Table VIII. Valence Energies of Rhodiacyclopentadiene Model Complexes

Geometry[a]	Valence energy, eV $Rh(H_2O)ClL_2C_4(CF_3)_4$	 $RhClL_2C_4(CF_3)_4$
Opposite equilibrium distortion		−11,157.330
Symmetric	−11,738.170	−11,162.606
Equilibrium	−11,738.169	−11,171.992
Distortion	−11,738.957	−11,159.426
Extreme distortion	−11,735.925	

[a] For a more detailed description of these geometries see ref 21.

A second objective of these calculations was to see if the apparent nonequivalence of the Rh-C bonds was electronic in origin rather than the result of packing forces in the solid state. To that end, the valence energies were calculated for a series of models of the five- and six-coordinate complexes incorporating varying degrees of distortion of the rhodiacyclopentadiene ring from the observed geometry. The various geometries used ranged from that in which both Rh-C distances were made equal and C_1-C_2 was the same as C_3-C_4 ("symmetrized" configuration) to one in which the differences between Rh-C_1 and Rh-C_4 and C_1-C_2 and C_3-C_4 were considerably greater than observed ("extreme distortion").[21] The results of these calculations are presented in Table VIII and it is apparent that the experimental geometry of the ring represents the configuration of minimum energy in each case. These minima are rather shallow however.

In summary, the structural and computational results appear to form a consistent body of data although it would be very desirable to have structural data on larger numbers of derivatives of the tetrakis(trifluoromethyl)rhodiacyclopentadiene moiety which incorporate a variety of ligands in the sixth position in the equatorial plane in order to check further the validity of our computational results. Such complexes are in hand and structural studies are planned in the near future.

Acknowledgments. We are indebted to Dr. Charles Fritchie for the use of the diffractometer and to Drs. L. C. Cusachs and Haven Aldrich for performing the molecular orbital calculations and for much helpful discussion.

Registry No. $Rh(H_2O)Cl(As(CH_3)_3)_2C_4(CF_3)_4$, 41184-52-5.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy of \$2.00 for microfiche, referring to code number INORG-73-2649.

Contribution from the Department of Chemistry,
Montana State University, Bozeman, Montana 59715

Crystal and Molecular Structure of Trinitrato-1,2-bis(pyridine-2-aldimino)ethanegadolinium(III)[1]

G. D. SMITH, C. N. CAUGHLAN,* MAZHAR-UL-HAQUE, and F. A. HART

Received April 16, 1973

The crystal and molecular structure of trinitrato-1,2-bis(pyridine-2-aldimino)ethanegadolinium(III), $[Gd(NO_3)_3(C_{14}H_{14}N_4)]$, has been determined by X-ray analysis. The crystals are orthorhombic, space group *Pbca* with $a = 14.774$ (3), $b = 16.072$ (5), $c = 16.198$ (3) Å, and $Z = 8$. The structure was solved from Patterson and three-dimensional electron-density syntheses and refined by least squares to $R = 0.033$ using 1478 observed reflections. Gadolinium is ten-coordinated. The coordination polyhedron approximates a distorted pentagonal bipyramid, where four of the five equatorial positions are occupied by the nitrogen atoms of the tetradentate amine ligand, the remaining three positions being occupied by the three bidentate nitrate groups.

Introduction

There has been a recent increase of interest in structural aspects of lanthanide complexes. Among other factors this can be ascribed to the tendency of these compounds to adopt high coordination numbers and novel coordination polyhedra,[2] to their possibilities in laser technology,[3] to the study of the Stark-split fluorescence spectra of Eu(III) complexes in relation to the symmetry of the coordination sphere,[4] and particularly to the use of certain lanthanide complexes as nmr shift reagents.[5] We here report and discuss the structure of $[Gd(NO_3)_3(dpae)]$, where dpae = 1,2-bis(pyridine-2-aldimino)ethane, $C_5H_4N{\cdot}CH{:}NCH_2CH_2N{:}CH{\cdot}C_5H_4N$.

The compounds $[MX_3(dpae)]$ ($X = NO_3$, Cl, NCS; M = Y, La-Lu except Pm) have been previously reported.[6] Their properties were described and on the basis of chemical evidence and infrared spectra, it was suggested[6a] that the nitrates probably had an irregular pentagonal-bipyramidal structure, in which one equatorial and two axial positions would be occupied by the three bidentate nitrate groups. A detailed knowledge of this ten-coordinate polyhedron should be of interest, for comparatively few examples of this coordination number are known. Also, it was desirable firmly to establish the mode or modes of coordination of the nitrate groups. Finally, a comparison with the structures of the rather analogous but less sterically constrained bipyridine complexes

---

(1) For a preliminary communication, see Mazhar-ul-Haque, F. A. Hart, and C. N. Caughlan, *Chem. Commun.*, 1240 (1970).

(2) E. L. Muetterties and C. M. Wright, *Quart. Rev., Chem. Soc.*, 21, 109 (1967).

(3) H. Samelson, A. Lempicki, C. Brecker, and V. Brophy, *Appl. Phys. Lett.*, 5, 173 (1964).

(4) S. Bjorklund, N. Filipescu, N. McAvoy, and J. Degnana, *J. Phys. Chem.*, 72, 970 (1968).

(5) C. C. Hinckley, *J. Amer. Chem. Soc.*, 91, 5160 (1969).

(6) (a) D. A. Durham and F. A. Hart, *J. Inorg. Nucl. Chem.*, 31, 145 (1969); (b) E. Butter, B. Lorenz, and F. Hoyer, *J. Prakt. Chem.*, 34, 30 (1966).

$[M(NO_3)_3(bipy)_2]$ (M = La,[7] Tb[8]) might help to develop general principles in this area of structural coordination chemistry.

Experimental Section

A nearly cylindrical crystal, 0.12 mm in diameter and 0.5 mm in length, was used to collect the data. The crystal was mounted along the cylindrical axis which coincided with the *b* axis of the unit cell. Weissenberg and precession photographs showed the space group to be *Pbca*, since the systematic absences were $0kl$ for $k \neq 2n$. $h0l$ for $l \neq 2n$, and $hk0$ for $h \neq 2n$. The cell dimensions were obtained by least-squares refinement of 25 2θ values measured on a diffractometer using Mo Kα radiation ($\lambda = 0.71069$ Å).

Crystal Data. $Gd(NO_3)_3(C_5H_4N{\cdot}CH{:}NCH_2CH_2N{:}CH{\cdot}C_5H_4N)$: mol wt 581.3; orthorhombic; $a = 14.774$ (3), $b = 16.072$ (5), $c = 16.198$ (3) Å; $d_{\text{measd}} = 2.03$ g cm^{-3} (by flotation in a mixture of CCl_4 and $CHBr_3$); $Z = 8$; $d_{\text{calcd}} = 2.01$ g cm^{-3}; Mo Kα radiation $\lambda = 0.71069$ Å; μ(Mo Kα) = 36.3 cm^{-1}; $F(000) = 2264$.

The intensities were measured on a General Electric XRD-5 diffractometer equipped with a scintillation counter as a detector using Mo Kα radiation. The θ–2θ scan technique was used for the collection of the data. Each reflection was scanned for 60 sec at a scan rate of 2°/min; the background was determined by a 30-sec count on each side of the peak. Three standard reflections were measured every 2 hr and showed no systematic change. Of the 2156 reflections measured, 1478 were considered observed by the criterion $I > 3\sigma(I)$. The data were corrected for Lorentz and polarization factors.[9] An absorption correction was made using Tompa's method;[10] transmission factors ranged from 0.82 to 0.83. No correction was made for extinction. The scattering factors for the nonhydrogen atoms were taken from ref 11a and for hydrogen atoms from ref 11b. Both real and imaginary terms for Gd were included.

Structure Analysis and Refinement. The position of the gadolinium atom was determined from a three-dimensional Patterson function and all the oxygen, nitrogen, and carbon atoms were located from two successive three-dimensional Fourier syntheses.

Refinement of positional and isotropic temperature factors by block-diagonal least-squares methods reduced the *R* to 0.08. A weighting scheme suggested by Stout and Jensen[12]

$$\sigma^2(F) = \frac{1}{4Lp}\left[\frac{\sigma^2(I) + (0.02I)^2}{I}\right]; w = 1/\sigma^2$$

for the diffractometer data was used throughout the refinement, the function minimized being $\Sigma w(|F_o| - |F_o|)^2$. Refinement of positional and anisotropic thermal parameters reduced the *R* to 0.05. A three-dimensional difference synthesis showed positions for all the 14 hydrogen atoms. A final refinement of the positional and anisotropic temperature factors for nonhydrogen atoms and the positional and isotropic temperature factors for hydrogen atoms using full-matrix least squares reduced the *R* to 0.033 and the weighted *R* to 0.034.

S, the standard deviation of an observation of unit weight, was calculated to be 1.62. This would at first indicate that the weights are poorly estimated. A δR plot was constructed according to the method of Abrahams and Keve[13] and was found to be linear with a slope of 1.53 and an intercept of −0.007. Examination of the normal probability plot and the table of calculated and observed structure factors indicates that the discrepancy between *S* and the slope is apparently due to relatively large errors in collection of several intensities.

Table I. Atomic Coordinates with Their Standard Deviations in Parentheses

Atom	*x*	*y*	*z*	*B*, Å^2
Gd(1)	0.20280 (3)	0.17714 (3)	0.10978 (3)	
O(2)	0.1255 (5)	0.1862 (4)	0.2449 (4)	
O(3)	0.2274 (5)	0.0926 (4)	0.2380 (4)	
N(4)	0.1643 (7)	0.1259 (6)	0.2795 (5)	
O(5)	0.1437 (6)	0.0991 (5)	0.3454 (5)	
O(6)	0.2835 (6)	0.2797 (4)	0.0251 (4)	
O(7)	0.2401 (6)	0.1766 (5)	−0.0439 (4)	
N(8)	0.2763 (7)	0.2461 (6)	−0.0439 (6)	
O(9)	0.3071 (6)	0.2778 (5)	−0.1053 (5)	
O(10)	0.0699 (6)	0.2258 (5)	0.0256 (6)	
O(11)	0.1151 (6)	0.3107 (5)	0.1151 (5)	
N(12)	0.0631 (7)	0.2951 (7)	0.0592 (7)	
O(13)	0.0095 (7)	0.3469 (6)	0.0341 (5)	
N(14)	0.3001 (6)	0.2733 (4)	0.1977 (4)	
C(15)	0.2690 (8)	0.3409 (6)	0.2343 (6)	
C(16)	0.3239 (9)	0.3960 (7)	0.2794 (6)	
C(17)	0.4131 (10)	0.3783 (7)	0.2833 (7)	
C(18)	0.4470 (8)	0.3083 (7)	0.2441 (7)	
C(19)	0.3887 (7)	0.2580 (6)	0.2009 (6)	
C(20)	0.4209 (7)	0.1808 (7)	0.1619 (6)	
N(21)	0.3646 (6)	0.1340 (5)	0.1240 (5)	
C(22)	0.3964 (8)	0.0513 (7)	0.0982 (7)	
C(23)	0.3356 (9)	0.0213 (7)	0.0286 (7)	
N(24)	0.2409 (7)	0.0346 (5)	0.0564 (5)	
C(25)	0.1860 (9)	−0.0245 (6)	0.0547 (6)	
C(26)	0.0930 (8)	−0.0112 (6)	0.0831 (6)	
C(27)	0.0265 (9)	−0.0732 (7)	0.0799 (6)	
C(28)	−0.0576 (8)	−0.0578 (8)	0.1074 (7)	
C(29)	−0.0779 (10)	0.0199 (9)	0.1390 (7)	
C(30)	−0.0078 (10)	0.0803 (8)	0.1374 (7)	
N(31)	0.0748 (6)	0.0656 (5)	0.1127 (5)	
H(15)	0.200 (5)	0.347 (4)	0.232 (4)	3.5 (19)
H(16)	0.293 (5)	0.446 (4)	0.319 (4)	1.7 (15)
H(17)	0.449 (4)	0.415 (4)	0.317 (4)	1.0 (15)
H(18)	0.503 (5)	0.304 (4)	0.250 (4)	3.2 (18)
H(20)	0.488 (7)	0.171 (7)	0.159 (6)	9.7 (33)
H(22)	0.376 (6)	0.019 (6)	0.158 (5)	6.1 (26)
H(22′)	0.449 (6)	0.058 (6)	0.071 (5)	7.0 (28)
H(23)	0.341 (5)	−0.036 (5)	0.016 (4)	3.2 (19)
H(23′)	0.345 (6)	0.056 (6)	−0.016 (6)	6.9 (29)
H(25)	0.205 (4)	−0.074 (3)	0.035 (3)	0.3 (12)
H(27)	0.058 (5)	−0.117 (4)	0.057 (4)	2.5 (17)
H(28)	−0.111 (8)	−0.109 (8)	0.112 (7)	9.8 (37)
H(29)	−0.132 (7)	0.050 (7)	0.166 (7)	6.5 (36)
H(30)	−0.014 (5)	0.124 (4)	0.167 (4)	0.8 (18)

Results and Discussion

The final positional and anisotropic thermal parameters are given in Tables I and II. The bond distances and angles are shown in Tables III and IV.[14] Figure 1 shows an ORTEP drawing of the molecule.

Coordination Polyhedron. In this complex Gd(III) is ten-coordinated, two oxygen atoms from each nitrate group being bonded to gadolinium, together with four nitrogen atoms from the ligand.

In agreement with the suggestion that, in purely geometrical terms,[15] small bidentate groups such as nitrate tend to occupy one coordination position in a fairly symmetrical polyhedron, the observed polyhedron may be very approximately described as a pentagonal bipyramid with N(4) and

---

(7) A. R. Al-Karaghouli and J. W. Wood, *J. Amer. Chem. Soc.*, **90**, 6548 (1968).

(8) D. S. Moss and S. P. Sinha, *Z. Phys. Chem. (Frankfurt am Main)*, **63**, 190 (1969).

(9) Computer programs used were by F. R. Ahmed and coworkers [NCR-2, Data Reduction and Tape Generation; NCR-8, Fourier for Distorted and Undistorted Nets; NCR-10, Structure Factor Least Squares (Block Diagonal); and NCR-12, Scan of Interatomic Distances and Angles, National Research Council, Ottawa, Ontario, Canada], Busing and Levy (ORFLS), and Carrol K. Johnson (ORTEP). These programs were locally modified for use with the XDS Sigma 7 computer. Other programs were written locally by C. N. Caughlan, E. L. Enwall, and G. D. Smith. The *R* factor is defined as $R = \Sigma|F_o - F_c|/\Sigma|F_o|$ while the weighted *R* factor is defined as $R_w = [\Sigma w(F_o - F_c)^2]^{1/2}/[\Sigma wF_o{}^2]^{1/2}$. *S*, the standard deviation of an observation of unit weight, is given by $S = [\Sigma w\Delta^2/N\theta - NV]^{1/2}$ where Nθ is the number of observations and NV is the number of parameters.

(10) J. De Meulemaer and J. Tompa, *Acta Crystallogr.*, **19**, 1014 (1965).

(11) (a) "International Tables for X-ray Crystallography," Vol. III, Kynoch Press, Birmingham, 1962, pp 202, 211; (b) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(12) G. H. Stout and L. H. Jensen, "X-ray Structure Determination," Macmillan, New York, N. Y., 1968, p 457.

(13) S. C. Abrahams and E. T. Keve, *Acta Crystallogr., Sect. A*, **27**, 157 (1971).

(14) See paragraph at end of paper regarding supplementary material.

(15) J. G. Bergman and F. A. Cotton, *Inorg. Chem.*, **5**, 1208 (1966).

Table II. Anisotropic Thermal Parameters[a] with Their Standard Deviations in Parentheses

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Gd(1)	0.00409 (3)	0.00223 (2)	0.00311 (2)	−0.00002 (3)	0.00002 (3)	−0.00010 (2)
O(2)	0.0049 (5)	0.0036 (10)	0.0036 (3)	0.0005 (4)	−0.0003 (3)	0.0007 (3)
O(3)	0.0058 (6)	0.0038 (4)	0.0035 (3)	0.0002 (4)	0.0013 (4)	0.0003 (3)
N(4)	0.0060 (7)	0.0053 (6)	0.0016 (4)	−0.0021 (5)	0.0009 (4)	0.0001 (4)
O(5)	0.0080 (6)	0.0069 (5)	0.0045 (4)	0.0007 (4)	0.0021 (4)	0.0017 (4)
O(6)	0.0126 (8)	0.0042 (4)	0.0032 (3)	−0.0029 (5)	0.0003 (5)	−0.0004 (3)
O(7)	0.0118 (7)	0.0034 (3)	0.0049 (4)	−0.0030 (4)	0.0006 (4)	−0.0011 (3)
N(8)	0.0084 (8)	0.0034 (4)	0.0034 (4)	−0.0003 (5)	0.0004 (5)	0.0006 (4)
O(9)	0.0116 (7)	0.0047 (4)	0.0051 (4)	−0.0011 (5)	0.0007 (6)	0.0006 (4)
O(10)	0.0094 (8)	0.0029 (4)	0.0120 (7)	0.0002 (5)	−0.0053 (6)	−0.0007 (4)
O(11)	0.0093 (7)	0.0046 (4)	0.0062 (4)	0.0028 (5)	−0.0035 (5)	−0.0012 (4)
N(12)	0.0043 (7)	0.0051 (6)	0.0053 (6)	0.0015 (6)	0.0002 (5)	0.0015 (5)
O(13)	0.0104 (8)	0.0071 (6)	0.0067 (5)	0.0035 (6)	0.0000 (5)	0.0007 (4)
N(14)	0.0045 (5)	0.0027 (3)	0.0031 (3)	−0.0004 (4)	−0.0004 (4)	0.0000 (3)
C(15)	0.0058 (8)	0.0043 (6)	0.0031 (4)	0.0001 (6)	0.0001 (5)	−0.0007 (4)
C(16)	0.0069 (9)	0.0039 (5)	0.0022 (4)	−0.0007 (6)	0.0006 (6)	0.0003 (4)
C(17)	0.0068 (10)	0.0034 (6)	0.0047 (6)	−0.0015 (6)	−0.0014 (7)	−0.0002 (4)
C(18)	0.0047 (7)	0.0050 (6)	0.0046 (5)	−0.0003 (7)	−0.0015 (5)	−0.0001 (5)
C(19)	0.0042 (7)	0.0033 (5)	0.0029 (4)	−0.0002 (6)	0.0000 (5)	0.0001 (4)
C(20)	0.0045 (7)	0.0048 (6)	0.0023 (4)	−0.0001 (6)	0.0000 (5)	0.0011 (5)
N(21)	0.0056 (6)	0.0029 (4)	0.0036 (4)	0.0000 (4)	0.0006 (4)	−0.0005 (3)
C(22)	0.0066 (8)	0.0044 (6)	0.0044 (6)	0.0007 (6)	0.0018 (6)	−0.0005 (5)
C(23)	0.0077 (10)	0.0039 (6)	0.0047 (6)	0.0007 (6)	0.0008 (7)	−0.0015 (5)
N(24)	0.0059 (7)	0.0027 (4)	0.0041 (4)	−0.0004 (5)	0.0000 (5)	0.0000 (4)
C(25)	0.0069 (9)	0.0019 (5)	0.0046 (5)	0.0009 (6)	0.0005 (6)	−0.0012 (4)
C(26)	0.0060 (8)	0.0027 (5)	0.0032 (5)	−0.0002 (6)	−0.0012 (5)	0.0000 (4)
C(27)	0.0098 (10)	0.0034 (5)	0.0037 (5)	−0.0014 (7)	−0.0014 (6)	0.0007 (4)
C(28)	0.0076 (9)	0.0056 (7)	0.0040 (5)	−0.0029 (7)	−0.0011 (7)	0.0009 (6)
C(29)	0.0069 (10)	0.0061 (8)	0.0037 (6)	−0.0014 (9)	−0.0004 (6)	−0.0005 (5)
C(30)	0.0086 (11)	0.0043 (6)	0.0033 (6)	−0.0018 (8)	−0.0003 (6)	−0.0018 (5)
N(31)	0.0049 (6)	0.0035 (4)	0.0038 (4)	−0.0010 (4)	0.0009 (5)	−0.0006 (4)

[a] In the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Table III. Bond Distances with Their Standard Deviations in Parentheses

Atoms	Dist, Å	Atoms	Dist, Å
Gd(1)-O(2)	2.473 (7)	C(17)-H(17)	0.96 (6)
Gd(1)-O(3)	2.508 (6)	C(18)-C(19)	1.37 (2)
Gd(1)-O(6)	2.454 (7)	C(18)-H(18)	0.84 (7)
Gd(1)-O(7)	2.550 (7)	C(19)-C(20)	1.47 (1)
Gd(1)-O(10)	2.515 (9)	C(20)-N(21)	1.28 (1)
Gd(1)-O(11)	2.509 (8)	C(20)-H(20)	1.00 (10)
Gd(1)-N(14)	2.546 (7)	N(21)-C(22)	1.47 (1)
Gd(1)-N(21)	2.500 (9)	C(22)-C(23)	1.52 (2)
Gd(1)-N(24)	2.513 (8)	C(22)-H(22)	1.14 (9)
Gd(1)-N(31)	2.606 (8)	C(22)-H(22′)	0.90 (9)
O(2)-N(4)	1.26 (1)	C(23)-N(24)	1.48 (2)
O(3)-N(4)	1.27 (1)	C(23)-H(23)	0.95 (8)
O(5)-N(4)	1.19 (1)	C(23)-H(23′)	0.92 (10)
O(6)-N(8)	1.25 (1)	N(24)-C(25)	1.25 (1)
O(7)-N(8)	1.24 (1)	C(25)-C(26)	1.46 (2)
O(9)-N(8)	1.21 (1)	C(25)-H(25)	0.90 (5)
O(10)-N(12)	1.24 (1)	C(26)-C(27)	1.40 (2)
O(11)-N(12)	1.21 (1)	C(26)-N(31)	1.35 (1)
O(13)-N(12)	1.22 (1)	C(27)-C(28)	1.34 (2)
N(14)-C(15)	1.32 (1)	C(27)-H(27)	0.92 (7)
N(14)-C(19)	1.33 (1)	C(28)-C(29)	1.38 (2)
C(15)-C(16)	1.41 (2)	C(28)-H(28)	1.14 (12)
C(15)-H(15)	1.02 (7)	C(29)-C(30)	1.42 (2)
C(16)-C(17)	1.35 (2)	C(30)-N(31)	1.31 (2)
C(16)-H(16)	1.12 (7)	C(30)-H(30)	0.86 (8)
C(17)-C(18)	1.39 (2)		

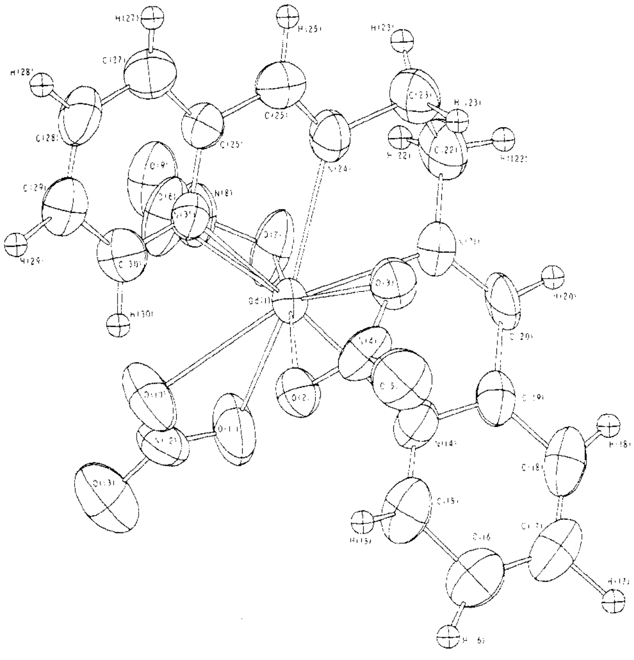

Figure 1. ORTEP drawing of trinitrato-1,2-bis(pyridine-2-aldimino)-ethanegadolinium(III) with thermal ellipsoids scaled to include 50% probability. For clarity, an isotropic temperature factor of 1.0 has been assigned to all hydrogens.

N(8) (Figure 1) lying near the axis and N(12), N(14), N(21), N(24), and N(31) lying near the equator. This approach, however, does not give a very close description of the structure in the present instance. Thus, if the pentagonal bipyramid is defined as above by Gd and N(4), N(8), N(12), N(14), N(21), N(24), and N(31) [N(4)-Gd(1)-N(21) = 91.2°], angular deviations of the Gd-ligand vectors from regular geometry lie in the approximate range 0-30°; this represents a considerable distortion.

The structure is best discussed in terms of, firstly, the constraints within the two types of ligand (nitrate and tetramine) and, secondly, their mutual interaction when coordinated.

Nitrate Groups. These are planar and the N-O interatomic distances are in the case of two groups within the range 1.21-1.25 Å. The third group, centered on N(4), has two longer distances of 1.27 and 1.26 Å and one shorter at 1.19 Å. The O-N-O interatomic angles in the case of the group centered

Table IV. Valence Angles with Their Standard Deviations in Parentheses

Atoms	Angle, deg	Atoms	Angle, deg
O(2)-Gd(1)-O(3)	50.6 (2)	Gd(1)-N(14)-C(15)	123.6 (6)
O(2)-Gd(1)-O(6)	132.8 (2)	Gd(1)-N(14)-C(19)	117.7 (6)
O(2)-Gd(1)-O(7)	164.6 (2)	C(15)-N(14)-C(19)	118.4 (8)
O(2)-Gd(1)-O(10)	95.8 (3)	N(14)-C(15)-C(16)	123.4 (10)
O(2)-Gd(1)-O(11)	71.4 (2)	N(14)-C(15)-H(15)	114.1 (39)
O(2)-Gd(1)-N(14)	74.3 (2)	C(16)-C(15)-H(15)	122.2 (39)
O(2)-Gd(1)-N(21)	112.1 (2)	C(15)-C(16)-C(17)	117.1 (11)
O(2)-Gd(1)-N(24)	117.5 (3)	C(15)-C(16)-H(16)	120.8 (36)
O(2)-Gd(1)-N(31)	71.9 (2)	C(17)-C(16)-H(16)	121.3 (36)
O(3)-Gd(1)-O(6)	139.2 (2)	C(16)-C(17)-C(18)	120.2 (11)
O(3)-Gd(1)-O(7)	140.8 (2)	C(16)-C(17)-H(17)	115.8 (39)
O(3)-Gd(1)-O(10)	136.9 (3)	C(18)-C(17)-H(17)	123.9 (39)
O(3)-Gd(1)-O(11)	120.7 (2)	C(17)-C(18)-C(19)	119.0 (11)
O(3)-Gd(1)-N(14)	77.5 (2)	C(17)-C(18)-H(18)	111.9 (52)
O(3)-Gd(1)-N(21)	68.6 (2)	C(19)-C(18)-H(18)	129.1 (52)
O(3)-Gd(1)-N(24)	76.0 (3)	N(14)-C(19)-C(18)	121.8 (9)
O(3)-Gd(1)-N(31)	73.6 (2)	N(14)-C(19)-C(20)	117.2 (9)
O(6)-Gd(1)-O(7)	49.6 (2)	C(18)-C(19)-C(20)	120.8 (9)
O(6)-Gd(1)-O(10)	82.4 (3)	C(19)-C(20)-N(21)	119.5 (9)
O(6)-Gd(1)-O(11)	72.3 (3)	C(19)-C(20)-H(20)	118.1 (60)
O(6)-Gd(1)-N(14)	68.3 (2)	N(21)-C(20)-H(20)	121.8 (60)
O(6)-Gd(1)-N(21)	76.9 (3)	Gd(1)-N(21)-C(20)	120.2 (7)
O(6)-Gd(1)-N(24)	108.1 (3)	Gd(1)-N(21)-C(22)	122.0 (6)
O(6)-Gd(1)-N(31)	145.6 (3)	C(20)-N(21)-C(22)	117.4 (9)
O(7)-Gd(1)-O(10)	68.9 (3)	N(21)-C(22)-C(23)	107.8 (9)
O(7)-Gd(1)-O(11)	98.5 (3)	N(21)-C(22)-H(22)	94.9 (45)
O(7)-Gd(1)-N(14)	115.2 (2)	N(21)-C(22)-H(22′)	107.9 (58)
O(7)-Gd(1)-N(21)	83.2 (3)	C(23)-C(22)-H(22)	109.2 (46)
O(7)-Gd(1)-N(24)	67.2 (3)	C(23)-C(22)-H(22′)	100.7 (58)
O(7)-Gd(1)-N(31)	99.9 (3)	H(22)-C(22)-H(22′)	134.4 (73)
O(10)-Gd(1)-O(11)	49.4 (3)	C(22)-C(23)-N(24)	106.6 (9)
O(10)-Gd(1)-N(14)	123.7 (3)	C(22)-C(23)-H(23)	114.8 (46)
O(10)-Gd(1)-N(21)	152.0 (3)	C(22)-C(23)-H(23′)	107.4 (59)
O(10)-Gd(1)-N(24)	105.8 (3)	N(24)-C(23)-H(23)	106.6 (46)
O(10)-Gd(1)-N(31)	70.0 (3)	N(24)-C(23)-H(23′)	107.0 (59)
O(11)-Gd(1)-N(14)	75.7 (3)	H(23)-C(23)-H(23′)	114.0 (74)
O(11)-Gd(1)-N(21)	136.7 (3)	Gd(1)-N(24)-C(23)	116.5 (7)
O(11)-Gd(1)-N(24)	155.2 (3)	Gd(1)-N(24)-C(25)	123.7 (7)
O(11)-Gd(1)-N(31)	102.3 (3)	C(23)-N(24)-C(25)	119.7 (9)
N(14)-Gd(1)-N(21)	65.0 (3)	N(24)-C(25)-C(26)	119.4 (10)
N(14)-Gd(1)-N(24)	128.3 (3)	N(24)-C(25)-H(25)	118.4 (35)
N(14)-Gd(1)-N(31)	144.8 (2)	C(26)-C(25)-H(25)	122.1 (35)
N(21)-Gd(1)-N(24)	64.2 (3)	C(25)-C(26)-C(27)	122.9 (10)
N(21)-Gd(1)-N(31)	120.1 (3)	C(25)-C(26)-N(31)	115.6 (9)
N(24)-Gd(1)-N(31)	62.7 (3)	C(27)-C(26)-N(31)	121.6 (10)
Gd(1)-O(2)-N(4)	98.0 (6)	C(26)-C(27)-C(28)	120.4 (11)
Gd(1)-O(3)-N(4)	96.0 (6)	C(26)-C(27)-H(27)	101.8 (43)
O(2)-N(4)-O(3)	115.1 (8)	C(28)-C(27)-H(27)	137.8 (44)
O(2)-N(4)-O(5)	124.2 (9)	C(27)-C(28)-C(29)	119.3 (12)
O(3)-N(4)-O(5)	120.7 (9)	C(27)-C(28)-H(28)	121.9 (61)
Gd(1)-O(6)-N(8)	99.7 (6)	C(29)-C(28)-H(28)	118.5 (61)
Gd(1)-O(7)-N(8)	95.2 (6)	C(28)-C(29)-C(30)	116.9 (12)
O(6)-N(8)-O(7)	115.3 (9)	C(28)-C(29)-H(29)	138.5 (62)
O(6)-N(8)-O(9)	121.6 (10)	C(30)-C(29)-H(29)	104.6 (62)
O(7)-N(8)-O(9)	122.9 (10)	C(29)-C(30)-N(31)	124.3 (12)
Gd(1)-O(10)-N(12)	96.0 (7)	C(29)-C(30)-H(30)	118.2 (51)
Gd(1)-O(11)-N(12)	97.2 (7)	N(31)-C(30)-H(30)	114.9 (51)
O(10)-N(12)-O(11)	117.4 (10)	Gd(1)-N(31)-C(26)	118.5 (6)
O(10)-N(12)-O(13)	121.2 (11)	Gd(1)-N(31)-C(30)	124.0 (8)
O(11)-N(12)-O(13)	121.3 (11)	C(26)-N(31)-C(30)	117.4 (10)

on N(12) lie within 3° of 120° but the other two groups show distortions of up to 4.9° from ideality. It is significant that the only two small O-N-O angles [O(2)-N(4)-O(3) = 115.1°; O(6)-N(8)-O(7) = 115.3°] are those which involve the two coordinated oxygen atoms of the nitrate group in question, these two oxygen atoms probably being squeezed toward one another by repulsion from other oxygen and nitrogen ligand atoms in the coordination sphere. A further and perhaps more powerful cause of this distortion is the reduction of inter-σ-bond electron-pair repulsion between these two N-O bonds consequent upon electron withdrawal in the sense N→O due to the inductive effect of coordination.[16] This reduction of the O-N-O angle also occurs in the ten-coordinate complex $[Ce(NO_3)_4(PPh_3)_2]$.[17] Of its four nitrate groups, three have one O-N-O angle significantly smaller than 120° (115.7, 114.9, and 117.0°) and in each case the two oxygen atoms involved are those coordinated to the Ce(IV) ion. A similar effect is observed in other complex nitrates and is discussed in a comprehensive review[16] on the structural chemistry of the nitrate ion.

The Gd-O bond lengths lie within the range 2.45-2.55 Å. The value predicted by addition of ionic radii is 1.40 + 0.94 = 2.34 Å. This tends to support the view that the bonding is primarily electrostatic. The compounds $[M(NO_3)_3(bipy)_2]$[7,8] have M-O distances of 2.60 (M = La) and 2.44-2.49 Å (M = Tb). After correction for the lanthanide contraction, these values agree very well with ours.

Tetradentate Amine. The pyridine rings show normal geometry. The average C-C and C-N bond lengths agree well with those reported for pyridine hydrochloride.[18] The bond angles of the pyridine rings appear to be normal within experimental error. Both pyridine groups are planar; the equations of the best least-squares planes are given in Table V.

The two $-CH_2\cdot N{:}CH\cdot C_5H_4N$ halves of the ligand are each essentially planar, but the planes of the two pyridine rings are mutually inclined at a dihedral angle of 28°. The bond angles at the two saturated carbon atoms C(22) and C(23) are very little distorted [N(21)-C(22)-C(23) = 107.8°; C(22)-C(23)-N(24) = 106.6°]. The angles at the trigonally hybridized atoms C(20), N(21), N(24), and C(25) [C(19)-C(20)-N(21) = 119.5°; C(20)-N(21)-C(22) = 117.4°; C(23)-N(24)-C(25) = 119.7°; N(24)-C(25)-C(26) = 119.4°] also show little strain. The bond lengths in the chain C(19)-C(20)-N(21)-C(22)-C(23)-N(24)-C(25)-C(26) are normal.

The mutual noncoplanarity of the two halves of the amine ligand is probably caused by the requirement that all four Gd-N bond lengths should be similar for maximum stability. The Gd-N distance expected from the structures of $[La(NO_3)_3(dipyridyl)_2]$ (La-N = 2.66, 2.65 Å) and $[Tb(NO_3)_3(dipyridyl)_2]$ (Tb-N = 2.46, 2.54 Å) is about 2.52 Å after allowing for the lanthanide contraction. In this work we find Gd-N distances of 2.55 [N(14)], 2.50 [N(21)], 2.51 [N(24)], and 2.61 Å [N(31)], in good agreement with expectation. If, however, the tetradentate amine had remained planar, a Dreiding molecular model shows that the Gd-N distance for the pyridine nitrogen atoms would be about 2.2 Å if Gd-N(21) and Gd-N(24) remain at 2.5 Å. The buckling of this ligand is thus readily explained by the necessity to seek the best Gd-N bond length rather than by invoking interligand repulsion.

Coordination Polyhedron. There is little or no evidence for directed covalent bonding in lanthanide complexes, so the bonding in this compound is probably best considered from an electrostatic viewpoint. Thus, the primary consideration will be the avoidance of unduly short interatomic distances between coordinated atoms. Further basic requirements are that the internuclear distance between a pair of oxygen atoms in any of the nitrate groups must necessarily remain almost unchanged on coordination and that the tetramine must coordinate as two pairs of nitrogen atoms, each pair forming part of a rigid planar aromatic system. However, as discussed above, the four nitrogen atoms cannot be coplanar and the

(16) C. C. Addison, N. Logan, and S. C. Wallwork, *Quart. Rev., Chem. Soc.*, **25**, 289 (1971).

(17) Mazhar-ul-Haque, C. N. Caughlan, F. A. Hart, and R. Van Nice, *Inorg. Chem.*, **10**, 115 (1971).

(18) P. C. Rerat, *Acta Crystallogr.*, **15**, 427 (1962).

Table V

Equations of Least-Squares Planes:[a] $A\bar{X} + B\bar{Y} + C\bar{Z} = D$

Plane	Atoms	*A*, Å	*B*, Å	*C*, Å	*D*, Å	*S*, Å^2
1	O(2), O(3), N(4), O(5)	0.6547	0.6233	0.4277	4.778	0.9013×10^{-4}
2	O(6), O(7), N(8), O(9)	0.8830	−0.4442	0.1519	1.757	0.4342×10^{-3}
3	O(10), O(11), N(12), O(13)	0.6756	0.3556	−0.6458	1.715	0.4123×10^{-3}
4	N(14), C(15), C(16), C(17), C(18), C(19)	0.1529	0.5368	−0.8297	0.393	0.3943×10^{-3}
5	C(26), C(27), C(28), C(29), C(30), N(31)	0.2661	−0.2964	0.9172	1.648	0.8225×10^{-3}

Dihedral Angles

Planes	Angle, deg	Planes	Angle, deg	Planes	Angle, deg
1 and 2	68.5	1 and 3	67.2	2 and 3	70.1

[a] *S* = sum of squares of deviation of atoms from plane; *D* = origin to plane distance in angstroms. All atoms given equal weight.

Table VI. Mutual Contacts of Coordinated Atoms in Å[a]

	O(2)	O(3)	O(6)	O(7)	O(10)	O(11)	N(14)	N(21)	N(24)	N(31)
O(2)		[2.13 (1)]				2.91 (1)	3.03 (1)			2.98 (1)
O(3)	[2.13 (1)]						3.16 (1)	2.82 (1)	3.09 (1)	3.06 (1)
O(6)				[2.10 (1)]						
O(7)			[2.10 (1)]		2.87 (1)	3.83 (1)		3.35 (1)	2.80 (1)	
O(10)				2.87 (1)		[2.10 (1)]				2.94 (1)
O(11)	2.91 (1)			3.83 (1)	[2.10 (1)]		3.10 (1)			
N(14)	3.03 (1)	3.16 (1)				3.10 (1)		[2.71 (1)]		
N(21)		2.82 (1)		3.35 (1)			[2.71 (1)]		[2.66 (1)]	
N(24)		3.09 (1)		2.80 (1)				[2.66 (1)]		[2.66 (1)]
N(31)	2.98 (1)	3.06 (1)			2.94 (1)				[2.66 (1)]	

[a] Brackets indicate constraint arising from NO_3 or tetramine stereochemistry.

position of the two pairs is closely circumscribed if strain in the chain N(21)-C(22)-C(23)-N(24) is to be avoided. These requirements of the tetramine seem to prevent the adoption of a structure with higher molecular symmetry, in contrast to $[M(NO_3)_3(bipy)_2]$ (M = La or Tb) which have C_2 molecular symmetry.

The contact distances of the ligand atoms with neighboring ligand atoms are listed in Table VI. The general features of these contacts within the coordination sphere are the following. Firstly, four ligand atoms each have four near neighbors while the other six have five near neighbors. Secondly, the contacts fall into three groups. Thus, two oxygen atoms in the same nitrate group have the smallest separation: 2.10-2.13 Å. The linked nitrogen atoms have separations of 2.66-2.71 Å, while the separations which have no intraligand constraints but only interligand constraints have larger contact distances between 2.80 and 3.35 Å. This distinction between what may be called "forced" and "natural" contacts emphasizes the desirability of the presence of bidentate or multidentate ligands if the coordination numbers of the lanthanides are to exceed nine, which is the usual maximum with monodentate ligands only. Other nonbonded contacts are well clear of the sum of the van der Waals radii, except seven O-H contacts (2.34-2.58 Å) which are less than the sum of the van der Waals radii of O and H (2.60 Å).

Acknowledgment. We wish to thank Montana State University for a grant of computer time.

Registry No. $[Gd(NO_3)_3(dpae)]$, 22534-57-2.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-73-2654.