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CRYSTAL STRUCTURE OF CERIUM MAGNESIUM NITRATE HYDRATE

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Crystal Structure of Cerium Magnesium Nitrate Hydrate*

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According to single-crystal x-ray diffraction data, crystals of $\text{Ce}_2\text{Mg}_3(\text{NO}_3)_{12}\cdot 24\text{H}_2\text{O}$ are rhombohedral, space group $R\bar{3}$. The hexagonal cell with $a = 11.004 \pm 0.006$, $c = 34.592 \pm 0.012$ Å contains 3 formula units. Atomic parameters were refined by least squares, and interatomic distances were corrected for thermal motion. The average N—O bond distance in nitrate is 1.26 Å. The Ce atoms, on the 3-fold axis at $z = \pm 0.2497$, are each surrounded by 12 oxygen atoms at an average distance of 2.64 Å. These oxygen atoms, belonging to 6 nitrate ions, are at the corners of a somewhat irregular icosahedron. The Mg atoms are of two kinds, located respectively at the origin and on the 3-fold axis at $z = \pm 0.4279$. Each Mg atom is surrounded by 6 water molecules with the

oxygen atoms at the corners of an octahedron with an average Mg—O distance of 2.07 Å. One-fourth of the water molecules are not coordinated to cations.

Evidence for the hydrogen atom positions from the diffraction data indicates that 6 of the 8 independent hydrogen atoms are involved in normal hydrogen bonds.

INTRODUCTION

Cerium magnesium nitrate hydrate is a typical member of the extensive series of double nitrates of generic formula $T_2D_3(NO_3)_{12} \cdot 24H_2O$, where T is a trivalent cation (e. g., Bi or an ion of the 4f group) and D is a divalent cation (e. g., Mg or an ion of the 3d group). Double nitrate crystals have been used extensively in experiments involving magnetic cooling, nuclear alignment, or paramagnetic resonance.¹ Large crystals are easy to grow, and the cations are at sites of favorable symmetry and sufficiently far enough apart for these purposes. Considerable information pertaining to the structure has been obtained from the resonance experiments and by x-ray diffraction, but the complete structure has not been determined previously. Lack of this information has hindered the interpretation of paramagnetic resonance studies.² We investigated this structure because of the wide interest in these substances and because of our interest in hydrogen bonding in salt hydrates.

We have obtained x-ray diffraction data for a single crystal of cerium magnesium nitrate hydrate of sufficient accuracy to locate all of the atoms including hydrogen. These data showed immediately a discrepancy

with previous reports of the symmetry. The other double nitrates are expected to have structures very similar to that reported here for the cerium magnesium salt.

EXPERIMENTAL

An aqueous solution of cerous nitrate and magnesium nitrate in the correct proportions was allowed to evaporate, and single crystals of the double nitrate grew readily in the form of thick hexagonal plates. X-ray photographs obtained with the Weissenberg technique and copper radiation established the diffraction symmetry of the crystal. A single crystal of approximate dimensions $0.09 \times 0.20 \times 0.15$ mm was used for collecting intensity data. Intensities were measured with a General Electric XRD-5 goniostat equipped with a scintillation counter and a pulse-height discriminator; MoK α radiation was used throughout. The unit cell dimensions are based on $\lambda = 0.70926$ Å for MoK α_1 .

The 2381 independent reflections permitted by the space group in the sphere with $\sin\theta/\lambda$ less than 0.705 ($2\theta < 60^\circ$) were measured with counting times of 20 sec each. Of these, 561 were assigned zero intensity. Reflections with odd l are systematically weaker than those of even l , especially at large diffraction angles. Zero intensity was assigned to only one reflection with even l . Among the 478 odd- l reflections for $50^\circ < 2\theta < 60^\circ$, 327 were recorded as zero and 119 as 0.5 counts/sec (the smallest increment recorded by the scaler). None was stronger than 2 counts/sec. In the same angular range, only 2 of the 457 even- l reflections were recorded as 2 counts/sec or less.

Such a large block of zero or nearly-zero intensities was considered undesirable in the least-squares calculations, and we arbitrarily assigned zero weight to the 788 reflections which were measured as less than 2.5 counts/sec and for which 2θ exceeded 40° . Unit weight was assigned to each of the remaining 1593 reflections, including 109 recorded as zero.

No corrections were made for either absorption or extinction, but the crystal was dipped in liquid nitrogen in an endeavor to reduce the latter. With $\mu = 22.7 \text{ cm}^{-1}$ for Mo radiation, μr is 0.23 or less. Thus absorption, though small, is not negligible and is a limiting factor in the accuracy of the intensity data.

Calculations were made with IBM-709 and 7090 computers using a full-matrix least-squares program written by P. K. Gantzell, R. A. Sparks and K. N. Trueblood, with minor changes, and Fourier and distance programs written by Zalkin. We minimized $\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2$.

Atomic scattering factors were taken as the values given by Ibers³ for Mg^{+2} and neutral N, O and H, and the values given by Thomas and Umeda⁴ for Ce^{+3} . Dispersion is unimportant for these atoms with Mo radiation,⁵ and no dispersion correction was made.

UNIT CELL AND SPACE GROUP

The primitive cell containing one formula unit $\text{Ce}_2\text{Mg}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$ is rhombohedral with dimensions:

$$a(r) = 13.165 \pm 0.006 \text{ \AA}, \quad \alpha(r) = 49.37^\circ.$$

The corresponding hexagonal cell containing three formula units has dimensions:

$$a = 11.004 \pm 0.006 \text{ \AA}, \quad c = 34.592 \pm 0.012 \text{ \AA}.$$

These results are compared in Table I with some previous measurements. In the often-quoted but unpublished work of Powell⁶ the weak odd- ℓ reflections were overlooked, and the c dimension was assigned half of its correct value. Except for this error, which was recognized by Culvahouse, Unruh and Sapp⁷ and by Swanson, et al.,⁸ the various results are in reasonable agreement.

From our x-ray data the density is calculated as 2.10 g cm^{-3} . A measurement by a flotation method gave 2.08 g cm^{-3} .

Reflections are absent unless $h-k-\ell = 3n$, showing that the primitive lattice is rhombohedral. No further systematic absences were observed. A careful examination of the Weissenberg photographs and of the data collected with the goniostat confirmed the 3-fold symmetry but showed that there are no vertical mirror planes, in direct contradiction to the result of Culvahouse, Unruh and Sapp.⁷ Thus the Laue group is $\bar{3} (C_{3i})$. These facts leave the choice of space group between the centrosymmetric $R\bar{3} (C_{3i}^2)$ and the noncentric $R3 (C_3^4)$. Crystal morphology⁹ suggests a center of symmetry; while the point group is listed as $\bar{3}m$ ("trigonal skalenoe'drisch") the observed faces are equally consistent with point group $\bar{3}$ because of the absence of general forms. On the other hand, the observed faces would correspond to equal development of four non-equivalent pairs of forms if the point group were 3. The success of our structure determination confirms $\bar{3}$ as the point group and $R\bar{3}$ as the space group.

DETERMINATION OF THE STRUCTURE

A three-dimensional Patterson function was calculated from the observed intensities after correction for Lorentz and polarization effects.

The hexagonal unit cell contains 6 Ce atoms which are identical according to magnetic evidence.¹⁰ The only 6-fold set available is

$$6(c): \pm(0,0,z) + (0,0,0; \frac{1}{3}, \frac{2}{3}, \frac{2}{3}; \frac{2}{3}, \frac{1}{3}, \frac{1}{3}).$$

We selected $z = 0.25$ because any other value is inconsistent with the weak reflections with l odd. There is also a huge Patterson peak at $0,0,\frac{1}{2}$, but it turned out that much of this peak is due to many pairs of light atoms.

Paramagnetic resonance data¹¹ indicate that there are two different types of divalent ions. The 9 Mg atoms must be assigned to a 3-fold set and a 6-fold set. Without loss of generality, the 3-fold set is chosen as

$$\text{Mg}(1) \text{ in } 3(a): (0,0,0) + (0,0,0; \frac{1}{3}, \frac{2}{3}, \frac{2}{3}; \frac{2}{3}, \frac{1}{3}, \frac{1}{3}).$$

The Patterson function contains peaks corresponding to Ce-Mg interactions with Mg(2) in 6(c) with $z = 0.43$ (or 0.07). The choice 0.07 places Mg atoms unreasonably close together and does not fit possible Mg-Mg interactions in the Patterson function. The parameter 0.43 places pairs of Mg atoms nearly equidistant from each other and from neighboring Ce atoms along the 3-fold axis, and is confirmed by the subsequent refinement.

All other atoms are in general positions

$$18(f): \pm(x,y,z; -y,x-y,z; y-x,-x,z) + (0,0,0; \frac{1}{3}, \frac{2}{3}, \frac{2}{3}; \frac{2}{3}, \frac{1}{3}, \frac{1}{3}).$$

The structure requires 2 sets of N atoms, 10 sets of oxygen atoms, and 8 sets of H atoms.

From the Patterson function we chose coordinates for 5 sets of oxygen atoms. The parameters of the 8 sets of atoms so far located were refined by least squares using 617 low-angle reflections. Three

cycles reduced $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ to 0.40. With phases determined by these 8 atoms, an electron density function showed the locations of the 2 sets of N atoms and the remaining 5 sets of O atoms.

With these 15 atoms, 617 reflections and isotropic temperature factors of the form $\exp(-B\lambda^{-2}\sin^2\theta)$ least-squares refinement resulted in $R = 0.086$ after three cycles. Further refinement with all the data (1593 terms selected as described earlier) after 3 cycles gave $R = 0.064$. These 15 atoms were given anisotropic temperature factors of the form $\exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - 2\beta_{12}hk - 2\beta_{13}hl - 2\beta_{23}kl)$. The atoms on the 3-fold axis (*i. e.*, Ce and Mg) had their parameters constrained so that

$$\beta_{11} = \beta_{22} = 2\beta_{12}, \text{ and } \beta_{13} = \beta_{23} = 0.$$

As a result of 3 cycles, R fell to 0.040.

An electron density difference function, with all atoms except H subtracted out, was calculated using the results of the anisotropic refinement. From this difference function, 7 of the 8 hydrogen positions (all in general sets 18(f)) were unambiguously determined. The eighth proved to be more difficult to determine as the difference function was confused in the appropriate region, leaving a choice of two locations. The more likely of these had much too high a peak height, possibly due to an incorrect thermal description of the oxygen atoms, but it was more reasonable on the basis of bond geometry.

Three cycles of least squares refinement were calculated with all 23 atoms, 15 of which had anisotropic temperature factors and the remaining 8 (the H atoms) isotropic temperature factors. With 149 independent parameters and using all the data (weighted as described earlier) the final R was 0.036. The observed and calculated structure factors from

this last refinement are compared in Table II. Coordinates of atoms are listed in Table III, and thermal parameters are given in Tables IV and V. Standard deviations of the parameters of the heavy atoms were calculated assuming that the discrepancies in the structure factors represent random errors and with neglect of the hydrogen parameters. Limitations of our computer programs did not permit us to estimate the standard deviations of the hydrogen parameters by the method of least squares. From the results for O—H bond distances, we estimate that the standard deviations of H coordinates correspond to about 0.2 Å.

DESCRIPTION OF THE STRUCTURE

A section through the structure parallel to c and $[\bar{1}10]$ is shown in Fig. 1. The structure consists of Ce atoms surrounded by nitrate ions, and Mg atoms surrounded by water. One set of water molecules (w_4) is not closely associated with any cation, but participates in the hydrogen bonding which connects the nitrate ions and water.

Much of the structure nearly repeats with a translation of $c/2$. Only the Mg and H atoms diverge substantially from this pattern. The Ce positions conform to this false translation within 0.01 Å. This repetition explains the general weakness of the odd- l reflections.

The symmetry of the Ce environment (the site symmetry) is $3 (C_3)$, but it can be considered to be more symmetrical if for some purpose only some of the neighbors are important. If one considers only Ce neighbors, the site symmetry is $3m (C_{3v})$ and very nearly $\bar{3}m (D_{3d})$. The nearest Ce neighbors are 3 at 8.56 Å and 3 at 8.59 Å. If one considers also the Mg atoms, the site symmetry is still $3m$, but deviates drastically from $\bar{3}m$. The nearest Mg neighbors (Fig. 2) are 1 at 6.17 Å,

3 each at 6.36, 6.98 and 8.31 Å, and 1 at 8.64 Å.

The nearest neighbors of the Ce atom are oxygen atoms of nitrate ions (Fig. 3) arranged at the 12 corners of an irregular icosahedron. Their positions conform closely to inversion symmetry so that the site symmetry is approximately $\bar{3}$ (C_{3i}) if only the nitrate ions are considered. The coordination by nitrate ions was predicted by Bleaney et al.¹² from paramagnetic resonance data, but with a different number and arrangement of neighbors. From spectroscopic data Judd¹³ deduced icosahedral symmetry of these neighbors in qualitative agreement with our result. According to Hellwege and Hellwege¹⁴ spectroscopic data show the symmetry of the crystal field to be C_{3v} . To make the 12 oxygen atoms conform to vertical mirror planes or to make the icosahedron regular requires that they be moved distances of the order of 0.5 Å. This result may indicate a limitation of the precision with which crystal field effects can be used to determine the symmetry of atomic locations.

The 12-fold coordination of Ce, which may seem higher than normal, is permitted by the fact that two oxygen atoms in the same nitrate ion are closer together than when not bonded to each other. The distances of these neighbors from Ce are nearly equal (Table VI) and average 2.63 Å before correction for thermal motion. If a thermal correction is made on the assumption that O "rides on" Ce, the average distance is 2.64 Å. The accuracy of this assumption is dubious, but in any case the thermal correction is not a large effect.

The N—O bond distances are listed in Table VII. In each of the two independent nitrate ions the oxygen not next to Ce is observed at a shorter distance and with larger thermal motion than the others. For these bonds the assumption that O "rides on" N seems plausible. Correction on this

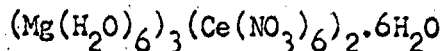
basis brings the bond lengths more nearly together, but leaves a discrepancy which is of doubtful significance. The average distance 1.26 Å is estimated to be accurate within 0.01 Å including uncertainty in the thermal correction. We do not know of any other more accurate determination of this bond distance in nitrate ion.

There are two distinctly different types of Mg atoms in the structure. The atoms Mg(1) at the origin have site symmetry $\bar{3}$ (C_{3i}). If only Ce and Mg neighbors are considered, the site symmetry is $\bar{3}m$ (D_{3d}). The neighbors (Fig. 4) include 6 Ce at 6.98 Å (at the corners of a trigonal antiprism) and 2 Ce at 8.64 Å. The nearest Mg neighbors are 6 Mg(2) at 7.15 Å.

The atoms Mg(2) have site symmetry 3 (C_3). Considering only Ce and Mg neighbors, this symmetry is $3m$ (C_{3v}). The neighbors (Fig. 5) include 1 Ce at 6.17 Å and 3 Ce each at 6.36 and 8.31 Å. The nearest Mg neighbors are 1 Mg(2) at 4.99 Å and 3 Mg(1) at 7.15 Å. This arrangement is rather different from that suggested by Culvahouse *et al.*⁷ on the basis of paramagnetic resonance data.

Each kind of Mg has six water neighbors. The oxygen atoms are at the corners of an octahedron which would be regular if bond angles were changed by less than 1° for Mg(1) and by up to 5° for Mg(2). The Mg—O distances (Table VIII) agree closely. Correction for thermal motion with the assumption that O "rides on" Mg changes them only a small amount. The average corrected distance 2.07 Å agrees closely with the similar distances observed^{15,16} in $Mg(NH_4)_2(SO_4)_2 \cdot 6H_2O$ and $MgSO_4 \cdot 6H_2O$. That the divalent ions are octahedrally hydrated was already established by paramagnetic resonance,¹⁷ and nuclear magnetic resonance experiments¹⁸ showed that water was distant from the cerium sites.

We may formulate this substance as



as a concise indication of the coordination of Mg and Ce and the chemically distinct nature of the fourth set of water molecules.

HYDROGEN BONDING

Hydrogen bonding is extensive in this crystal, but it does not seem to dominate the structure as much as it does in many hydrated salts. Six of the 8 H atoms are involved in normal hydrogen bonds with lengths ranging from 2.78 to 2.98 Å (Table IX). The angles that these bonds make with each other and with the O—Mg vectors are listed in Table X. In each case the angles are appropriate for reasonable orientations of the water molecules with their dipoles away from the Mg atoms.

The accuracy of the hydrogen positions does not justify a detailed listing of the distances and angles to these atoms. The O—H bond distances range from 0.5 to 0.9 Å. The O—H bonds make angles of 8° to 29° with the O—O vectors of the corresponding hydrogen bonds. These results are as good as can be expected if the standard deviations of hydrogen coordinates correspond to 0.2 Å.

For O(W4) no neighbor is at a suitable distance and angle for the second H atom to make a normal hydrogen bond. Two neighbors, O(N22) at 2.98 Å and O(N21) at 3.09 Å, are close enough for weak bonding, but at poor angles. The hydrogen atom H(2W4) is directed within 28° of O(N21) and within 40° of O(N22). This kind of arrangement (Fig. 6) has been called a "bifurcated hydrogen bond". In the present case, the distances suggest that the bonding is weak.

For the second hydrogen of O(W3), the bonding situation is even poorer. The O(W3)-H(2W3) vector is within 29° of another O(W3) at 3.20 Å and within 54° of O(N22) at 3.08 Å. This hydrogen atom was the one most in doubt in the difference function, but its position corresponds to an H—O—H angle of 111° for the water molecule and an H—O—Mg angle of 120° . We conclude that it is not significantly involved in hydrogen bonding.

The hydrogen bonding ties the structure together as follows. Water (W2) is bonded to two oxygen atoms of two different nitrate ions. Water (W3) is bonded through only a single hydrogen bond to the interstitial water (W4). Water (W1) is bonded to a nitrate ion and to water (W4). Water (W4) accepts two hydrogen bonds and makes a third to nitrate. Its "bifurcated bond" involves oxygen atoms of two other nitrate ions. The effect of all these hydrogen bonds is to tie all parts of the structure together.

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Table I. Cell dimensions and axial ratios of Ce-Mg salt.

a, Å	c, Å	c/a	Reference
11.004	34.592	3.144	This work.
10.88	34.44 ^a	3.165 ^a	Powell (Ref. 6).
11.030	34.65	3.141	Swanson <u>et al.</u> (Ref. 8).
--	--	3.0756 ^a	Groth (Ref. 9).

^aValue doubled to conform with correct cell.

Table II. Observed structure factor magnitudes (FOB) and calculated structure factors (FCA). An asterisk (*) marks each reflection which was given zero weight.

(Table to be reproduced photographically in three parts.)

31 0 -17*	12 92 90	22 143-140	18 76 -74	12 87 80	23 0 4*	25 20 3*	7 0 10*	8 64 65	17 0 7*
34 93 -97	15 19 -15*	25 18 -5*	21 34 24*	15 35 -33*	26 59 -57	28 115 114	10 85 -85	11 0 -11*	20 87 81
37 21 21*	18 93 -93	28 118 120	24 102 104	18 70 -69				14 68 -68	
	21 0 18*	31 0 -9*	27 0 -9*	21 37 37*	H,K=11, 1	H,K=12,-6	H,K=13,13	17 0 7*	H,K=14,-5
H,K= 9,-3	24 89 81	34 84 -83	30 90 -90	27 0 -10*	L FOB FCA	L FOB FCA	L FOB FCA	20 61 59	L FOB FCA
L FOB FCA	27 0 3*	37 0 11*		27 0 -10*	1 27 -20*	3 18 9*	2 36 -35	23 0 2*	1 0 -7*
3 21 -23				30 84 -87	4 81 81	6 166-167	5 29 11*		4 69 60
6 193-199	H,K= 9, 4	H,K=10,-5	L FOB FCA	33 0 8*	7 19 13*	9 0 2*	8 78 78	H,K=13,-3	7 0 14*
9 55 55	L FOB FCA	L FOB FCA	2 135-129		10 97-105	12 100 98	11 0 5*	L FOB FCA	10 78 -79
12 224 223	2 118-122	3 0 -1	5 0 16*	H,K=11,-6	13 20 1*	15 0 0*		1 0 -5*	13 0 -0*
15 16 -26	5 19 5*	6 195-194	8 53 49	L FOB FCA	16 103 105	18 138-133	H,K=13,12	4 100 102	16 90 92
18 105-106	8 72 80	9 32 25	11 19 -12*	2 106-105	19 0 3*	21 19 12*	L FOB FCA	7 34 26*	19 0 -3*
21 29 32*	11 0 -0*	12 180 174	14 64 -62	5 17 17*	22 69 -74	24 127 123	1 0 -15*	10 81 -76	
24 78 81	14 56 -56	15 17 -13*	17 0 14*	8 152 155	25 0 10*	27 20 -21*	4 49 50	13 0 -8*	H,K=14,-4
27 0 1*	17 0 9*	18 71 -71	20 106 106	11 0 14*		30 51 -46	7 0 6*	16 99 95	L FOB FCA
30 94-104	20 76 81	21 18 21*	23 0 1*	14 17 -26	H,K=11, 2		10 71 -76	19 0 1*	3 0 2*
33 0 5*	23 0 7*	24 114 113	26 55 -66	17 18 10*	L FOB FCA	H,K=12,-5	13 0 4*	22 70 -74	6 78 -78
36 58 58		27 0 -5*		20 109 106	0 94 101	L FOB FCA	16 47 53		9 0 8*
39 0 -10*	H,K= 9, 5	30 75 -76	H,K=10, 3	23 19 7*	3 0 -5*	2 81 -84		H,K=13,-2	12 105 109
	L FOB FCA	33 29 21*	L FOB FCA	26 101 -94	6 88 -94	5 40 39		L FOB FCA	15 0 -2*
	1 0 5*	36 69 66	1 19 -8*	29 0 -1*	9 0 8*	8 88 88	H,K=13,11	L FOB FCA	3 0 3*
H,K= 9,-2	4 113 113		4 128 130	32 65 71	12 97 99	11 0 8*	3 20 13*	6 79 -81	H,K=14,-3
L FOB FCA	2 99 -97		7 28 25*		15 20 14*	14 94 -89	6 91 -88	9 20 20*	L FOB FCA
2 99 -97	7 0 4*	H,K=10,-4	L FOB FCA	10 48 -49	H,K=11,-5	18 72 -72	17 19 -2*	9 0 3*	12 73 79
5 0 3	10 97 -95	L FOB FCA	13 0 -1*	13 0 -1*	L FOB FCA	21 0 3*	20 120 118	12 67 65	15 0 -14*
8 153 154	13 0 2*	2 125-124	5 10 13	16 95 97	1 0 -13*		23 20 17*	15 0 -1*	18 91 -89
11 16 11	16 59 66	5 10 13	8 150 149	19 0 6*	4 197 196	H,K=11, 3	26 70 -76	18 62 -67	21 0 8*
14 142-138	19 0 6*	8 150 149	11 0 -2*	22 87 -84	7 29 35*	L FOB FCA	29 0 -7*	21 0 17*	11 0 -6*
17 16 16*		11 0 -2*	14 116-119		10 137-132	2 58 -64			14 63 -61
20 150 145	H,K= 9, 6	17 17 19*	H,K=10, 4	13 17 11*	5 0 19*	H,K=12,-4	H,K=13,10	H,K=13,-1	H,K=14,-2
23 0 3*	L FOB FCA	20 68 63	L FOB FCA	16 99 93	8 77 78	L FOB FCA	L FOB FCA	L FOB FCA	L FOB FCA
26 96 -98	0 62 68	23 0 -11*	0 102 122	19 18 -1*	11 0 -3*	1 25 -25*	2 104-113	5 0 -7*	1 21 2*
29 0 16*	3 0 11*	26 79 -78	3 0 8*	22 97-101	14 73 -75	4 91 99	5 19 17*	8 61 58	4 86 89
32 98 98	6 72 -79	29 0 5*	6 61 -67	25 19 8*		7 31 -21*	8 68 73	11 0 -1*	7 0 19*
35 0 2*	9 0 2*	32 75 76	9 0 3*	28 69 63	H,K=12,12	10 37 -37	11 0 1*	14 75 -78	10 56 -53
38 51 -51	H,K=10,10	L FOB FCA	12 77 80	31 0 -4*	L FOB FCA	13 0 9*	14 49 -49	17 0 1*	
	L FOB FCA	2 81 -83	15 0 -10*	34 94 -91	3 0 -3*	16 112 113	17 0 -5*		H,K=15,10
H,K= 9,-1	L FOB FCA	5 17 23*	H,K=10,-3		6 102-104	19 0 -4*	20 75 76	H,K=13, 0	L FOB FCA
L FOB FCA	8 159 161	1 0 6	L FOB FCA	H,K=10, 5	H,K=11,-4	9 28 9*	22 97-101	L FOB FCA	1 0 -4*
1 0 3	5 17 23*	4 104 97	2 73 -75	3 0 1*	L FOB FCA	12 87 85	25 20 6*	1 0 -5*	4 51 60
4 153 155	8 159 161	1 0 6	L FOB FCA	H,K=11,-4	L FOB FCA	15 0 -1*	28 102 110	H,K=13,-9	7 0 21*
7 0 0	11 35 -11*	4 104 97	5 0 -2*	6 134-131	18 58 -48			L FOB FCA	4 69 71
10 118-115	14 72 -68	7 32 30	8 56 58	9 24 19*	21 0 9*	H,K=12,-3	1 0 -1*	10 79 -86	H,K=15,-9
13 0 -4*	17 37 35*	10 154-153		12 167 170		L FOB FCA	4 111 112		L FOB FCA
16 200 199	20 75 76	13 24 -26*		15 18 5*	H,K=12,11	3 0 2*	7 19 15*	H,K=14,12	3 0 -4*
19 38 36	23 19 -3*	16 147 144	H,K=11,11	18 85 -86	L FOB FCA	6 95 -92	10 99 -97	L FOB FCA	6 51 -46
22 167-165	26 119-111	19 30 32*	L FOB FCA	21 26 17*	2 68 -64	9 18 15*	13 20 -17*	2 51 -50	9 0 10*
25 0 -1*	29 0 -6*	22 110-106	1 0 -10*	4 155 157	24 77 74	5 27 27*	12 70 67	16 96 94	5 0 19*
28 117 119	32 67 70	25 0 4*	7 49 42	27 20 -17*	8 92 95	15 0 -8*	19 0 7*	8 56 51	H,K=15,-8
31 0 -4*		28 109 108	10 126-123	30 61 -57	11 19 0*	18 89 -93	22 75 -77		L FOB FCA
34 64 -62	H,K=10,-9	31 0 -16*	13 19 -5*	33 21 19*	14 71 -69	21 20 17*	25 0 12*	H,K=14,11	2 46 -47
37 21 16*	L FOB FCA	34 68 -68	16 84 83		17 0 -3*	24 64 65		L FOB FCA	5 0 6*
	1 0 -9*		19 20 0*	H,K=11,-3	20 61 58	27 0 -8*	H,K=13,-8	1 0 -6*	8 47 54
H,K= 9, 0	4 62 63	H,K=10,-2	22 86 -86	L FOB FCA	23 0 5*		L FOB FCA	4 82 83	11 0 -10*
L FOB FCA	7 24 27*	3 0 2	25 0 6*	2 106 -98		H,K=12,-2	3 0 4*	7 0 10*	
0 136 136	10 196-194	6 88 -79	28 92 88	8 156 156	H,K=12,10	L FOB FCA	6 98 -96	10 51 -55	H,K=15,-7
3 16 21	13 25 -19*	9 29 36*		11 18 9*	L FOB FCA	2 133-134	9 0 15*	13 0 4*	L FOB FCA
6 176-174	16 151 149	12 199 196	H,K=11,10	14 80 -85	4 108 105	5 19 3*	12 102 98		1 0 -2*
9 16 14*	19 18 14*	15 24 -12*	L FOB FCA	17 18 12*	7 19 -1*	8 109 108	15 0 -4*	H,K=14,10	4 75 76
12 105 100	22 118-115	18 165-163	3 0 -5*	20 77 76	10 73 -70	14 51 -51	21 20 14*	3 0 6*	10 70 -76
15 17 -16*	25 0 1*	21 36 35*	6 106-105	23 0 4*	13 19 8*	17 0 10*	24 83 80	6 86 -87	
18 138-130	28 114 117	24 101 99	9 36 27*	26 92 -90	16 118 113	20 60 60		9 0 7*	H,K=15,-6
21 40 37	31 0 -10*	27 27 -17*	12 183 176	15 0 3*	29 0 -5*	23 20 -2*	H,K=13,-7	12 80 79	L FOB FCA
24 147 141*	34 60 -56	30 72 -72	15 0 9*	18 103-102	32 78 81	22 89 -89	L FOB FCA	15 0 -7*	3 0 1*
27 0 -14*		21 0 9*	21 0 9*	24 96 91	H,K=11,-2		2 53 -54		6 100 -99
30 81 -78	H,K=10,-8	27 21 -7*	28 92 88	5 24 23*	L FOB FCA	H,K=12,-9	5 27 28*	H,K=14,-9	9 0 -0*
33 0 15*	L FOB FCA	30 90 -86		8 156 156	1 0 4*	L FOB FCA	8 103 105	L FOB FCA	
36 73 77	3 16 12	2 151-155	H,K=11,-9	11 18 9*	4 152 153	1 0 1*	11 0 2*	2 82 -79	H,K=15,-5
	6 73 -68	5 0 -2*	L FOB FCA	14 80 -85	7 0 2*	3 0 11*	4 111 112	14 101-108	L FOB FCA
H,K= 9, 1	9 33 32*	8 94 97	H,K=11,-9	17 18 12*	10 79 -83	6 91 -88	7 0 10*	17 0 -5*	8 53 55
L FOB FCA	12 220 222	11 17 8*	L FOB FCA	20 77 76	13 0 7*	9 32 27*	12 104 103	20 103 100	11 0 -8*
2 122-125	15 17 -13*	14 108-116	5 17 12*	23 0 4*	16 148 141	15 27 -22*	18 95 -97	23 0 7*	14 77 -72
5 0 8*	18 113-111	17 18 -13*	8 148 146	11 18 12*	22 134-132	21 28 27*	22 55 -52	26 63 -67	17 0 8*
8 115 118	21 44 43	20 116 112	11 18 12*	25 0 -2*	24 70 69	27 0 -15*			
11 0 -2*	24 75 73	23 19 15*	14 112-115	28 84 77	31 0 -0*				
14 17 19	27 27 -20*	26 87 -79	17 19 -3*	20 78 79		H,K=12,-8	H,K=12, 0	4 94 93	4 68 82
17 18 16*	30 109-107	29 0 2*	23 0 3*	26 87 -85	H,K=11,-1	L FOB FCA	L FOB FCA	7 19 11*	7 20 22*
20 135 134	33 0 1*	32 72 78	26 87 -85	29 0 7*	L FOB FCA	0 98 102	0 98 102	10 93 -93	10 92 -86
23 19 22*			30 90 -86		L FOB FCA	2 136-131	3 0 3*	13 0 9*	13 0 -10*
26 101-105	H,K=10,-7	32 72 78			5 0 1*	6 118-112	6 118-112	16 90 85	16 87 90
29 0 4*	L FOB FCA				6 100 -97	8 123 123	9 28 11*	19 20 -8*	19 21 6*
32 72 77	2 81 -82				9 18 16*	11 18 8*	12 96 97	22 117-111	
	5 16 -13				12 140 138	14 81 -81	15 0 -1*	25 0 -4*	H,K=14,-7
H,K= 9, 2	8 124 122				15 26 -16*	17 0 3*	18 75 -73		L FOB FCA
L FOB FCA	11 16 8*				18 97 -96	20 51 57	21 0 10*		3 0 -5*
1 0 6*	14 75 -75				21 39 38*	23 20 -5*			L FOB FCA
4 97 101	17 0 11*				24 85 83	26 65 -61			6 99 -97
7 30 33*	20 87 87				27 21 -22*	29 0 14*			9 20 9*
10 96 -94	23 18 8*				19 37 39*				12 88 87
13 26 -20*	26 106-105				22 133-136				15 0 -3*
16 82 83	29 0 3*				25 0 -14*				18 75 -71
19 19 9*	32 105 103								21 21 14*
22 107-109	35 0 0*								
25 0 7*									
28 89 88	H,K=10,-6								
31 0 -7*	L FOB FCA								
	1 0 -12								
H,K= 9, 3	4 113 107								
L FOB FCA	7 28 25								
0 164 165	10 141-145								
3 0 -15*	13 0 -2*								
6 147-146	16 95 95								
9 26 20*	19 17 16*								

Table III. Atomic coordinates from least-squares refinement. Standard deviations are $\sigma(x) = \sigma(y) = 0.0005$ for O and N, $\sigma(z) = 0.0001$ for Mg(2), O, and N, and $\sigma(z) = 0.00002$ for Ce.

Atom ^a	x	y	z
Ce	0	0	0.24966
Mg(1)	0	0	0
Mg(2)	0	0	0.4279
O(N11)	-0.0563	0.1202	0.3089
O(N12)	0.0441	0.3454	0.3185
O(N13)	0.1088	0.2614	0.2712
O(N21)	0.1256	0.1782	0.1926
O(N22)	0.3500	0.3044	0.1844
O(N23)	0.2650	0.1526	0.2310
O(W1)	0.0128	0.1576	0.0349
O(W2)	0.1607	0.0173	0.3938
O(W3)	0.1567	0.1548	0.4609
O(W4)	0.1669	0.2282	0.1044
N(1)	0.0316	0.2450	0.3002
N(2)	0.2495	0.2136	0.2023
H(1W2)	0.0554	0.1962	0.0524
H(2W1)	-0.0065	0.2062	0.0278
H(1W2)	0.1761	0.0500	0.3813
H(2W2)	0.1649	-0.0535	0.3976
H(1W3)	0.2337	0.1977	0.4550
H(2W3)	0.1418	0.1874	0.4734
H(1W4)	0.2131	0.1871	0.1114
H(2W4)	0.1171	0.2006	0.1237

^aAtom O(N_i_j) is bonded to N(i); H(iW_j) is bonded to O(W_j).

Table IV. Anisotropic thermal parameters (each $\times 10^5$).

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ce	433	(433) ^a	28	(217)	(0)	(0)
Mg(1)	600	(600)	41	(300)	(0)	(0)
Mg(2)	582	(582)	31	(291)	(0)	(0)
O(N11)	582	620	48	136	33	7
O(N12)	1012	672	67	457	20	-85
O(N13)	631	496	51	226	54	5
O(N21)	502	1027	50	337	13	65
O(N22)	725	1104	71	157	37	130
O(N23)	623	889	42	408	27	73
O(W1)	1112	742	54	526	-43	-54
O(W2)	874	712	51	493	42	14
O(W3)	844	824	63	325	-26	-100
O(W4)	1103	1137	61	733	-11	-3
N(1)	474	618	32	290	25	-7
N(2)	426	568	46	168	23	3

^a Parentheses indicate parameters which are subject to constraints.

Table V. Isotropic thermal parameters of hydrogen atoms.

Atom	B, Å ²	Atom	B, Å ²
H(1W1)	3.6	H(1W3)	5.4
H(2W1)	4.0	H(2W3)	0.7
H(1W2)	1.3	H(1W4)	1.8
H(2W2)	1.2	H(2W4)	3.2

Table VI. Ce—O distances.

Atoms	Distance, ^a Å (uncorrected)	Distance, ^b Å (corrected)
Ce—O(N11)	2.675	2.680
Ce—O(N13)	2.612	2.616
Ce—O(N21)	2.636	2.643
Ce—O(N23)	2.616	2.622
Ave.	2.635	2.642

^aStandard deviations are 0.005 Å.

^bCorrected for thermal motion with assumption that O rides on Ce.

Table VII. Bond distances in nitrate ions.

Atoms	Distance, ^a Å (uncorrected)	Distance, ^b Å (corrected)
N(1)—O(N11)	1.259	1.270
N(1)—O(N12)	1.220	1.242
N(1)—O(N13)	1.268	1.272
N(2)—O(N21)	1.262	1.273
N(2)—O(N22)	1.225	1.251
N(2)—O(N23)	<u>1.257</u>	<u>1.268</u>
Ave.	1.248	1.263

^aStandard deviations are 0.008 Å.

^bCorrected for thermal motion with assumption that O rides on N.

Table VIII. Mg—O distances.

Atoms	Distance, ^a Å (uncorrected)	Distance, ^b Å (corrected)
Mg(1)—O(W1)	2.058	2.067
Mg(2)—O(W2)	2.056	2.061
Mg(2)—O(W3)	<u>2.058</u>	<u>2.070</u>
Ave.	2.057	2.066

^aStandard deviations are 0.005 Å.

^bCorrected for thermal motion with assumption that O rides on Mg.

Table IX. Hydrogen-bond distances.

Atoms	O—O distance, ^a Å
O(W1)—H(1W1)—O(W4)	2.82
O(W1)—H(2W1)—O(N12)	2.98
O(W2)—H(1W2)—O(N11)	2.96
O(W2)—H(2W2)—O(N13)	2.78
O(W3)—H(1W3)—O(W4)	2.81
O(W4)—H(1W4)—O(N23)	2.88
Ave.	2.87

^aStandard deviations are less than 0.01 Å.

Table X. Some bond angles.

Atoms	Angle
O(W4)—O(W1)—O(N12)	124°
O(N11)—O(W2)—O(N13)	98°
O(W4)—O(W1)—Mg(1)	121°
O(N12)—O(W1)—Mg(1)	108°
O(N11)—O(W2)—Mg(2)	125°
O(N13)—O(W2)—Mg(2)	112°
O(W4)—O(W3)—Mg(2)	120°
O(N23)—O(W4)—O(W1)	114°
O(N23)—O(W4)—O(W3)	94°

(Figure captions)

Fig. 1. Crystal structure of $\text{Ce}_2\text{Mg}_3(\text{NO}_3)_{12}\cdot 24\text{H}_2\text{O}$. Atoms of Ce and Mg which lie in a section parallel with \underline{c} and $[\bar{1}10]$ are shown, together with the nitrate ions and water molecules near this section. Examples are shown of each kind of hydrogen atom and bond.

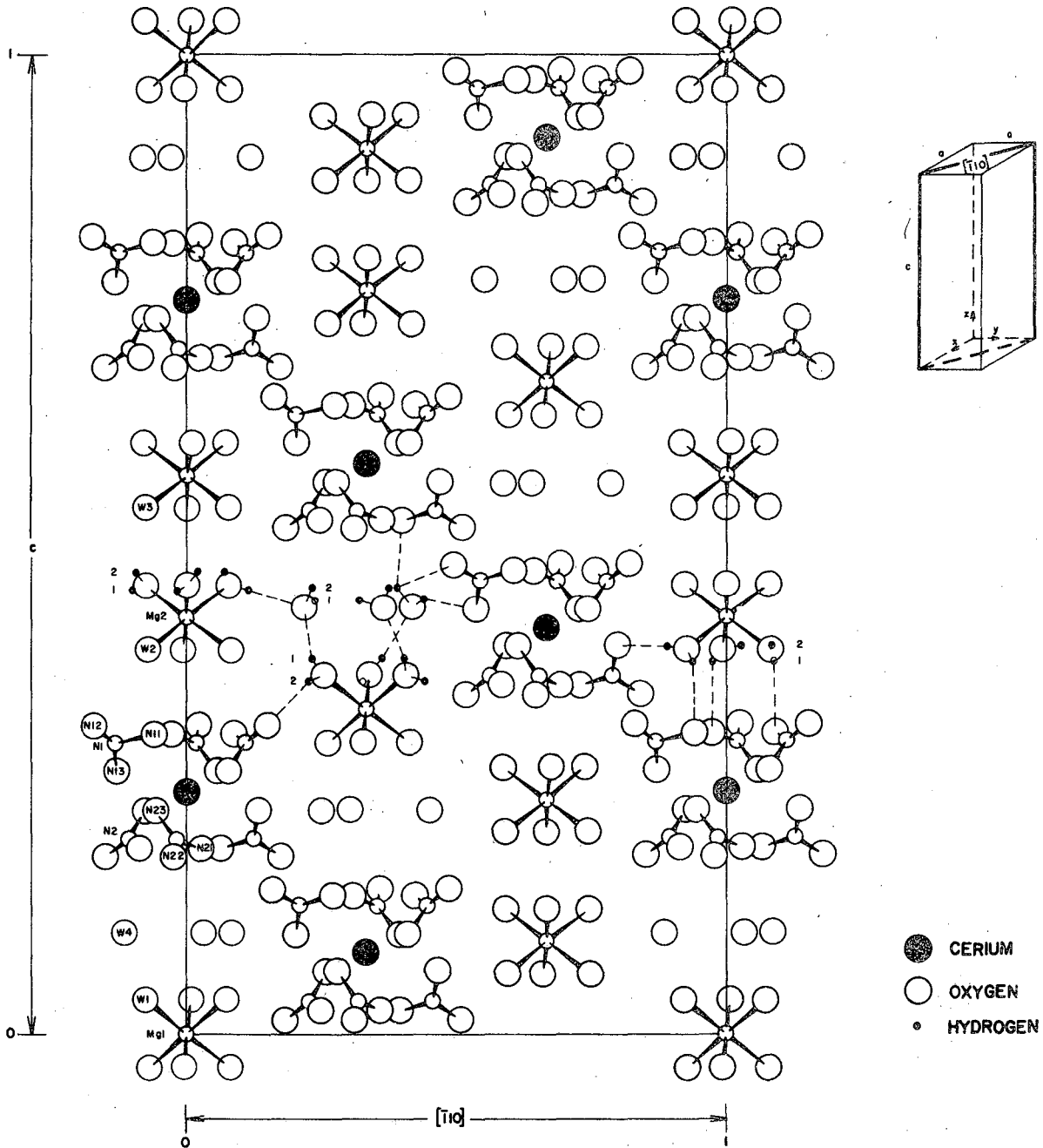
Fig. 2. The magnesium environment of the Ce atom. Distances are in Å.

Fig. 3. The coordination of the Ce atom by nitrate ions, viewed along the 3-fold axis. Alternate nitrate ions are above and below the Ce atom.

Fig. 4. The cerium environment of the Mg(1) atom (at origin). Distances are in Å.

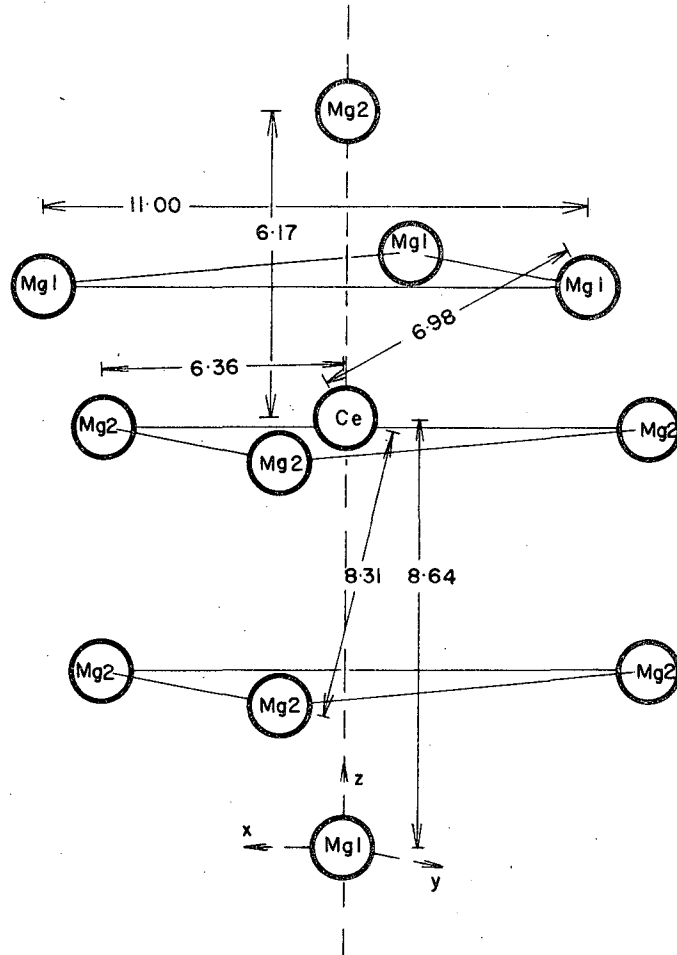
Fig. 5. The cerium environment of a pair of Mg(2) atoms. Distances are in Å.

Fig. 6. Environment of fourth water molecule showing proximity of H(2W4) to two oxygen atoms. Distances (in Å) are those calculated from the coordinates of H atoms found by least squares.



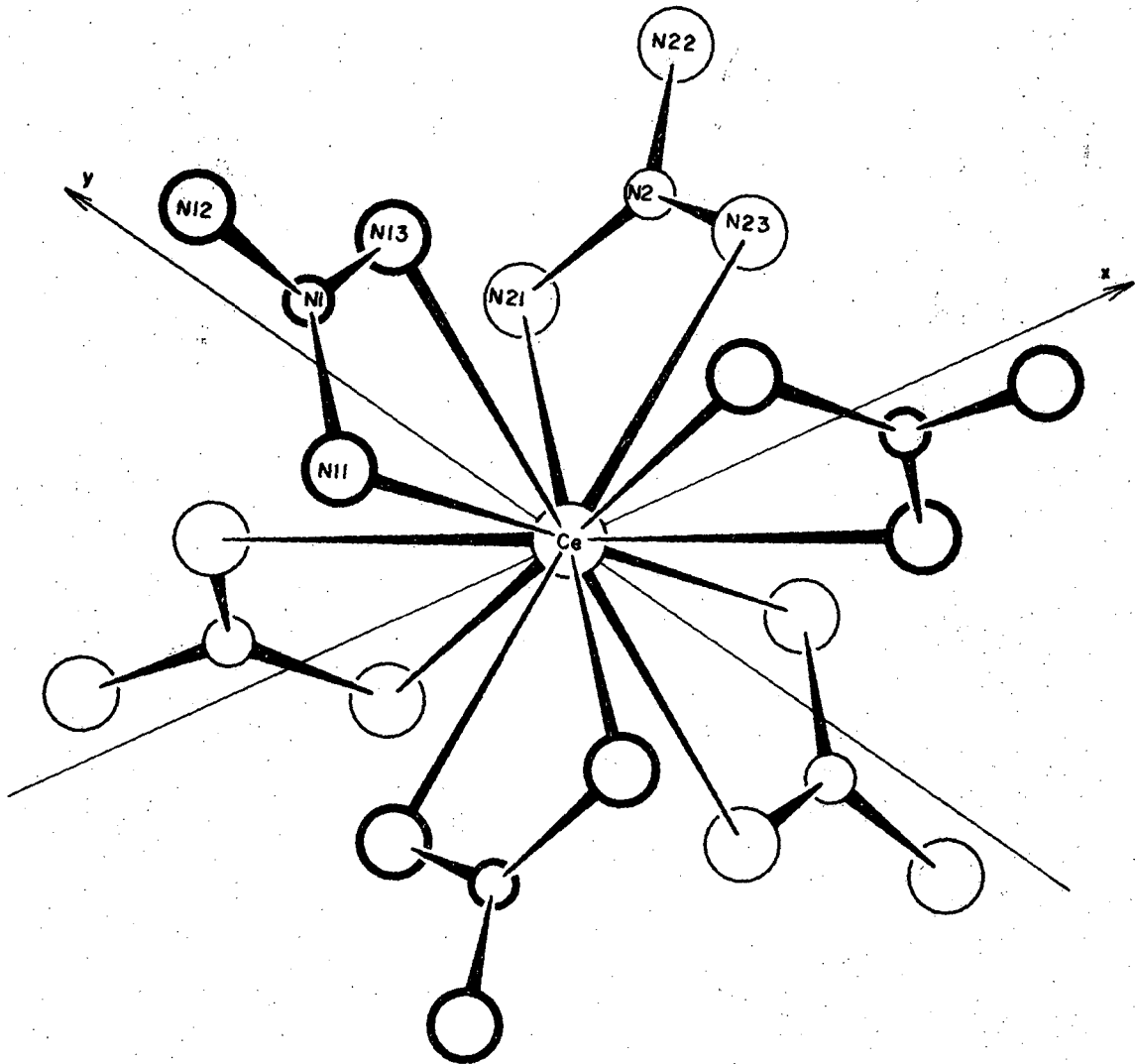
MUB-1437

Fig. 1



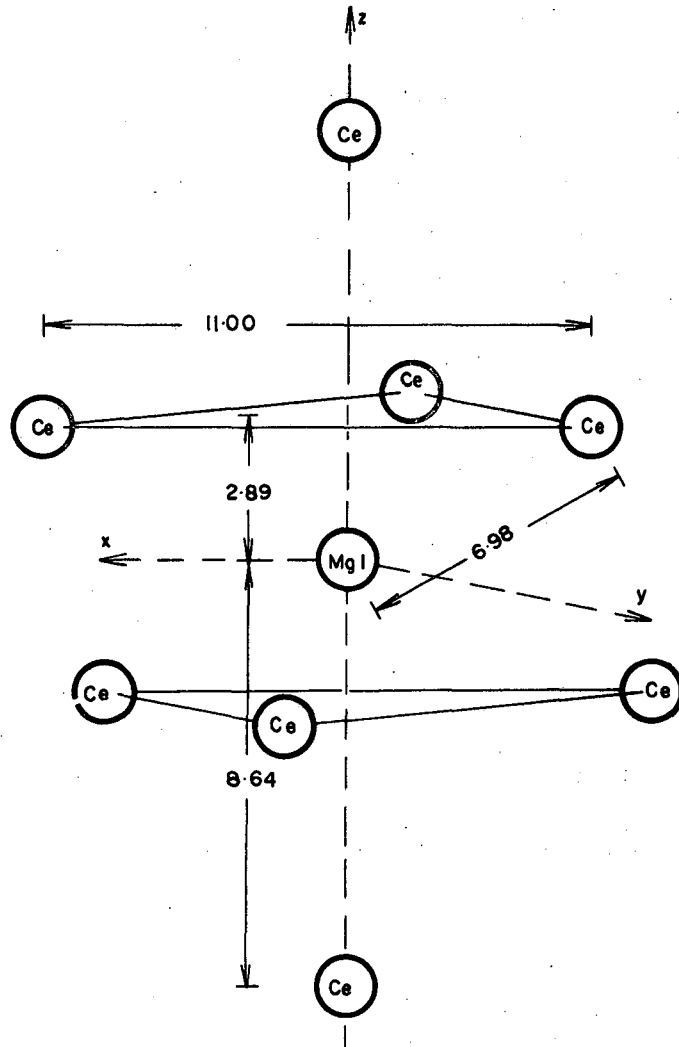
MU-28593

Fig. 2



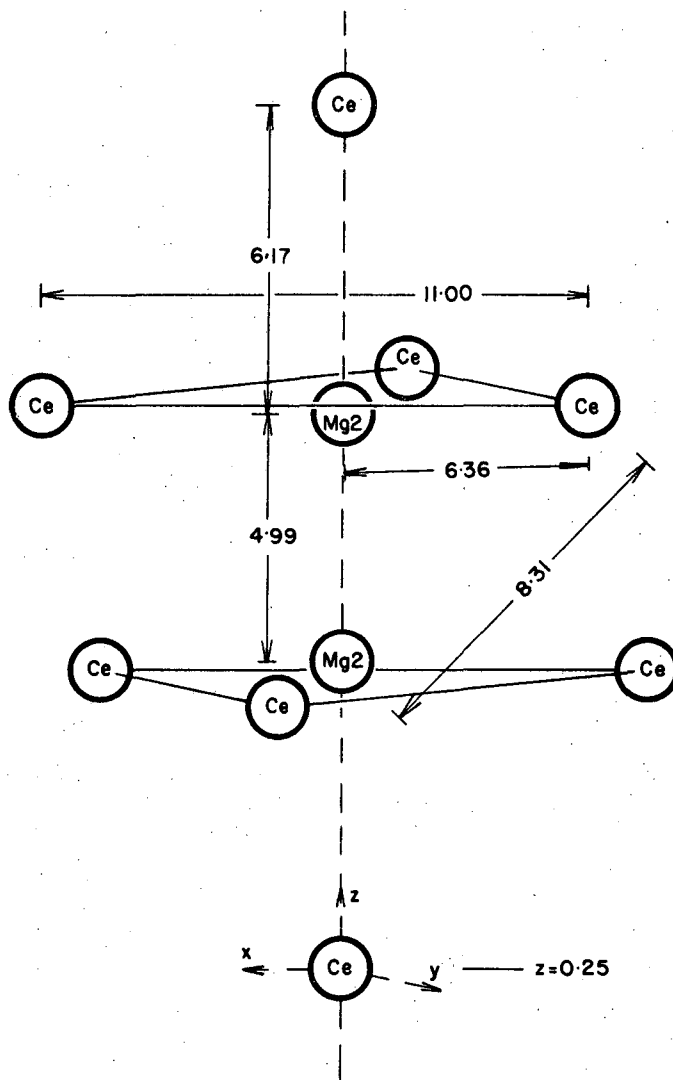
MUB-1436

Fig. 3



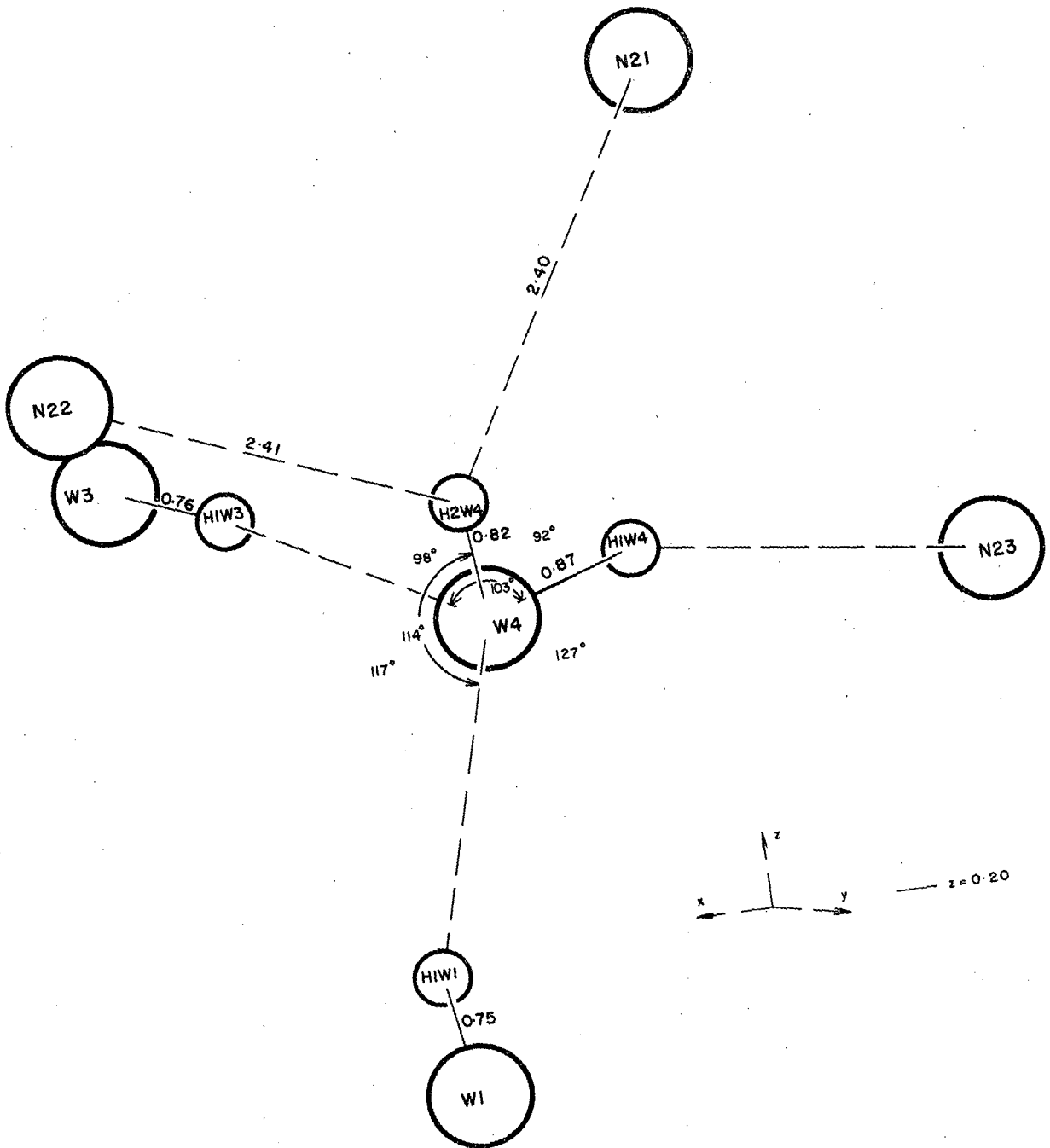
MU-28594

Fig. 4



MU-28595

Fig. 5



MUB-1435

Fig. 6

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