

# The Crystal Structure of Ceric Ammonium Nitrate<sup>1</sup>

By T. A. BEINEKE AND J. DELGAUDIO

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The crystal structure of ceric ammonium nitrate,  $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ , has been determined from three-dimensional single-crystal X-ray diffraction data collected by counter methods. The crystals are monoclinic, space group  $P2_1/n$  with unit cell parameters  $a = 13.061 \pm 0.007$ ,  $b = 6.842 \pm 0.004$ ,  $c = 8.183 \pm 0.004$  Å,  $\beta = 91.34 \pm 0.02^\circ$ ,  $\rho_0 = 2.49$ ,  $\rho_c = 2.490$  g/cm<sup>3</sup> for  $Z = 2$ . Block-diagonal anisotropic least-squares refinement led to a conventional  $R$  of 0.036 for 625 observed reflections. The structure is composed of ammonium cations and hexanitratocerate anions. The hexanitratocerate anions result from the bidentate coordination of six nitrate groups about each cerium atom. The approximate symmetry is  $T_h$ . The average Ce-O distance is  $2.508 \pm 0.007$  Å, the average N-O distance involving a coordinated oxygen is  $1.282 \pm 0.011$  Å, and the average N-O distance involving a noncoordinated oxygen is  $1.235 \pm 0.011$  Å.

## Introduction

Ceric ammonium nitrate has been employed by analytical chemists for years as an oxidation standard. Moreover, it has recently been used as an oxidant in the conversion of various alcohols and toluenes to the corresponding aldehydes.<sup>2-5</sup> In some of these oxidations, nitroaldehydes have been produced in high yields<sup>6</sup> indicating participation of the nitrate groups of the oxidant in the oxidation mechanism. X-Ray diffraction studies of concentrated aqueous solutions of ceric ammonium nitrate indicate a coordination number of 12 for cerium<sup>7</sup> which could only be possible if the ligands are multidentate with a short bite. Since bidentate 12-fold coordination by nitrate groups has been found in the cerium(III) salt,  $\text{Ce}_2\text{Mg}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$ ,<sup>8</sup> it is not unreasonable to expect some kind of nitratocerate complex ions in aqueous solutions of ceric ammonium nitrate. It is, therefore, apparent that a complete understanding of the mechanisms of oxidation by ceric ammonium nitrate depends on knowledge of the structure of the reactant species. To obtain this structural information, a single-crystal X-ray diffraction investigation of ceric ammonium nitrate was undertaken.

## Experimental Section

Crystals of ceric ammonium nitrate,  $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ , as obtained from the G. F. Smith Chemical Co. were small and badly twinned. Larger crystals were obtained by digesting the original material in concentrated nitric acid for several days. These larger crystals were also twinned, but a satisfactory single crystal was obtained by cleaving a twin with a razor blade. The visible satellite crystals were dissolved with a moist paper towel. The resultant single crystal was an almost perfect parallelepiped approximately 0.2 mm along each edge. The only visible forms were  $\{101\}$  and  $\{010\}$ . Because of its deliquescence the crystal

was mounted in a 0.2-mm soft-glass capillary with the  $a^*$  axis approximately collinear with the capillary axis.

Precession pictures made with Mo  $K\alpha$  radiation indicated monoclinic symmetry with systematic extinctions of  $h0l$  reflections for  $h + l$  odd and  $0k0$  reflections for  $k$  odd. The space group is  $P2_1/n$ . The unit cell dimensions at  $22^\circ$  were obtained from a least-squares refinement by means of the program LCR-2<sup>9</sup> of the  $2\theta$  settings of 18 reflections with  $2\theta > 100^\circ$  which had been accurately centered on a General Electric diffractometer using Cr  $K\alpha$  radiation ( $\lambda$  2.29092 Å for  $K\alpha$  and 2.28962 Å for  $K\alpha_1$ ). The unit cell parameters are  $a = 13.061 \pm 0.007$ ,  $b = 6.842 \pm 0.004$ ,  $c = 8.183 \pm 0.004$  Å,  $\beta = 91.34 \pm 0.02^\circ$ ,  $V = 731.1$  Å<sup>3</sup>. The estimated standard deviations include systematic errors in addition to random errors. The systematic errors were estimated by accounting for absorption and the residual error in the  $2\theta = 0$  instrument setting, in the least-squares refinement. The density of the crystals as measured by flotation was 2.49 g/cm<sup>3</sup>; the density calculated with  $Z = 2$  was 2.490 g/cm<sup>3</sup>. Space group  $P2_1/n$  with  $Z = 2$  requires  $\bar{1}$  point symmetry for the cerium positions. The cerium atoms were, therefore, located at 0, 0, 0 and  $1/2, 1/2, 1/2$ , where they contribute only to the reflections for which  $h + k + l = 2n$ . These reflections were, indeed, significantly more intense than the  $h + k + l = 2n + 1$  reflections on the precession and Weissenberg photographs.

A General Electric XRD-5 X-ray unit equipped with a single-crystal orienter and scintillation counter was used with Mo  $K\alpha$  radiation ( $\lambda$  0.7107 Å) in the moving-crystal-moving-counter mode ( $\theta, 2\theta$  coupling) to measure intensities. A 100-sec scan covering  $3.33^\circ$  was used for each reflection. Strong peaks were corrected for nonlinearity of the counting system by assuming a dead time of  $10^{-8}$  sec. Individual backgrounds were measured by the same scanning procedure with  $\omega$  offset by  $1.8^\circ$ . The take-off angle was  $3.0^\circ$  and the diffracted beam aperture was  $2.2^\circ$ . Two standard reflections were monitored throughout the process of intensity measurement as a check for decomposition. Decomposition was negligible. Two crystallographically independent octants of data were measured out to  $2\theta = 40^\circ$  ( $(\sin \theta)/\lambda = 0.481$ ) where the reflections for which  $h + k + l = 2n + 1$  could not be distinguished above the background. Because these reflections result from the scattering of the light atoms only, it was assumed that the intensities of the reflections for which  $h + k + l = 2n$  in this region of reciprocal space and beyond resulted only from cerium scattering. Since the positions of the ceriums had been determined by symmetry, data in the region  $2\theta > 40^\circ$  were considered of little value and were not measured. Reflections were considered observed if, in addition to giving a definite peak on the recorder trace,  $F_o > 2\sigma(F_o)$  (*vide infra*). A total of 690 reflections were recorded of which 625 were considered observed. An unobserved reflection having failed either of the above two tests was given a threshold value for  $F_o$  equiva-

(1) Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

(2) W. S. Trahanovsky and L. B. Young, *J. Chem. Soc.*, 5777 (1965).

(3) W. S. Trahanovsky and L. B. Young, *J. Org. Chem.*, **31**, 2023 (1966).

(4) L. B. Young and W. S. Trahanovsky, *ibid.*, **32**, 2349 (1967).

(5) W. S. Trahanovsky, L. B. Young, and G. L. Brown, *ibid.*, **32**, 3865 (1967).

(6) W. S. Trahanovsky, L. M. Smith, and P. J. Flash, 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967, Abstract S166.

(7) R. D. Larsen and G. H. Brown, *J. Phys. Chem.*, **68**, 3060 (1964).

(8) A. Zalkin, J. D. Forrester, and D. H. Templeton, *J. Chem. Phys.*, **39**, 2881 (1963).

(9) D. E. Williams, "Lcr-2, a Fortran Lattice Constant Refinement Program," Ames Laboratory, Ames, Iowa, USAEC Report No. IS-1052.

lent to  $2\sigma(F_o)$  or  $F_o$ , whichever was larger. Unobserved reflections were included in the least-squares refinement only if  $F_o$  was larger than the threshold  $F_c$ . Only three unobserved reflections had  $F_o > F_c$  and were included in the final cycle of refinement.

A streak correction<sup>10</sup> was applied to 38 reflections which occurred along densely packed radial reciprocal lattice rows. The approximate crystal dimensions and the linear absorption coefficient for Mo  $K\alpha$  radiation,  $\mu = 33.4 \text{ cm}^{-1}$ , were used to compute absorption corrections.<sup>11</sup> The transmission factors,  $A$ 's, which ranged from 0.446 to 0.620, were applied along with the usual Lorentz-polarization corrections to reduce the intensities to structure factors. An attempt was made to account for systematic as well as random errors in the assignment of standard deviations to the intensity data. The formula used was

$$\sigma(I) = \frac{1}{A} [C_T + C_B + C_S + (K_T C_T)^2 + (K_B C_B)^2 + (K_S C_S)^2 + (K_A I)^2]^{1/2}$$

where  $C_T$ ,  $C_B$ ,  $C_S$ ,  $I$ , and  $A$  are, respectively, the total counts, background counts, streak counts, the intensity corrected for Lorentz-polarization and absorption effects, and the transmission factor.  $K_T$ ,  $K_B$ ,  $K_S$ , and  $K_A$  are, respectively, the estimated errors in the total counts, background counts, streak counts, and the transmission factor. Based on experience in this laboratory,  $K_T$  and  $K_B$  were assigned values of 0.02;  $K_S$ , 0.10; and  $K_A$ , 0.03.  $\sigma(F)$  was computed from  $\sigma(I)$  for each reflection by the method of finite differences<sup>10</sup>

$$\sigma(F) = (L_p)^{-1/2} [(I + \sigma(I))^{1/2} - I^{1/2}]$$

### Structure Determination

If the cerium atoms are considered alone, the structure is body centered. A straightforward application of the heavy-atom method would, therefore, lead to a body-centered structure which would obviously be the superposition of the true structure and its image after rotation by  $180^\circ$  about the  $b$  axis. Chemical intuition would probably permit one to extract the true structure from the result; however, the direct method<sup>12-16</sup> appeared to offer an easier solution in this case.

The scattering factors used in this investigation were those of Hanson, *et al.*,<sup>17</sup> for neutral N and also O. The  $\text{Ce}^{4+}$  scattering factor of Thomas and Umeda<sup>18</sup> was used for cerium. The effects of anomalous dispersion are reasonably expected to be minimal in this structure. The only anomalous scatterer is the cerium atom which, because of its location at a center of symmetry, contributes an approximately constant imaginary component of 3.0 electrons to only half of the structure factors. In view of these considerations, as well as the uncertainty in values for  $f'$  and  $f''$ , anomalous dispersion was neglected. The only structural parameters which could be affected are the temperature factors for the Ce atom. Ceric ammonium nitrate is obviously not a structure of equal scatterers as is presumed

by Sayer's equation,<sup>12</sup> but this difficulty is easily avoided by subtracting the contribution due to the cerium atoms from each reflection for which  $h + k + l = 2n$  under the assumption that the signs of these reflections are all plus. In order to subtract the cerium contribution, however, the scale factor, which can be determined by Wilson's method,<sup>19</sup> must be accurately known. Wilson's method also depends on the assumption of a random structure of equal scatterers, but this is altogether reasonable for the  $h + k + l = 2n + 1$  reflections to which the cerium atoms do not contribute. The data were, therefore, divided into two sets according to the parity of  $h + k + l$ . The light-atom reflections ( $h + k + l = 2n + 1$ ) were scaled in the usual way and yielded a scale factor of 0.2904 and an isotropic temperature factor of 3.44. For the cerium reflections ( $h + k + l = 2n$ ), the contribution of the cerium to each reflection is  $2f_{\text{Ce}}$ . Consequently,  $4f_{\text{Ce}}^2$  was added to  $\Sigma_i f_i^2$  for the light atoms in the scaling of the cerium reflections. The scale factor for these reflections was 0.3553; the isotropic temperature factor, 1.37. The scale factors agree rather well, and the geometric mean, 0.321, was used along with the isotropic temperature factor, 1.37, due mainly to the cerium, to subtract the scattering power of the ceriums from all of the cerium reflections. The scale factor as determined in the final least-squares cycle was 0.3292; the final isotropic temperature factor for cerium was 1.82.

The data were then recombined, rescaled, and reduced to a set of normalized unitary structure factors,  $E$ 's.<sup>20</sup> The distribution of the  $E$ 's is given in Table I.

TABLE I  
DISTRIBUTION OF NORMALIZED UNITARY STRUCTURE FACTORS

	Theoret	Obsd	%		
			Theoret	Obsd	
$\langle E^2 \rangle$	1.000	0.944	$ E  > 3$	0.3	0.3
$\langle  E^2 - 1  \rangle$	0.968	0.884	$ E  > 2$	5.0	2.6
$\langle  E  \rangle$	0.798	0.797	$ E  > 1$	32.0	31.0

The 78  $E$ 's which were greater than 1.5 were arranged in the usual Sayer relationships. Thirty-five of these  $E$ 's (those for which  $h + k + l = 2n$ ) had signs determined in the subtraction of the cerium scattering. Ordinarily in monoclinic crystals three signs can be assigned arbitrarily to reflections of three independent parity groups to determine the origin of the unit cell.<sup>16</sup> Two of these degrees of freedom, however, were used in the selection of 0, 0, 0 and  $1/2, 1/2, 1/2$  as cerium positions from among the four equivalent sets of special positions in space group  $P2_1/n$ . The one remaining degree of freedom represents the selection of either 0, 0, 0 or  $1/2, 1/2, 1/2$  as the origin. Thus, one of the reflections, for which  $h + k + l = 2n + 1$ , 450, was given a plus sign. The signs of 20 light-atom reflections were obtained by checking for consistency in the Sayer rela-

(19) A. J. C. Wilson, *Nature*, **150**, 152 (1942).

(20) This and subsequent calculations, unless otherwise noted, were performed on an IBM 360 Model 50 computer with the crystallographic programs written by F. R. Ahmed, S. R. Hall, M. E. Pippy, and C. P. Saunderson of the National Research Council, Ottawa, Ontario, Canada.

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(18) L. H. Thomas and K. Umeda, *J. Chem. Phys.*, **26**, 293 (1957).

TABLE II  
 FINAL PARAMETERS AND STANDARD DEVIATIONS (IN PARENTHESES)<sup>a</sup>

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>b</i> <sub>11</sub>	<i>b</i> <sub>22</sub>	<i>b</i> <sub>33</sub>	<i>b</i> <sub>12</sub>	<i>b</i> <sub>13</sub>	<i>b</i> <sub>23</sub>
Ce(1)	5000	5000	5000	26 (1)	107 (2)	66 (2)	2 (2)	-13 (2)	3 (2)
N(2)	6776 (6)	2408 (13)	4620 (11)	35 (6)	126 (21)	144 (19)	-25 (20)	-59 (16)	-43 (33)
O(3)	6153 (5)	2239 (10)	5781 (8)	32 (5)	172 (20)	114 (15)	29 (16)	13 (13)	39 (26)
O(4)	6647 (5)	3928 (10)	3719 (8)	40 (5)	147 (19)	105 (14)	22 (17)	10 (14)	44 (26)
O(5)	7454 (5)	1241 (11)	4344 (10)	39 (5)	148 (21)	236 (19)	78 (17)	4 (16)	-94 (31)
N(6)	3884 (6)	2267 (12)	2834 (10)	46 (6)	153 (23)	75 (16)	-2 (20)	18 (16)	87 (32)
O(7)	4836 (5)	2110 (9)	3131 (8)	26 (5)	128 (18)	130 (14)	0 (15)	-24 (13)	-51 (26)
O(8)	3462 (5)	3754 (10)	3496 (8)	32 (5)	170 (20)	121 (14)	19 (16)	-19 (13)	-34 (27)
O(9)	3385 (5)	1134 (11)	2007 (9)	58 (6)	157 (21)	127 (15)	-93 (18)	-67 (15)	-43 (28)
N(10)	4465 (6)	2507 (13)	7804 (11)	30 (6)	160 (23)	156 (20)	25 (20)	18 (17)	-22 (35)
O(11)	4093 (5)	2238 (10)	6371 (8)	50 (5)	147 (19)	84 (13)	-16 (16)	-43 (13)	1 (25)
O(12)	4983 (5)	4097 (11)	7964 (8)	51 (6)	186 (20)	81 (14)	-29 (18)	-40 (14)	40 (28)
O(13)	4364 (6)	1431 (10)	8946 (9)	75 (7)	154 (20)	123 (15)	27 (19)	40 (16)	200 (28)
N(14)	1614 (6)	2639 (14)	5288 (11)	45 (7)	155 (23)	148 (19)	8 (21)	-3 (18)	47 (34)

<sup>a</sup> All values have been multiplied by 10<sup>4</sup>. The temperature factors have the form:  $\exp[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)]$ .

tionships. The sign of one cerium reflection appeared inconsistent and was removed from the data set. There remained 55 *E*'s for which signs had been determined. These reflections were used to compute an *E* map in which 12 of the 13 light atoms were visible. The coordinates of these 12 light atoms (all but O(12)) were used as starting parameters along with the ceriums for two isotropic block-diagonal least-squares cycles, one utilizing only low-angle data; the second, all data. An electron density map was then computed which clearly showed the remaining oxygen.

The structure was refined by block-diagonal least-squares techniques with the NRC least-squares program which minimized the function  $\sum w(|F_o| - |F_c|)^2$ . For each isotropic atom one 4 × 4 block containing positional parameters and the isotropic temperature factor was used. Two blocks were used for each anisotropic atom. The first was a 3 × 3 block of positional parameters; the second, a 6 × 6 block of anisotropic temperature factors. The weighting scheme was  $\sqrt{w} = \sigma(F)^{-1}$ . Unobserved reflections were weighted exactly the same as observed reflections if  $F_o \geq F_c$ . They were, however, given weights of zero if  $F_o < F_c$ . With all atoms given isotropic temperature factors the refinement led to a conventional *R* factor,  $R_1 = \sum(|F_o| - |F_c|)/\sum|F_o|$ , of 0.049 and a weighted *R* factor,  $R_2 = (\sum w(|F_o| - |F_c|)^2/\sum w F_o^2)^{1/2}$ , of 0.064. When the ceriums were given anisotropic temperature factors and all other atoms remained isotropic, *R*<sub>1</sub> was reduced to 0.044; *R*<sub>2</sub>, to 0.061. With all atoms anisotropic, *R*<sub>1</sub> = 0.036 and *R*<sub>2</sub> = 0.050. The average shift was 0.07σ; the maximum shift was 0.3σ in the final cycle. The average standard deviation of an observation of unit weight was 2.68 which indicates a slight underestimation of errors. Using Hamilton's<sup>21</sup> significance test, both the hypothesis that all atoms are isotropic as well as the hypothesis that all but the ceriums are isotropic can be rejected at the 0.005 level. The final positional and thermal parameters along with their estimated standard deviations are listed in Table II. Experience in this laboratory indicates

that the block-diagonal approximation leads to standard deviations which are consistently underestimated by a factor of 0.8. Consequently the standard deviations listed in Table II as well as all estimated errors derived from them should be multiplied by 1.2 to correspond with values derived from the more conventional full-matrix least-squares techniques. The structure factors computed from these parameters are compared with the observed values in Table III. A comparison of the observed and calculated *F*'s for the more intense reflections indicated the absence of extinction effects. Consequently, no extinction correction was made. Two reflections, 202 and -426, showed large discrepancies between calculated and observed *F*'s. These reflections were remeasured and yielded the same results. Reflection 202 was obviously absent on the precession photographs. It was therefore concluded that the peak recorded on the diffractometer resulted from a multiple reflection, and it was given a weight of zero in the least-squares refinement. Reflection -426 was listed as unobserved because  $F_o < 2\sigma(F)$ , whereas a well-defined peak appeared on the recorder trace. This error presumably resulted from an anomalously high background measurement possibly including the white streak from another reflection. This reflection was also given a weight of zero.

A difference Fourier map was computed at the conclusion of the refinement in an attempt to locate the hydrogens. The largest peaks, both positive and negative, occurred in the vicinity of the cerium position and ranged from -0.4 to 1.1 e/Å<sup>3</sup>. Elsewhere, the noise level was about 0.2 e/Å<sup>3</sup>. There was an area of positive density 0.2 e/Å<sup>3</sup> around N(14), but chemically reasonable hydrogen positions could not be assigned.

## Results

Ceric ammonium nitrate is composed of ammonium cations and hexanitratocerate anions in which the nitrate groups are apparently tightly held by the cerium atoms. The symmetry of the hexanitratocerate ion closely approximates T<sub>h</sub> with a  $\bar{3}$  axis parallel to the

(21) W. C. Hamilton, *Acta Cryst.*, **18**, 502 (1965).

TABLE III  
OBSERVED AND CALCULATED STRUCTURE FACTORS<sup>a</sup>

0 K 0	1 594 553	6 -37* -15	9 K 1	4 166 182	4 317 114	2 796 852	1 8 K 3	3 623 688	-8 K 5	3 544 547	4 117 119
2 452 -401	2 -144* 1	0 594 598	5 709 705	5 451 454	3 228 -174	3 491 491	1 933 704	5 181 -184	1 491 478	4 -75* -19	0 472 471
4 657 -672	3 484 498	-1 K 1	1 -105* -99	6 45 -44	8 K 2	4 451 465	2 144 -158	2 76 -46	5 489 499	3 318 -34	5 K 5
6 152 117	12 K 0	0 1508 1466	2 522 528	3 286 -290	-2 K 2	0 450 452	4 -71* -2	0 K 4	0 599 586	0 599 533	1 284 277
1 K 0	0 798 749	2 678 661	4 514 513	0 461 398	1 214 -212	1 127 1317	9 K 3	0 399 399	-7 K 4	1 48 -55	2 721 721
1 1104 -1035	1 -174* -174	3 219 207	1 174* 174	1 1170 1080	2 750 721	2 1149 1215	2 225 -225	3 246 246	2 635 -622	4 464 458	3 -15* 9
2 99 -44	4 801 814	10 K 1	2 587 999	3 86 102	2 402 419	3 383 356	4 -69* -6	0 522 523	2 611 650	1 -44* -10	3 118 107
3 1207 1238	1 102 -124	3 159 146	3 583 464	4 510 532	3 374 355	4 581 588	2 733 746	4 842 859	3 149 -149	4 290 280	3 K 6
4 -230* -84	1 396 392	6 424 399	2 84 93	5 229 228	2 645 667	5 481 492	3 203 197	5 174 -183	3 149 -149	1 546 543	2 178 178
5 221 212	-11 K 1	0 K 1	1 422 474	2 9* -4	1 98 -41	6 131 -121	10 K 3	1 K 4	-4 K 5	1 565 455	3 497 494
6 95* 9	0 803 772	1 1214 1149	0 428 416	-1 K 2	3 478 482	0 109 108	1 698 703	1 523 522	2 -38* -8	3 568 568	4 K 6
0 316 0	1 -75* 20	2 126 -98	0 428 416	2 121 104	4 56 -40	0 139 -126	2 145 96	3 528 537	4 -45* -13	7 K 5	0 395 393
1 210 350	2 190 180	3 819 827	1 -138* 62	2 943 549	2 121 -961	2 1149 1215	3 290 283	4 186 -152	5 557 553	1 626 631	2 617 614
2 695 654	3 189 -204	4 399 -31	3 -36* 8	4 188 186	0 288 265	3 58 25	5 917 505	6 442 488	7 40 -44	1 205 -202	2 110 116
3 182 164	-10 K 1	0 K 1	1 12 K 1	5 569 567	1 167 -150	4 581 588	0 351 311	0 552 488	-5 K 5	1 706 162	3 537 528
4 848 828	1 454 458	2 123 -124	3 12 K 1	6 442 438	0 721 612	5 86 83	1 145 -149	2 K 4	0 886 689	3 148 -150	4 848 848
5 118 141	0 6 87 -74	1 1473 1314	2 325 315	3 175 -162	1 144 140	4 202 202	0 455 415	1 170 -181	3 49 52	2 88 85	3 537 528
6 45* 441	3 611 621	4 395 395	-12 K 2	5 -70* -8	-11 K 2	6 553 550	-10 K 4	2 504 497	4 557 553	5 442 453	6 618 667
0 K 0	-9 K 1	1 1149 1124	0 865 840	1 324 314	2 90* -15	3 785 810	-9 K 3	4 145 -149	5 46 -39	6 442 453	7 99 97
1 995 983	0 1022 973	2 325 315	3 175 -162	1 144 140	1 519 525	1 615 617	0 3 K 3	1 170 -181	3 49 52	4 281 266	5 684 667
2 462 -464	1 63 -31	3 819 827	4 399 -31	5 -70* -8	-11 K 2	6 553 550	0 3 K 3	2 504 497	4 557 553	5 442 453	6 618 667
3 854 887	2 259 271	5 389 391	3 369 391	4 404 398	2 88 83	4 807 793	-9 K 4	5 46 -39	6 442 453	7 99 97	8 485 475
4 135 136	3 200 -202	6 404 398	2 88 83	3 369 391	4 404 398	5 442 453	0 1012 991	1 54 45	2 281 266	3 684 667	4 848 848
5 588 561	4 592 589	0 K 1	1 1149 1124	2 325 315	3 175 -162	4 202 202	3 333 318	4 145 -149	5 46 -39	6 442 453	7 99 97
6 -95* 31	-9 K 1	1 1149 1124	0 865 840	1 324 314	2 90* -15	3 785 810	-9 K 3	4 145 -149	5 46 -39	6 442 453	7 99 97
0 K 0	1 345 363	2 -35* 65	3 156 -155	4 156 -155	1 754 727	1 126 113	1 K 3	0 593 552	1 130 127	2 1011 1030	3 374 374
1 568 486	2 187 -187	3 734 737	4 331 -331	5 377 376	6 404 398	7 404 398	0 3 K 3	1 130 127	2 1011 1030	3 374 374	4 464 458
2 954 866	3 69 -42	4 464 458	5 464 458	6 464 458	7 464 458	8 464 458	1 K 3	2 1011 1030	3 374 374	4 464 458	5 464 458
3 1239 1257	4 -53* 8	5 491 477	3 -39* -29	4 814 839	5 814 839	6 814 839	-10 K 3	3 374 374	4 464 458	5 464 458	6 464 458
4 439 -438	5 462 463	6 404 398	7 464 458	8 464 458	9 464 458	10 464 458	0 3 K 3	4 464 458	5 464 458	6 464 458	7 464 458
5 221 224	-7 K 1	0 865 840	1 324 314	2 90* -15	3 785 810	4 145 -149	-9 K 4	5 46 -39	6 442 453	7 99 97	8 485 475
6 947 527	1 986 1036	2 334 336	3 435 437	4 435 437	5 435 437	6 435 437	0 3 K 3	1 145 -149	2 281 266	3 684 667	4 848 848
0 K 0	2 705 745	3 819 827	4 399 -31	5 -70* -8	-11 K 2	6 553 550	0 3 K 3	1 145 -149	2 281 266	3 684 667	4 848 848
1 1088 1126	3 454 476	4 300 295	5 -43* 30	6 542 510	7 474 474	8 474 474	0 3 K 3	2 281 266	3 684 667	4 848 848	5 464 458
2 9 K 4	3 69 -42	4 300 295	5 -43* 30	6 542 510	7 474 474	8 474 474	0 3 K 3	2 281 266	3 684 667	4 848 848	5 464 458
3 473 500	4 300 295	5 -43* 30	6 542 510	7 474 474	8 474 474	9 474 474	0 3 K 3	2 281 266	3 684 667	4 848 848	5 464 458
4 246 227	5 510 477	6 135 -122	7 135 -122	8 135 -122	9 135 -122	10 135 -122	0 3 K 3	2 281 266	3 684 667	4 848 848	5 464 458
5 510 477	6 135 -122	7 135 -122	8 135 -122	9 135 -122	10 135 -122	11 135 -122	0 3 K 3	2 281 266	3 684 667	4 848 848	5 464 458
6 135 -122	7 135 -122	8 135 -122	9 135 -122	10 135 -122	11 135 -122	12 135 -122	0 3 K 3	2 281 266	3 684 667	4 848 848	5 464 458
0 K 0	1 358 383	2 452 448	3 435 437	4 435 437	5 435 437	6 435 437	0 3 K 3	1 145 -149	2 281 266	3 684 667	4 848 848
1 1385 1281	4 -45* 41	5 398 393	6 -72* -95	7 333 363	8 333 363	9 333 363	0 3 K 3	1 145 -149	2 281 266	3 684 667	4 848 848
2 216 212	3 454 476	4 -45* 41	5 398 393	6 -72* -95	7 333 363	8 333 363	0 3 K 3	1 145 -149	2 281 266	3 684 667	4 848 848
3 795 828	4 -45* 41	5 398 393	6 -72* -95	7 333 363	8 333 363	9 333 363	0 3 K 3	1 145 -149	2 281 266	3 684 667	4 848 848
4 222 -176	-5 K 1	1 1422 1360	2 752 790	3 296 -296	4 384 382	5 118 113	6 518 518	0 3 K 3	1 145 -149	2 281 266	3 684 667
5 435 448	0 224 211	1 472 461	2 752 790	3 296 -296	4 384 382	5 118 113	6 518 518	0 3 K 3	1 145 -149	2 281 266	3 684 667
6 -73* 16	1 672 672	2 1000 1000	3 73 476	4 207 213	5 -6 K 2	6 4 K 2	7 1015 1027	8 2 96 -115	9 3 593 611	10 2 500 500	11 3 246 246
0 K 0	1 358 383	2 452 448	3 435 437	4 435 437	5 435 437	6 435 437	0 3 K 3	1 145 -149	2 281 266	3 684 667	4 848 848
1 1385 1281	4 -45* 41	5 398 393	6 -72* -95	7 333 363	8 333 363	9 333 363	0 3 K 3	1 145 -149	2 281 266	3 684 667	4 848 848
2 216 212	3 454 476	4 -45* 41	5 398 393	6 -72* -95	7 333 363	8 333 363	0 3 K 3	1 145 -149	2 281 266	3 684 667	4 848 848
3 795 828	4 -45* 41	5 398 393	6 -72* -95	7 333 363	8 333 363	9 333 363	0 3 K 3	1 145 -149	2 281 266	3 684 667	4 848 848
4 222 -176	-5 K 1	1 1422 1360	2 752 790	3 296 -296	4 384 382	5 118 113	6 518 518	0 3 K 3	1 145 -149	2 281 266	3 684 667
5 435 448	0 224 211	1 472 461	2 752 790	3 296 -296	4 384 382	5 118 113	6 518 518	0 3 K 3	1 145 -149	2 281 266	3 684 667
6 -73* 16	1 672 672	2 1000 1000	3 73 476	4 207 213	5 -6 K 2	6 4 K 2	7 1015 1027	8 2 96 -115	9 3 593 611	10 2 500 500	11 3 246 246
0 K 0	1 358 383	2 452 448	3 435 437	4 435 437	5 435 437	6 435 437	0 3 K 3	1 145 -149	2 281 266	3 684 667	4 848 848
1 1385 1281	4 -45* 41	5 398 393	6 -72* -95	7 333 363	8 333 363	9 333 363	0 3 K 3	1 145 -149	2 281 266	3 684 667	4 848 848
2 216 212	3 454 476	4 -45* 41	5 398 393	6 -72* -95	7 333 363	8 333 363	0 3 K 3	1 145 -149	2 281 266	3 684 667	4 848 848
3 795 828	4 -45* 41	5 398 393	6 -72* -95	7 333 363	8 333 363	9 333 363	0 3 K 3	1 145 -149	2 281 266	3 684 667	4 848 848
4 222 -176	-5 K 1	1 1422 1360	2 752 790	3 296 -296	4 384 382	5 118 113	6 518 518	0 3 K 3	1 145 -149	2 281 266	3 684 667
5 435 448	0 224 211	1 472 461	2 752 790	3 296 -296	4 384 382	5 118 113	6 518 518	0 3 K 3	1 145 -149	2 281 266	3 684 667
6 -73* 16	1 672 672	2 1000 1000	3 73 476	4 207 213	5 -6 K 2	6 4 K 2	7 1015 1027	8 2 96 -115	9 3 593 611	10 2 500 500	11 3 246 246
0 K 0	1 358 383	2 452 448	3 435 437	4 435 437	5 435 437	6 435 437	0 3 K 3	1 145 -149	2 281 266	3 684 667	4 848 848
1 1385 1281	4 -45* 41	5 398 393	6 -72* -95	7 333 363	8 333 363	9 333 363	0 3 K 3	1 145 -149	2 281 266	3 684 667	4 848 848
2 216 212	3 454 476	4 -45* 41	5 398 393	6 -72* -95	7 333 363	8 333 363	0 3 K 3	1 145 -149	2 281 266	3 684 667	4 848 848
3 795 828	4 -45* 41	5 398 393	6 -72* -95	7 333 363	8 333 363	9 333 363	0 3 K 3	1 145 -149	2 281 266	3 684 667	4 848 848
4 222 -176	-5 K 1	1 1422 1360	2 752 790	3 296 -296	4 384 382	5 118 113	6 518 518	0 3 K 3	1 145 -149	2 281 266	3 684 667
5 435 448	0 224 211	1 472 461	2 752 790	3 296 -296	4 384 382	5 118 113	6 518 518	0 3 K 3	1 145 -149	2 281 266	3 684 667
6 -73* 16	1 672 672	2 1000 1000	3 73 476	4 207 213	5 -6 K 2	6 4 K 2	7 1015 1027	8 2 96 -115	9 3 593 611	10 2 500 500	11 3 246 246
0 K 0	1 358 383	2 452 448	3 435 437	4 435 437	5 435 437	6 435 437	0 3 K				

TABLE IV  
 BOND DISTANCES (Å) IN CERIC AMMONIUM NITRATE<sup>a</sup>

Bond	Uncor	Cor <sup>b</sup>	Bond	Uncor	Cor <sup>b</sup>
	for therm vib	for therm vib		for therm vib	for therm vib
Ce(1)-O(3)	2.490	2.497	N(2)-O(3)	1.271	1.280
Ce(1)-O(4)	2.524	2.530	N(2)-O(4)	1.284	1.287
Ce(1)-O(7)	2.506	2.510	N(2)-O(5)	1.218	1.243
Ce(1)-O(8)	2.482	2.488	N(6)-O(7)	1.266	1.272
Ce(1)-O(11)	2.509	2.514	N(6)-O(8)	1.283	1.289
Ce(1)-O(12)	2.504	2.512	N(6)-O(9)	1.210	1.235
			N(10)-O(11)	1.272	1.280
			N(10)-O(12)	1.286	1.286
			N(10)-O(13)	1.199	1.225

Av 2.503 ± 2.508 ±  
0.015° 0.014

<sup>a</sup> Standard deviations are ±0.007 Å for Ce-O bonds and ±0.011 Å for N-O bonds. <sup>b</sup> Ce-O distances, correction made on basis that oxygen atoms ride on cerium; N-O distances, oxygens assumed to ride on nitrogens. <sup>c</sup> Error is the root-mean-square deviation for equivalent distances, *i.e.*,  $\sqrt{\Sigma(x - \bar{x})^2/(n - 1)}$ .

 TABLE V  
 BOND ANGLES (DEG) IN CERIC AMMONIUM NITRATE<sup>a</sup>

O(3)-Ce(1)-O(4)	50.9	O(4)45504-N(14)-O(5)65602 <sup>c</sup>	65.4
O(7)-Ce(1)-O(8)	50.9	O(4)45504-N(14)-O(8)55501	124.2
O(11)-Ce(1)-O(12)	50.6	O(4)45504-N(14)-O(9)55503	149.0
O(3)-Ce(1)-O(7)	66.5	O(4)45504-N(14)-O(12)45404	115.9
O(3)-Ce(1)-O(8) <sup>b</sup>	69.9	O(4)45504-N(14)-O(13)55603	96.4
O(3)-Ce(1)-O(11)	66.6	O(5)65602-N(14)-O(8)55501	86.7
O(3)-Ce(1)-O(12)	65.4	O(5)65602-N(14)-O(9)55503	140.3
O(4)-Ce(1)-O(7)	65.1	O(5)65602-N(14)-O(12)45404	89.6
O(4)-Ce(1)-O(8')	67.5	O(5)65602-N(14)-O(13)55603	161.8
O(4)-Ce(1)-O(11')	67.5	O(8)55501-N(14)-O(9)55503	58.5
O(4)-Ce(1)-O(12')	69.0	O(8)55501-N(14)-O(12)45404	110.9
O(7)-Ce(1)-O(11)	69.2	O(8)55501-N(14)-O(13)55603	103.9
O(7)-Ce(1)-O(12')	66.8	O(9)55503-N(14)-O(12)45404	86.1
O(8)-Ce(1)-O(11)	65.0	O(9)55503-N(14)-O(13)55603	56.6
O(8)-Ce(1)-O(12')	68.3	O(12)45404-N(14)-O(13)55603	100.0
O(3)-N(2)-O(4)	115.2		
O(3)-N(2)-O(5)	124.1		
O(4)-N(2)-O(5)	120.7		
O(7)-N(6)-O(8)	114.6		
O(7)-N(6)-O(9)	124.5		
O(8)-N(6)-O(9)	120.9		
O(11)-N(10)-O(12)	113.9		
O(11)-N(10)-O(13)	125.6		
O(12)-N(10)-O(13)	120.5		

<sup>a</sup> The standard deviations are 0.2° for O-Ce-O angles and 0.6° for O-N-O angles. <sup>b</sup> The primes indicate atoms inverted through the center of symmetry at the cerium position. <sup>c</sup> These are the angles about the ammonium ion which represent possible hydrogen bonds. Each atom number except the vertex atom is followed by the atom designator code which defines the symmetry operation which relates the atom to the original coordinates. See text for description of atom designator code.

vibration along with the root-mean-square displacements are tabulated in Table VI.

If the symmetry of the anion were exactly  $T_h$ , the nitrate groups would define three mutually perpendicular planes. The least-squares planes for the nitrate groups are given in Table VII. These planes were calculated with each atom given unit weight. Since the distances of the atoms from these planes are all about an order of magnitude smaller than their standard deviations, the nitrate groups are definitely planar. As can be seen from the equations, the sense of the normals to these planes is such that each normal has a positive component along the crystallographic *b* axis. The angles between these planes are: plane 1-plane 2, 94.75°; plane 1-plane 3, 96.39°; plane 2-

 TABLE VI  
 RMS AMPLITUDES AND PRINCIPAL AXES OF THE  
 THERMAL ELLIPSOIDS (ALL VALUES × 10<sup>3</sup>)

Atom	Rms displacement, Å	Row vectors (direction cosines) <sup>a</sup>		
		<i>l</i>	<i>m</i>	<i>n</i>
Ce(1)	135	711	-83	699
	159	121	993	-5
	162	693	-88	-715
N(2)	127	723	504	473
	185	474	-859	191
	244	-503	-87	860
O(3)	158	931	-364	-34
	186	-177	-531	829
	218	320	765	559
O(4)	167	391	-756	525
	183	793	-13	-610
	209	468	655	594
O(5)	124	685	-715	-140
	222	-718	-630	-294
	290	122	302	-946
N(6)	129	-171	-529	831
	199	927	-373	-47
	212	334	762	554
O(7)	142	901	247	356
	168	346	-904	-250
	221	-260	-348	901
O(8)	159	933	-170	318
	189	-75	771	633
	220	-352	-614	706
O(9)	112	-596	-627	-501
	216	-73	664	-744
	268	-799	407	442
N(10)	151	-916	372	152
	200	-390	-914	-113
	232	-97	163	-982
O(11)	146	499	122	858
	185	-108	-973	202
	226	860	-194	-473
O(12)	147	-423	99	-901
	196	-561	-809	174
	237	712	-579	-398
O(13)	103	51	731	-681
	234	-751	477	456
	278	658	488	573
N(14)	182	367	851	-375
	199	-925	-376	52
	231	96	-366	-926

<sup>a</sup> The direction cosines *l*, *m*, and *n* are referred to an ortho-normal coordinate system the axes of which are parallel to the crystallographic *a*, *b*, and *c*\* axes, respectively.

plane 3, 96.19°. The central cerium atom deviates by -0.3259, -0.1301, and -0.3679 Å from planes 1, 2, and 3, respectively.

### Discussion

The averages of chemically equivalent bond distances, corrected for thermal vibration, are compared in Table VIII with the distances found in the solution study of ceric ammonium nitrate<sup>7</sup> and the single-crystal investigations of  $Ce_2Mg_3(NO_3)_{12} \cdot 24H_2O$ <sup>8</sup> and cerium(IV) acetylacetonate.<sup>25</sup> It is immediately apparent that the Ce-O distances are 0.13 Å shorter in ceric ammonium nitrate than in  $Ce_2Mg_3(NO_3)_{12} \cdot 24H_2O$  but 0.11 Å longer than in the eight-coordinated cerium(IV) acetylacetonate. That the Ce-O distances are shorter

TABLE VII  
 LEAST-SQUARES PLANES FOR NITRATE GROUPS

Plane	Atom	Distance from plane, Å <sup>a</sup>	Eq of planes <sup>b</sup>
1	N(2)	0.0007	0.61225X + 0.51413Y + 0.60066Z - 8.4813 = 0
	O(3)	-0.0002	
	O(4)	-0.0002	
	O(5)	-0.0003	
2	N(6)	0.0014	0.20507X + 0.54469Y - 0.81317Z + 0.0131 = 0
	O(7)	-0.0005	
	O(8)	-0.0004	
	O(9)	-0.0005	
3	N(10)	-0.0011	-0.83612X + 0.48875Y + 0.24903Z + 2.3217 = 0
	O(11)	0.0003	
	O(12)	0.0003	
	O(13)	0.0004	

<sup>a</sup> The standard deviations of distances from the plane are 0.008 Å for nitrogens and 0.007 Å for oxygens. <sup>b</sup> These equations refer to an orthonormal coordinate system defined by vectors parallel to the crystallographic axes *a*, *b*, and *c*\*. The parameters *X*, *Y*, and *Z* are in Ångström units.

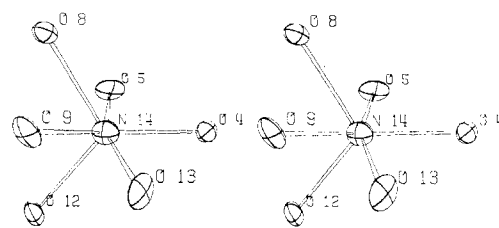


Figure 2.—Locations of possible hydrogen bonds about N(14). The atom designator codes have been left out of this drawing since the atom numbers uniquely define the atoms. The corresponding atom designator codes are listed in Table IX.

number *SN*. For the identity operation, *SN* = 1; for inversion through the center of symmetry at 0, 0, 0, *SN* = 2; for rotation and translation by the 2<sub>1</sub> screw at *x* = 1/4, *z* = 1/4, *SN* = 3; and for reflection and translation by the *n*-glide plane at *y* = 1/4, *SN* = 4. Atoms in neighboring unit cells are designated by crystal lattice translation digits, *TA*, *TB*, and *TC*. The origin is designated by zeros for all three digits.

 TABLE VIII  
 AVERAGE BOND DISTANCES (Å)

Bond	Ceric ammonium nitrate			Cerium(IV) acetylacetonate <sup>c</sup>	Sum of Slater radii <sup>d</sup>
	This work	Soln study <sup>a</sup>	Ce <sub>2</sub> Mg <sub>3</sub> (NO <sub>3</sub> ) <sub>12</sub> ·24H <sub>2</sub> O <sup>b</sup>		
Ce-O	2.508 ± 0.007	2.85	2.642 ± 0.005	2.40 ± 0.03	2.45
All N-O's	1.267 ± 0.011	1.35	1.263 ± 0.008		1.25
N-O(coordinated) <sup>e</sup>	1.282 ± 0.011		1.271 ± 0.008		
N-O(lone) <sup>f</sup>	1.235 ± 0.011		1.246 ± 0.008		

<sup>a</sup> R. D. Larsen and G. H. Brown, *J. Phys. Chem.*, **68**, 3060 (1964). <sup>b</sup> A. Zalkin, J. D. Forrester, and D. H. Templeton, *J. Chem. Phys.*, **39**, 2881 (1963). <sup>c</sup> B. Matkovic and D. Grdenic, *Acta Cryst.*, **16**, 456 (1962). <sup>d</sup> J. C. Slater, *J. Chem. Phys.*, **41**, 3199 (1964). <sup>e</sup> Coordinated O refers to those oxygens which are bonded to the cerium atom. <sup>f</sup> Lone O is the remaining uncoordinated oxygen.

in the cerium(IV) compounds with respect to the cerium(III) compounds is expected since the electronic configuration of cerium(IV) is that of the noble gas xenon while cerium(III) has one additional electron. The difference between the two cerium(IV) compounds probably results from increased steric interactions in the 12-coordinated compound when compared with the 8-coordinated compound. The larger Ce-O distances found in the solution study are impossible to assess since very few details and no standard deviations were given in that report.<sup>7</sup>

Even with correction for thermal vibration, the N-O distances to the noncoordinated oxygen atoms are significantly shorter than to the coordinated oxygens as shown in Table VIII. Since the inequality of N-O distances has been observed in Ce<sub>2</sub>Mg<sub>3</sub>(NO<sub>3</sub>)<sub>12</sub>·24H<sub>2</sub>O<sup>8</sup> and in several other structures<sup>26,27</sup> as well, there is little doubt that it is a real effect. This is probably a lengthening of the N-O bonds to the coordinating oxygens due to the reduction of bond order which accompanies donation of electron density from these bonds to the Ce-O bonds.

In discussing hydrogen bonding and interionic nonbonded distances the convention of Johnson<sup>22</sup> is used. Each symmetry operation is assigned a symmetry

 TABLE IX  
 HYDROGEN-BOND DISTANCES AND ALL  
 NONBONDED INTERIONIC DISTANCES LESS THAN 3.5 Å

Possible hydrogen-bond distances about N(14) <sup>a</sup>		Nonbonded interionic distances less than 3.500 Å <sup>a</sup>	
N(14)-O(5)65602	2.933	N(2)-O(9)55504	3.005
N(14)-O(8)55501	2.953	N(2)-O(11)65602	3.465
N(14)-O(13)55603	2.965	O(3)-O(9)65602	2.985
N(14)-O(4)45504	3.004	O(3)-O(9)55504	3.256
N(14)-O(9)55503	3.040	O(3)-N(6)65602	3.285
N(14)-O(12)45404	3.062	O(3)-O(7)65602	3.372
		O(4)-O(5)65503	3.209
		O(4)-N(14)66602	3.354
		O(4)-O(9)55504	3.479
		O(5)-O(13)55404	2.984
		O(5)-O(9)55504	3.054
		O(5)-N(10)55404	3.061
		O(5)-O(11)65602	3.168
		O(5)-O(11)55404	3.439
		N(6)-O(13)55401	3.307
		O(7)-O(13)65602	3.152
		O(7)-O(11)65602	3.309
		O(7)-N(14)55404	3.330
		O(7)-N(10)65602	3.381
		O(7)-O(13)55401	3.497
		O(8)-O(9)55503	2.931
		O(9)-O(13)55401	2.846
		N(10)-N(14)55504	3.428
		O(11)-N(14)55501	3.348
		O(13)-O(13)65702	3.072
		O(13)-N(14)55504	3.178

(26) T. Ueki, A. Zalkin, and D. H. Templeton, *Acta Cryst.*, **20**, 836 (1966).  
 (27) J. C. Taylor, M. H. Mueller, and R. L. Hitterman, *ibid.*, **20**, 842 (1966).

<sup>a</sup> The first atom listed for each distance has *ADC* = 55501. See text for description of *ADC*.

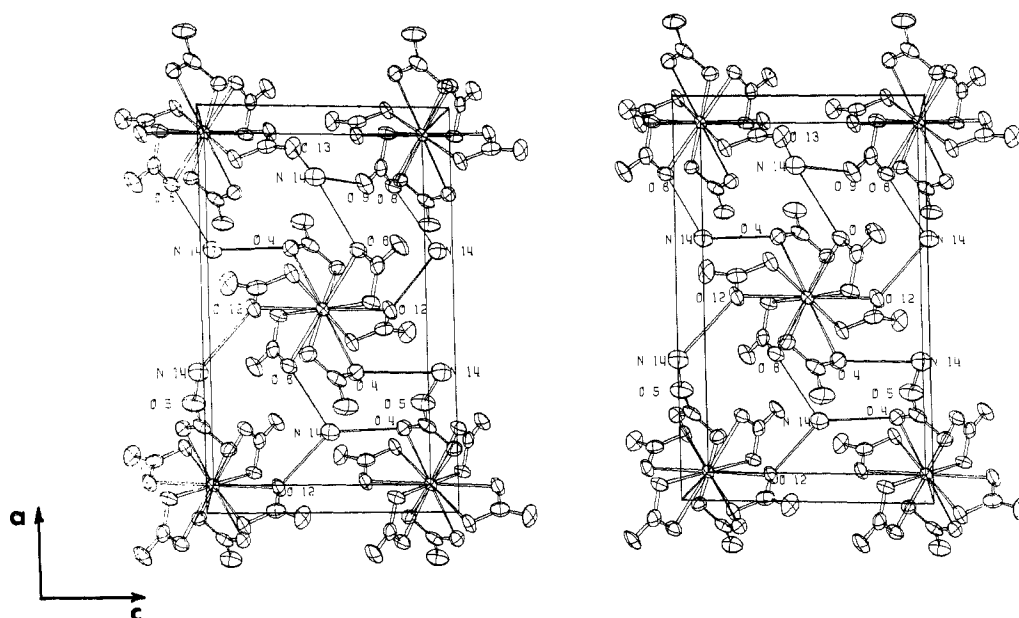


Figure 3. Packing diagram of ceric ammonium nitrate. The  $b$  axis points out of the plane of the paper.

Translation in the positive direction one unit cell along the  $a$  axis makes  $TA = 1$  and similarly for the other two axes. The atom designator code,  $ADC$ , is

$$ADC = (TA + 5) \times 10^4 + (TB + 5) \times 10^3 + (TC + 5) \times 10^2 + SN$$

Hence, the original parameters operated on only by the identity operator have  $ADC = 55501$ .

Six  $\text{NH}_4\text{-O}$  distances range from 2.933 to 3.062 Å; the next closest oxygen is 3.178 Å from N(14). The first six distances indicate the locations where hydrogen bonds are possible, but the seventh results from the fact that the oxygen is on the same nitrate group as the oxygen involved in the 3.062 Å distance. These distances along with the important nonbonded distances are listed in Table IX. Either the hydrogens are disordered or two of them must be involved in bifurcated hydrogen bonds. Since the hydrogens could not be located in the difference map, possibly the result of the first alternative, it is not possible to distinguish between these two possibilities. The arrangement of the six oxygens about N(14) is shown in Figure 2.

If O(13)55603 and O(9)55503 shared one hydrogen and O(8)55501 and O(5)65602, another, the hydrogens could approach a tetrahedral arrangement about N(14). Each hexanitratocerate ion is involved in 12 hydrogen bonds as indicated in Figure 3. The coordinating oxygens can be divided into two groups. The first group includes O(4), O(8), O(12), and the corresponding atoms related to these by the center of symmetry at the cerium position. These atoms are close to the equator of the hexanitratocerate ion when the  $\bar{3}$  axis parallel to the crystallographic  $b$  axis is chosen as the polar axis. Oxygens of the first group are referred to as equatorial oxygens. The second group includes O(3), O(7), O(11), and the centrosymmetrically related atoms. These atoms are closest to the polar axis and are called polar oxygens. Every equatorial oxygen is involved in a hydrogen bond, whereas no polar oxygen is hydrogen bonded. Each noncoordinating oxygen is also hydrogen bonded primarily in the direction of the  $b$  axis. In this way the structure is held together by a three-dimensional network of hydrogen bonds.