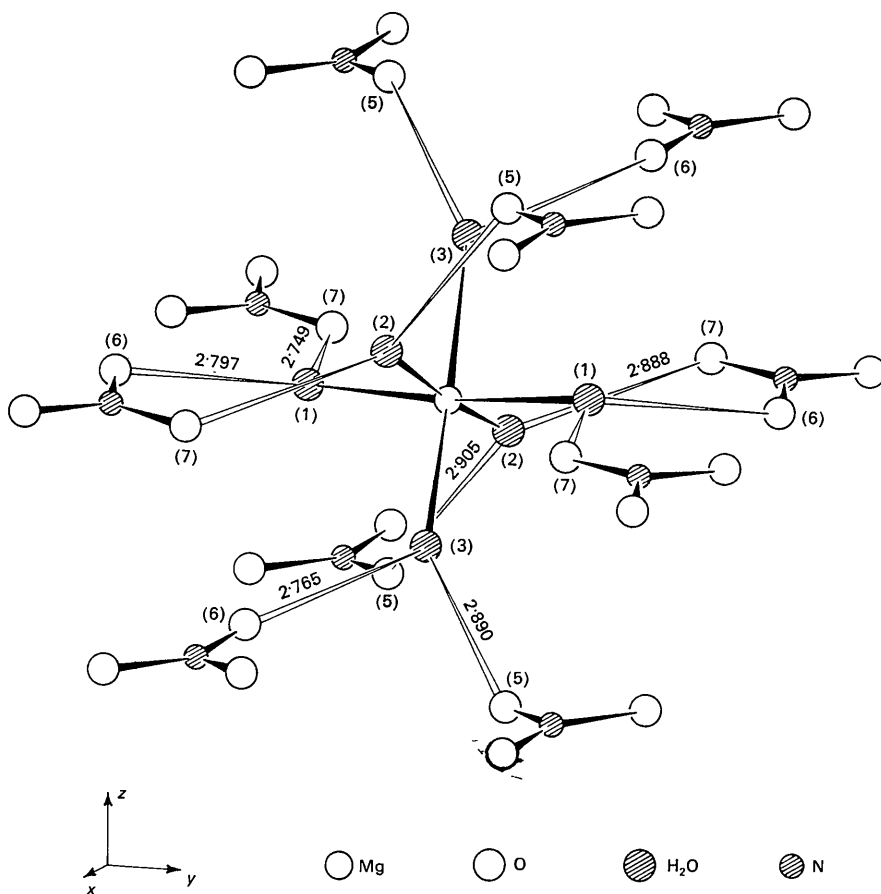


Fig. 4. Hydrogen bonds (Å) radiating from the hexaquomagnesium cation. Hollow cones indicate hydrogen bonds, filled cones other bonds.

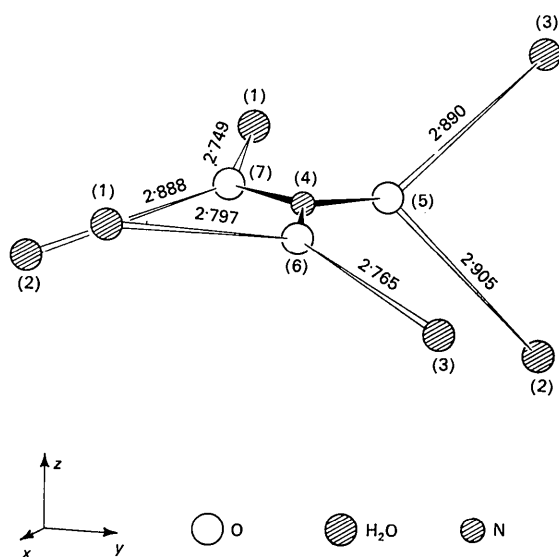


Fig. 5. Hydrogen bonds (Å) pointing towards the oxygen atoms of the nitrate anion. Hollow cones indicate hydrogen bonds, filled cones other bonds.

(Ferrari, Braibanti, Manotti Lanfredi & Tiripicchio, 1967) where the three N-O bonds are practically equal (1.242(9) Å). It is difficult to find an explanation for this different behaviour, if any, of the nitrate group. Neither are the results quoted in the literature all concordant because according to the results of Barclay, Sabine & Taylor (1965) the three non-equivalent N-O bonds are 1.21, 1.26, 1.26 Å, according to Taylor & Mueller (1965) 1.207, 1.271, 1.271 Å and 1.231, 1.260, 1.260 Å and according to Britton & Dunitz (1965) 1.202, 1.272, 1.309 Å, while according to Sass, Vidale & Donohue (1957) and Komiyama & Lingafelter (1964) the three N-O bonds are equivalent with 1.218 and 1.258 Å respectively.

The hexaquocations are bound to the nitrate groups by hydrogen bonds OH-O (Fig. 4). Each water molecule forms two hydrogen bonds. The hydrogen bonds are in the range 2.75-2.90 Å. Each oxygen atom of the nitrate group (Fig. 5) forms two hydrogen bonds with different water molecules.

The differences between the structures of hexaquozinc nitrate, orthorhombic (Ferrari, Braibanti, Ma-

notti Lanfredi & Tiripicchio, 1967), and of hexaquomagnesium nitrate, monoclinic, are related to the different disposition of the nitrate groups with respect to the hexaquocation. Because the radii of the metal cations are practically equal, the actual origin of the different disposition of the nitrate groups can be sought in the hydrogen bonds radiating from the hexaquocations. The hydrogen bonds around magnesium are all very close to one plane containing the Mg-OH<sub>2</sub> bond. This is shown by the sum of the angles

formed by each water molecule with magnesium and with the two oxygen atoms of nitrate groups which are bound, *via* hydrogen bonds, to the water molecule (Table 7). In the zinc compound only two pairs of hydrogen bonds are in the same plane as the zinc-water bond and these correspond to the shortest Zn-OH<sub>2</sub> distances. It seems reasonable to assume that the tetrahedral oxygen atom of the water molecule can be bound to the cations in two ways, either by ion-dipole interaction (*a*) or by coordinative bond (*b*):

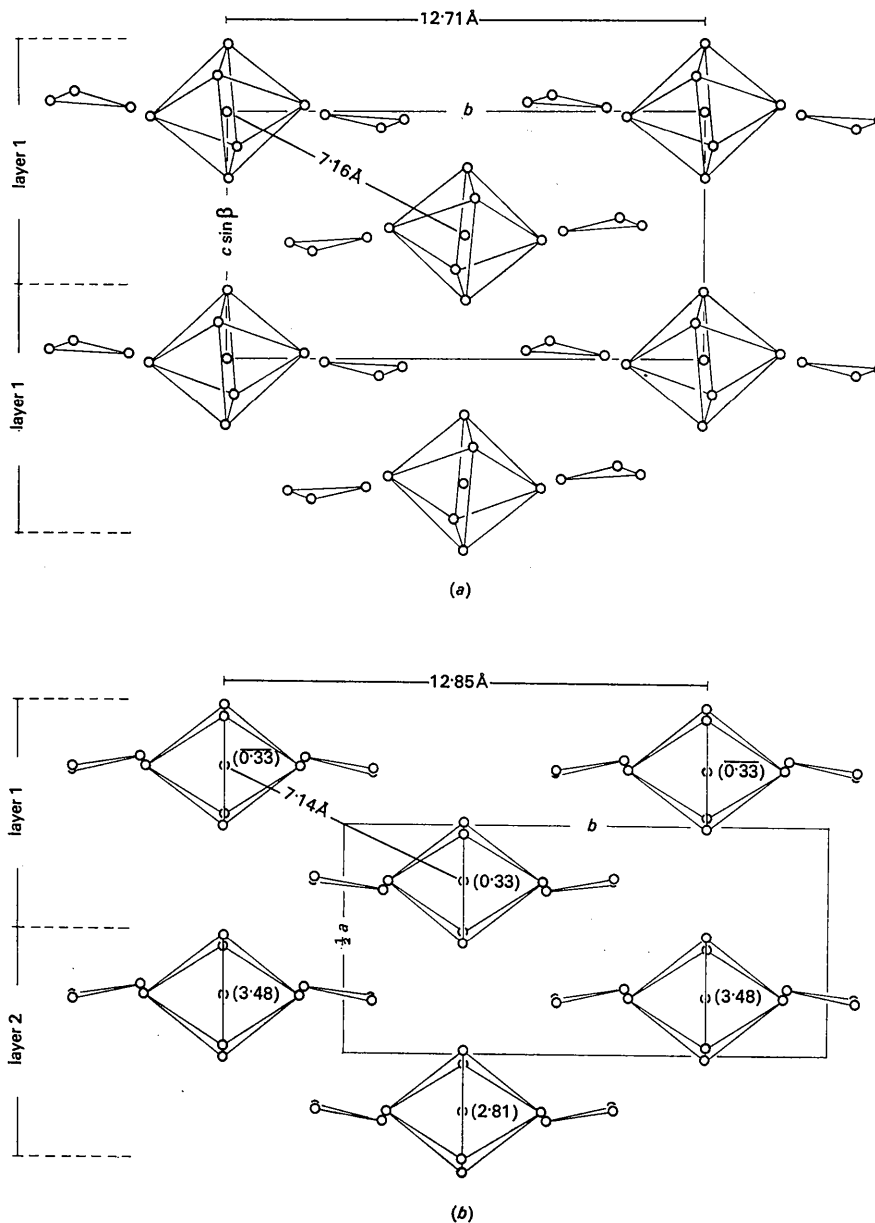
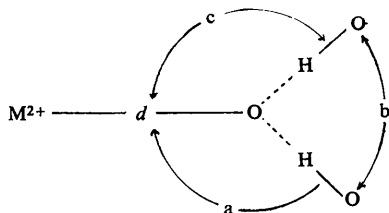


Fig. 6. Layers in the structures of hexaquometal(II) nitrates: (a) (100) projection of hexaquomagnesium nitrate, (b) (001) projection of hexaquozinc nitrate (values in parenthesis are *z* coordinates, in Å, of the zinc atoms).

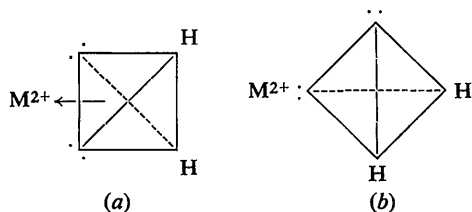
Table 7. *Metal-water bond lengths and angles around each water molecule of the hexaquomagnesium and hexaquozinc cation*



[Mg(OH <sub>2</sub> ) <sub>6</sub> ] <sup>2+</sup>				
a	b	c	Σ	d
126.5°	120.9°	107.1°	354.5°	2.053 Å
114.9	131.0	113.6	359.5	2.063
118.8	94.9	142.5	356.2	2.061
126.5	120.9	107.1	359.2	2.053
114.9	131.0	113.6	359.5	2.063
118.8	94.9	142.5	356.1	2.061

[Zn(OH <sub>2</sub> ) <sub>6</sub> ] <sup>2+</sup>				
a	b	c	Σ	d
111.9	123.4	111.9	347.2	2.104
100.4	98.6	100.4	299.4	2.129
94.0	92.4	94.0	280.4	2.130
112.0	116.2	112.0	340.2	2.083
133.1	93.8	132.9	359.8	2.064
133.1	93.8	132.9	359.8	2.064

$$\Sigma = a + b + c \text{ (degrees)}$$



If this assumption is valid then the cation  $Zn^{2+}$  should present both types of bonding probably, implying  $4s$  and  $4p$  orbitals for the coordinative bonds, while  $Mg^{2+}$  should present only the ion-dipole interactions. As a consequence of this the arrangement of the nitrate groups is determined by the position of the hydrogen atoms.

Apart from these different interactions between cation and water, followed by the arrangement of the nitrate groups, the two structures are very similar. In both lattices layers formed by a zigzag succession of hexaquocations and nitrate groups can be recognized. The distances between cations within the layers are practically equal in the two compounds (Fig. 6). The packing, however, of these layers is slightly different: in the magnesium compound all the layers are equally oriented and shifted  $c$  with respect to one another while in the zinc compound the layer 2, which is the mirror image of layer 1 with respect to (001), is shifted  $\frac{1}{2}a + \frac{1}{2}c$ .

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