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The Crystal and Molecular Structure of Trinitratobis(bipyridyl)lanthanum(III)

BY A. R. AL-KARAGHOULI AND J. S. WOOD*

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The crystal and molecular structure of trinitratobis(bipyridyl)lanthanum, $La(NO_3)_3(C_{10}H_8N_2)_2$, has been determined from 1514 independent X-ray diffraction data collected with a counter diffractometer. The material crystallizes in the orthorhombic space group *Pbcn* with four formula units in a cell of dimensions $a = 17.11$ (2) Å, $b = 9.18$ (1) Å, and $c = 14.92$ (2) Å; $\rho_{obsd} = 1.80$ (2) g cm^{-3} and $\rho_{calcd} = 1.805$ (4) g cm^{-3}. The structure has been refined by full-matrix least-squares techniques to a final (conventional) *R* value of 6.0% and to a weighted *R* value of 6.6% for the 1155 reflections above background. The molecules are located on twofold axes in the crystal but, because of a static disorder involving one nitrate group, have no inherent symmetry. The lanthanum atom is ten-coordinate being chelated by the two bipyridyl ligands and three bidentate nitrate groups. The averaged La–N and La–O bond distances are 2.66 (1) and 2.59 (1) Å, respectively. The relative stabilities of three ten-coordination polyhedra have been assessed on the basis of nonbonded ligand–ligand repulsion energies, namely, the bicapped square antiprism (D_{4d}), the bicapped dodecahedron (D_2), and a polyhedron of C_{2v} symmetry derived by the sharing of a trans pair of the four equatorial "B" positions of a dodecahedron between two pairs of ligands. The polyhedron in the lanthanum complex has features common to all three polyhedra but on the basis of adherence to various least-squares planes is probably best described in terms of the D_2 geometry.

Introduction

The stereochemistries of compounds containing high-coordination polyhedra have been the subject of several reviews,[1-3] and a variety of structural investigations of species containing the transition elements and the lanthanides have given information on the geometries of principally coordination number 8 and to a lesser extent other coordination numbers. One of the principal factors affecting the stability of the higher coordination number (from 10 upward) and also coordination number 8 for certain first-row transition metals is the presence of compact ligands, such as bidentate nitrate and carbonate ions, as for example in $Ce(NO_3)_6{}^{3-}$ [4] and in $Th(NO_3)_4 \cdot 5H_2O$.[5]

In order to investigate further some of these high-coordination geometries we have carried out structure analyses on two ten-coordinate complexes, *viz.*, the title compound and the pentanitratocerium(III) ion, $Ce(NO_3)_5{}^{2-}$. Preliminary results of the analyses of both these complexes have been reported,[6,7] and here we give further structural details for the bipyridyl complex and a discussion of ten-coordinate stereochemistry on the basis of ligand–ligand repulsions. There are now several other reports of structure determinations of ten-coordinate complexes,[8-13] including a compound indentical, apart from the central lanthanide, with that described here, namely, $Tb(NO_3)_3 \cdot (C_{10}H_8N_2)_2$.[10] This and other related complexes were first described by Sinha[14] while the lanthanum complex was first prepared by Labanov and Smirnova.[15] Further details including characterization by physical measurements were reported by Hart and Laming,[16] who, on the basis of infrared data, suggested that all nitrates might be bidentate and the molecule ten-coordinate.

Experimental Procedures

Crystalline $La(NO_3)_3(C_{10}H_8N_2)_2$ was prepared as described by Hart and Laming,[16] by the reaction of 2,2′-bipyridyl with $La(NO_3)_3 \cdot 6H_2O$ in alcoholic solution. *Anal.* Calcd for $LaC_{20}H_{16}N_7O_9$: C, 37.68; N, 15.38; H, 2.51. Found: C, 37.66; N, 15.42; H, 2.51. The transparent crystals were not very well formed and showed no pronounced morphological features. Preliminary Weissenberg and precession photographs taken with Mo Kα radiation indicated Laue symmetry *mmm* and gave the

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* Author to whom correspondence should be addressed at the University of Massachusetts.

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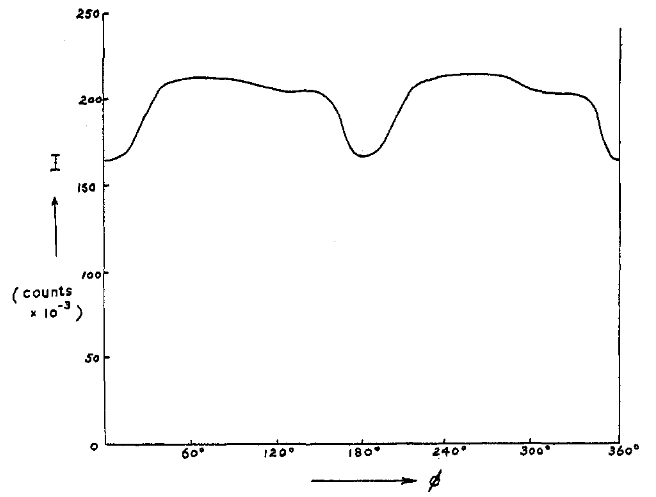

Figure 1.—Variation of intensity of the 600 reflection as a function of ϕ.

systematic absences $hk0$ for $h + k \neq 2n$, $h0l$ for $l \neq 2n$, and $0kl$ for $k \neq 2n$, which are consistent with the unique choice of the orthorhombic space group *Pbcn*. Preliminary cell constants were estimated from the films.

A wedge-shape crystal fragment of maximum dimension 0.3 mm was selected for intensity measurement and was mounted with the a^* axis coincident with the ϕ axis of a General Electric quarter-circle XRD-6, manually operated diffractometer. The crystal was placed 14.6 cm from the source and the distance from the crystal to the detector aperture (2°) was 16.5 cm. Unit cell dimensions were obtained from the 2θ values for the axial reflections, which were measured using a fine detector slit and zirconium-filtered Mo Kα radiation (λ 0.7107 Å). The averaged values are $a = 17.11$ (2), $b = 9.18$ (1), and $c = 14.92$ (2) Å with the standard deviations obtained from the distribution of individual values. The observed density (measured by flotation in a mixture of ethyl iodide and chloroform) of 1.80 (2) g cm^{-3} agrees well with the density calculated for 4 formula units per unit cell, namely, 1.805 (4) g cm^{-3}, and in the absence of any disorder the molecule is required to have C_2 or C_i point symmetry.

The integrated intensities of 1514 independent reflections within the sphere $2\theta_{\mathrm{Mo}} < 45°$ were measured at an instrument takeoff angle of 1° using the θ-2θ scan technique and a scan rate of 2°/min. A scintillation counter equipped with a pulse height analyzer set for a 95% window centered on the Mo Kα peak was used to measure the data. The instrument settings were computed using the program GESET[17] which also calculated the scan range for each reflection, using the formula $\Delta 2\theta = A + B \tan \theta$. The quantity A, chosen on the basis of the crystal mosaicity and source size, was given the value 1.8° while B, included to take account of spectral dispersion, was given the value 1°.[18] Stationary-background counts, B_1 and B_2, were taken at each limit of the 2θ scan, for half the scan time. From these readings and the measured peak counts, P, the net intensity, I, was calculated as $I = P - (B_1 + B_2)$. The intensities of two standard reflections were monitored after every 40 reflections and a small drop in intensity of approximately 3% was observed between the initial and final measurements. Of the 1514 independent reflections 348 had a net intensity of zero as given by the above formula. The assignment of standard deviations to both observed and unobserved reflections was made on the basis of an analysis of the agreement between $|F_o|$ and $|F_c|$ as outlined later.

Detailed absorption corrections were not made to the intensity data since the crystal faces could not be unambiguously indexed. The largest variations in the crystal dimensions were in the (100) plane and ϕ scans of the axial ($h00$) reflections indicated a maximum variation in intensity of *ca.* 23%. The form of the variation for the 600 reflection is illustrated in Figure 1. These axial scans were then used to derive an empirical absorption correction based on ϕ only,[19] the relative correction factors (for the F's) ranging from 1.0 to 1.13. The linear absorption coefficient for Mo Kα radiation is 19.2 cm^{-1}. The intensities were corrected for Lorentz and polarization factors.

Solution and Refinement of Structure

A three-dimensional Patterson map revealed the positions of the four lanthanum atoms located on the twofold axes in the crystal in the 4(e) special positions.[20] All light atoms were expected to be in general positions except for one nitrate group, which from space group requirements was also expected to have C_2 symmetry. However, the La–N and La–O vectors for this nitrate had much lower weight than predicted and subsequent solution of the structure indicated a static disorder with two "half" nitrates occupying general positions.

The atoms constituting the bipyridyl molecule and the ordered nitrate group (1) in general positions were located in two successive electron density maps. These maps indicated the disorder in nitrate group 2 but because of the overlapping of peaks it was difficult to derive coordinates for the four "half" atoms. Full-matrix least-squares refinement was therefore commenced and two cycles, in which the variables were the positional and isotropic thermal parameters of all atoms and with the nitrogen and terminal oxygen atoms of nitrate 2 constrained to be on the twofold axis, led to a residual R (defined as $\Sigma||F_o| - |F_c||/\Sigma|F_o|$) of 0.078. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ and the weighted R factor, $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{1/2}$, was 0.089 with unit weights. The thermal parameters for all atoms of nitrate 2 and for the terminal oxygen atom of nitrate 1 converged to high values, and examination of a difference Fourier map indicated that a more reasonable model for nitrate 2 would be one in which this group was displaced slightly from the twofold axis and treated as two half-nitrates in general positions. Coordinates for the four "half" atoms were accordingly derived from the Fourier maps.

Before continuing with this model variable weights for the individual reflections were introduced and these were chosen such that the quantity $\Sigma w(|F_o| - |F_c|)^2$ was essentially constant when the reflection data were analyzed over ranges of $|F_o|$. The standard deviations from which the weights were derived were calculated from the formula $\sigma(F_o) = A + B|F_o|$, and for the final cycles of refinement the constants had the values $A = 20.0$ and $B = 0$ for $0 < F_o < 7.0$, $A = 5.6$ and $B = -0.022$ for $7.0 \leqslant F_o < 90.0$, $A = 0.4$ and $B = 0.035$ for $90 \leqslant F_o < 250.0$, and $A = -33.0$ and $B = 0.168$ for $F_o \geqslant 250.0$.

The further cycles of refinement were carried out with the majority of the atoms assigned anisotropic thermal parameters and initially an attempt was made to refine the four "half" atoms of nitrate ion 2 anisotropically, in addition to the other atoms of the molecule. However, this led to a meaningless pattern of thermal behavior for this ion and to large oscillations in the positional parameters of oxygen atoms O(4) and O(5), which were strongly coupled in the least-squares matrix, presumably due to overlap. Accordingly the four "half" atoms were restrictued to isotropic thermal motion and refinement converged satisfactorily to give physically meaningful results with constraints on the model such that the positional and thermal parameters of O(4) and O(5) were varied in alternate cycles and not refined together. The remainder of the light atoms were refined anisotropically and the adoption of an anisotropic model gave significant improvement in R' at the 99.5% confidence level.[21]

Three cycles of refinement with this model (166 variables) converged to a final R value of 0.060 and an R' value of 0.066 calculated for the reflection data above background. The largest parameter shifts in the two final cycles were for the oxygen atoms O(4) and O(5), the maximum amounting to 0.43 of the corresponding standard deviation. However, in these last two cycles no other parameter shift exceeded 0.26σ and the coordinate shifts were much less than this. The standard deviation of an observation of unit weight was 2.152.

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(17) A diffractometer setting program by J. Kraut and S. T. Freer and included in the X-Ray 63 program system (J. M. Stewart and D. High, University of Maryland) as adapted for use on the Atlas computer system, Harwell, England. This system also incorporates the Busing–Martin–Levy full-matrix least-squares program ORFLS, which was used for all refinements, and the error function program ORFFE, which was used for calculating the orientation and magnitudes of the thermal ellipsoids and for the construction of Figure 2.

(18) T. C. Furnas "Single Crystal Orienter Instruction Manual," General Electric Co., Milwaukee, Wis., 1957.

(19) U. W. Arndt and B. T. M. Willis, "Single Crystal Diffractometry," Cambridge University Press, London, England, 1966, p 241.

(20) "International Tables for X-Ray Crystallography," Vol. 1, Kynoch Press, Birmingham, England, 1962.

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

A final difference Fourier map showed no anomalous features and indicated that the model adopted for the treatment of the disordered nitrate group was satisfactory. The highest peaks in the map, of a density *ca.* 0.8 e/Å^3, were situated close to the lanthanum atom. Three low-order reflections were omitted from the refinement as they showed errors presumably attributable to primary extinction.

The scattering factors used for this analysis were, for lanthanum, that tabulated by Cromer and Waber[22] and, for carbon, nitrogen, and oxygen, those given in ref 23. During the last two cycles, anomalous dispersion corrections were applied to the calculated structure factors for La ($\Delta f' = -0.44$ and $\Delta f'' = 2.86$).[24] The positional and anisotropic thermal parameters derived from the last cycle of least-squares refinement are listed in Tables I and II, along with the standard deviations derived from the inverse matrix of this last cycle.[25]

TABLE I

POSITIONAL PARAMETERS FOR $La(NO_3)_3(C_{10}H_8N_2)_2$ WITH STANDARD DEVIATIONS IN PARENTHESES

Atom	x	y	z
La	0	0.0969 (1)	0.25
N(1)	0.0761 (6)	−0.1331 (11)	0.3135 (7)
N(2)	0.1326 (6)	−0.0116 (12)	0.1733 (7)
C(1)	0.1489 (7)	−0.1646 (15)	0.2902 (8)
C(2)	0.1932 (9)	−0.2757 (18)	0.3308 (9)
C(3)	0.1565 (11)	−0.3578 (19)	0.3968 (11)
C(4)	0.0798 (9)	−0.3277 (17)	0.4225 (9)
C(5)	0.0413 (8)	−0.2114 (16)	0.3768 (8)
C(6)	0.1595 (8)	0.0912 (17)	0.1044 (9)
C(7)	0.2391 (9)	0.0925 (18)	0.0800 (10)
C(8)	0.2918 (8)	0.0073 (18)	0.1303 (11)
C(9)	0.2632 (7)	−0.0792 (16)	0.1999 (10)
C(10)	0.1836 (6)	−0.0753 (14)	0.2201 (8)
N(3)	0.0862 (6)	0.1899 (13)	0.4168 (8)
O(1)	0.0223 (5)	0.1269 (10)	0.4219 (6)
O(2)	0.1171 (5)	0.1959 (11)	0.3414 (6)
O(3)	0.1178 (7)	0.2357 (16)	0.4834 (7)
N(4)[a]	−0.0169 (10)	0.4193 (19)	0.2666 (12)
O(4)[a]	−0.0519 (15)	0.3407 (28)	0.3206 (20)
O(5)[a]	0.0304 (15)	0.3635 (26)	0.2152 (20)
O(6)[a]	−0.0260 (11)	0.5455 (23)	0.2643 (15)

[a] These atoms constitute the "half" nitrate ion which was refined isotropically (see text). The thermal parameters (in Å^2) are as follows: O(4), 6.42 (76); O(5), 6.26 (80); O(6), 6.86 (58), and N(4), 2.72 (40).

Results and Discussion

A view of the bis(bipyridyl)lanthanum trinitrate complex, illustrating the relative orientation and magnitudes of the thermal ellipsoids and giving the atom numbering system, is depicted in Figure 2. Qualitatively the pattern of thermal motion seems physically reasonable and the isotropic parameters obtained for the disordered nitrate group (2) are realistic and compare with those obtained for nitrate 1. Because of the disorder an individual complex molecule has no inherent symmetry although, in subsequent discussion of the geometry of the coordination polyhedron, C_2 point symmetry will be assumed.

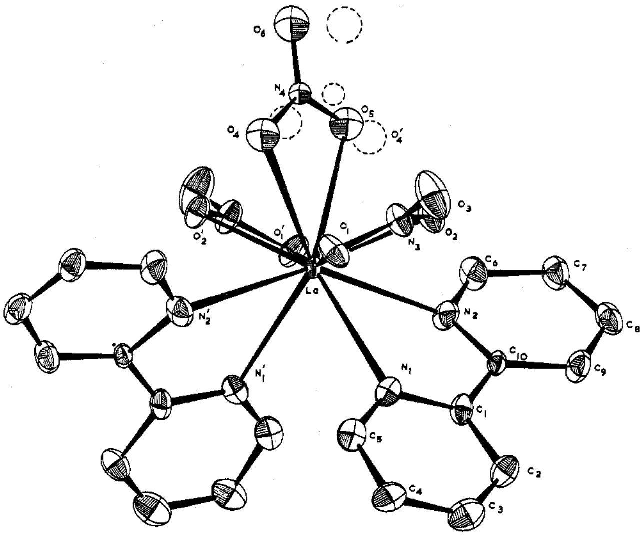

Figure 2.—The $La(NO_3)_3(C_{10}H_8N_2)_2$ molecule projected onto (001) and illustrating the orientations and relative magnitudes of the thermal ellipsoids. The position of one of the "half" nitrate ions is indicated by broken lines.

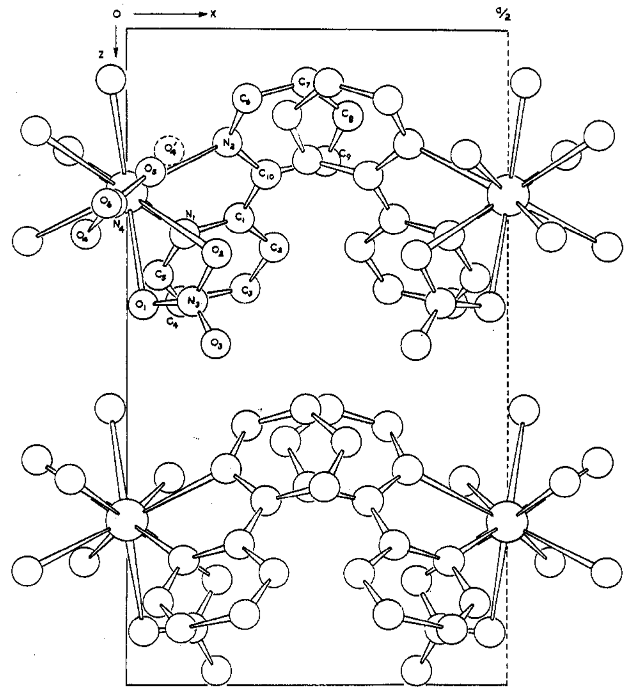

Figure 3.—The contents of one "half" unit cell projected onto the (010) plane illustrating the molecular packing. Only one of the "half" nitrates is included.

The static disorder of nitrate 2 appears to be a consequence of the molecular packing. The molecules stack "nose to tail" along the crystallographic two-fold axis such that the nitrate group occupies the region between the two bipyridyl rings 1 and 1'. The relevant intermolecular distances involved here are those between the terminal oxygen atom O(6) and N(1), C(4), and C(5) of the complex molecule with coordinates x, $1 + y$, z. These distances are 3.28 (2), 3.19 (2), and 3.08 (2) Å, respectively. A view of the contents of one half-unit cell projected onto (010) is illustrated in Figure 3. No mention is made of the presence of a similar static disorder in the isostructural terbium complex,[10] and it is possible that the significant changes in molecular dimensions lead to sufficient change in intermolecular contacts, to eliminate such a disorder.

The Coordination Geometry.—Details of the bond

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[22] D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).

[23] "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, Table 3.3.1A.

[24] D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).

[25] A listing of structure factor amplitudes will appear immediately following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth Street, N.W., Washington, D. C. 20036, by referring to code number INORG-72-2293. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

TABLE II

ANISOTROPIC THERMAL PARAMETERS (Å^2) FOR $La(NO_3)_3(C_{10}H_8N_2)_2$ WITH STANDARD DEVIATIONS IN PARENTHESES[a]

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
La	1.38 (4)	2.73 (4)	2.94 (5)	0	0.16 (4)	0
N(1)	3.09 (50)	3.44 (52)	2.57 (46)	0.45 (41)	−0.02 (38)	−0.32 (42)
N(2)	2.88 (44)	4.04 (54)	2.90 (47)	0.20 (45)	0.43 (38)	−0.40 (45)
C(1)	2.23 (51)	3.96 (63)	2.89 (52)	−0.06 (50)	0.01 (43)	−0.18 (52)
C(2)	4.93 (74)	5.49 (84)	3.32 (63)	1.62 (69)	−0.47 (58)	0.32 (64)
C(3)	7.02 (103)	5.71 (94)	4.52 (78)	1.94 (82)	−0.94 (73)	0.39 (70)
C(4)	6.09 (88)	4.51 (73)	3.14 (61)	1.11 (68)	−0.68 (61)	0.38 (60)
C(5)	3.93 (62)	4.87 (73)	2.08 (51)	0.29 (59)	−0.24 (49)	−0.46 (56)
C(6)	3.96 (58)	5.13 (91)	3.41 (61)	0.19 (60)	1.15 (52)	0.63 (60)
C(7)	3.47 (71)	5.93 (85)	5.85 (76)	−0.57 (67)	1.85 (64)	−0.95 (75)
C(8)	2.43 (58)	5.49 (81)	6.60 (87)	−0.75 (66)	1.55 (62)	−2.24 (75)
C(9)	2.41 (58)	4.69 (73)	5.46 (69)	0.43 (54)	1.23 (54)	−1.15 (69)
C(10)	1.85 (46)	3.56 (60)	3.38 (59)	0.70 (47)	−0.13 (42)	−1.24 (49)
N(3)	2.58 (51)	5.24 (62)	3.72 (58)	−1.05 (48)	−0.34 (47)	−0.44 (50)
O(1)	4.00 (51)	4.86 (49)	2.89 (35)	−1.82 (38)	0.25 (31)	−0.29 (35)
O(2)	2.64 (38)	5.89 (55)	3.14 (41)	−1.02 (38)	0.70 (35)	−0.52 (39)
O(3)	6.09 (63)	12.65 (102)	4.35 (55)	−4.14 (64)	−1.05 (51)	−0.86 (63)

[a] The form of the anisotropic thermal parameter is given by $\exp[-(\Sigma_i\Sigma_j h_ih_jr_i^*r_j^*B_{ij})/4]$ with i, j = 1, 2, 3 where r_i^* is the ith reciprocal axis.

distances and angles involving the metal atom and the equations of various weighted least-squares planes through the coordination polyhedron are listed in Table III. The lanthanum atom is ten-coordinate with average La–N and La–O bond distances of 2.66 (1) and 2.60 (1) Å, respectively.

TABLE III

DIMENSIONS OF THE COORDINATION POLYHEDRON WITH STANDARD DEVIATIONS IN PARENTHESES

(i) Bond Distances (Å) and Angles (Deg)

La–N(1)	2.655 (10)	La–N(2)	2.658 (9)
La–O(1)	2.608 (8)	La–O(2)	2.590 (8)
La–O(4)	2.628 (27)	La–O(5)	2.559 (26)
N(1)–La–N(2)	60.1 (3)	N(1)–La–N′(2)	91.8 (3)
N(1)–La–O(1)	70.2 (3)	N(1)–La–O(2)	73.2 (3)
N(2)–La–O(2)	70.7 (3)	N′(2)–La–O(1)	74.5 (3)
N(2)–La–O′(4)	77.9 (6)	O(2)–La–O′(4)	69.6 (6)
O_2–La–O(4)	75.6 (6)	O(2)–La–O(1)	48.0 (3)
O(1)–La–O(4)	64.2 (6)	O(4)–La–O(5)	48.4 (10)
O_1–La–O′(1)	167.9 (4)		
N(1)–La–N′(1)	74.6 (5)[a]	O(4)–La–O′(4)	63.2 (10)[a]
N(2)–La–N′(2)	145.7 (5)[a]	O(2)–La–O′(2)	138.9 (4)[a]

(ii) Intramolecular Nonbonded Distances (Å)[b]

a	N(1)–N′(1)	3.219 (14)	O(4)–O′(4)	2.755 (39)
m	N(1)–O(2)	3.128 (15)	N(2)–O′(4)	3.323 (30)
g	N(1)–N(2)	2.659 (14)	O(4)–O′(2)	2.976 (15)
g′	N(1)–N′(2)	3.814 (14)	O(4)–O(2)	3.197 (5)
b	N(2)–O(2)	3.037 (14)		
b′	O(1)–O(2)	2.115 (12)	O(1)–N′(2)	3.188 (13)
c	O(1)–N(1)	3.027 (12)	O(1)–O(4)	2.783 (14)

(iii) Equations of Least-Squares Planes[c]

Atoms	Plane	*l*	*m*	*n*	*d*
O(2), O′(2), N(1), N′(1)	1	−0.5730	0.0	0.8195	3.055
La, O(4), O′(4)	2	0.7391	0.0	0.6737	2.514
N(2), N′(2), O(4), O′(4)	3	0.5030	0.0	0.8640	3.220
La, N′(2), O(1), O(2)	4	0.3642	0.9292	0.0631	0.590

Distances from Planes (Å × 10^3)

1	O(2) (−25)	O′(2) (25)	N(1) (30)	N′(1) (−30)
3	O(4) (−475)	O′(4) (475)	N(2) (−155)	N′(2) (155)
4	La (0)	N(2) (−23)	O(2) (−27)	O(1) (45)

[a] These angles correspond to the trapezoidal plane angles $2\theta_A$ and $2\theta_B$ of dodecahedral geometry: J. L. Hoard and J. V. Silverton, *Inorg. Chem.*, **2**, 235 (1963). [b] The intramolecular distances are classified according to the polyhedron edges of the D_2 ten-coordinate geometry and these are indicated in Figure 4(ii). [c] Defined as $lX + mY + nZ = d$ where the orthogonal axes X, Y, and Z are coincident with the orthorhombic cell axes. The weights w_i assigned to the ith atom in calculating the least-squares planes were evaluated as $w_i = 1/(a\sigma_x b\sigma_y c\sigma_z)^{2/3}$.

The lanthanum–oxygen bond distances are comparable with the La–O distances found in the EDTA complexes $La(H_2O)_4HA$[8] and $La(H_2O)_3A^-$[26] (where H_4A = EDTA) and in $La_2(CO_3)_3 \cdot 8H_2O$,[11] while the La–N distances are appreciably shorter than those found in the EDTA complexes by *ca.* 0.1–0.2 Å. It appears that the steric constraints of the ligand are instrumental in producing the long La–N bonds in the latter complexes.

The La–O and La–N distances are significantly longer than the corresponding distances in the terbium complex,[10] but these differences are in keeping with the contraction in the size of the lanthanides on passing to higher members of the series, and in fact the differences are closely comparable with the difference in the ionic radii of the two metal ions, namely, 0.14 Å.

Ligand Geometries.—The bond distance and angle data and least-squares planes information, pertinent to the bipyridyl and nitrate ligands, are listed in Table IV. Although the standard deviations for nitrate 2 are appreciably higher than those of nitrate 1, the same trend in N–O bond distances is observed for both groups, namely, that the terminal bond is apparently shorter than the two N–O bonds involved in coordination to the metal. While in the present case the deviations from the D_{3h} geometry of the free ion are possibly only just significant and are consistent with the predominantly ionic binding of the nitrate, the features of C_{2v} geometry with a shorter terminal N–O bond (*vide supra*) and an O–N–O angle in the chelate ring <120° are now well characterized where nitrate functions as a bidentate ligand.[27] In the strongly covalent nitrates $Ti(NO_3)_4$[28] and $Co(NO_3)_3$[29] the terminal bonds average 1.19 Å while the two N–O bonds involving the coordinated oxygens are much longer and average 1.29 Å.

The lanthanum atom lies significantly out of the planes of both nitrate groups by 0.31 and 0.34 Å for

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TABLE IV

LIGAND DIMENSIONS

(a) Bipyridyl Molecule

(i) Distances (Å) and Angles (Deg)

Ring 1		Ring 2	
C(1)–N(1)	1.326 (15)	C(6)–N(2)	1.340 (20)
C(5)–N(1)	1.328 (16)	C(10)–N(2)	1.363 (16)
C(1)–C(2)	1.405 (20)	C(6)–C(7)	1.409 (20)
C(2)–C(3)	1.392 (23)	C(7)–C(8)	1.411 (21)
C(3)–C(4)	1.395 (24)	C(8)–C(9)	1.394 (22)
C(4)–C(5)	1.426 (20)	C(9)–C(10)	1.412 (17)
C(1)–C(10)	1.450 (17)		
C(1)–N(1)–C(5)	119.3 (10)	C(6)–N(2)–C(10)	119.4 (11)
N(1)–C(1)–C(2)	123.5 (11)	N(2)–C(6)–C(7)	122.4 (12)
C(1)–C(2)–C(3)	117.1 (13)	C(6)–C(7)–C(8)	117.3 (14)
C(2)–C(3)–C(4)	120.7 (15)	C(7)–C(8)–C(9)	119.2 (14)
C(3)–C(4)–C(5)	116.9 (13)	C(8)–C(9)–C(10)	119.0 (12)
C(4)–C(5)–N(1)	122.6 (11)	C(9)–C(10)–N(2)	121.4 (12)
N(1)–C(1)–C(10)	116.3 (10)	N(2)–C(10)–C(1)	116.3 (11)
C(2)–C(1)–C(10)	120.3 (11)	C(9)–C(10)–C(1)	121.9 (11)

(ii) Least-Squares Plane Parameters (Å)

	l	*m*	*n*	*d*
Ring 1	0.3318	0.6424	0.6908	2.873
Ring 2	0.1602	0.7574	0.6330	2.065

Distances (Å × 10^3)

C(1)	C(2)	C(3)	C(4)	C(5)	N(1)
(−8)	(8)	(−5)	(2)	(−2)	(5)
C(6)	C(7)	C(8)	C(9)	C(10)	N(2)
(−5)	(−11)	(16)	(−6)	(−11)	(16)

(b) Nitrate Ions

(i) Distances and Angles

$NO_3(1)$		$NO_3(2)$	
O(1)–N(3)	1.238 (14)	O(4)–N(4)	1.237 (31)
O(2)–N(3)	1.243 (14)	O(5)–N(4)	1.222 (31)
O(3)–N(4)	1.207 (16)	O(6)–N(4)	1.170 (27)
O(1)–N(3)–O(2)	117.1 (11)	O(4)–N(4)–O(5)	119.2 (25)
O(1)–N(3)–O(3)	120.6 (11)	O(4)–N(4)–O(6)	122.1 (21)
O(2)–N(3)–O(3)	122.5 (12)	O(5)–N(4)–O(6)	118.8 (22)

(ii) Least-Squares Plane Parameters (Å)

	l	*m*	*n*	*d*
$NO_3(1)$	0.4534	−0.8787	0.1493	0.083
$NO_3(2)$	0.7290	0.1273	0.6725	2.962

Distances (Å × 10^3)

O(1) (5)	O(2) (5)	O(3) (6)	N(3) (−18)
O(4) (−4)	O(5) (2)	O(6) (−2)	N(4) (11)

groups 1 and 2, respectively, although the two nitrates are themselves planar.

Each individual pyridine ring of the bipyridyl ligand is planar, but there is a rotation around the C(1)–C(10) bond to give a small dihedral angle of 12.4° between the two rings. A similar dihedral angle is found in the analogous terbium complex,[10] while a range of angles from 12 to 26° is found for angles involving the rings of the terpyridyl (terpy) ligands in $Eu(terpy)_3(ClO_4)_3$.[30] The lanthanum atom is displaced from the plane of ring 1 by 0.275 Å and from ring 2 by 0.97 Å. It would appear that these displacements and the nonplanarity of the bipyridyl (and terpyridyl) ligands arise at least to some extent from the size of the metal atom which does not allow it to be coplanar with the ligand, rather than from intraligand nitrogen lone pair interactions. The average C–N and C–C bond distances of 1.339 (12) and 1.406 (13) Å, respectively, compare with 1.36 and 1.39 Å determined for the free ligand[31] and the pattern of intra-ring angles is similar in both rings 1 and 2. One might anticipate that angles N(1)–C(1)–C(10) and N(2)–C(10)–C(1) would be 120° or slightly larger. That they are significantly less than this might be attributable to the formation of the chelate ring.

Discussion of Ten-Coordination Polyhedra.—Owing to the fixed separations of the donor atoms in the nitrate and bipyridyl ligands, the coordination polyhedron would not be expected to be very symmetrical. However, it is useful to discuss the structural results for this molecule and those for some other ten-coordinate species in terms of alternative idealized polyhedra. We have accordingly evaluated the relative stabilities of three such polyhedra on the basis of ligand–ligand repulsions, using the methods described by Hoard and Silverton in their treatment of eight-coordination.[32] The two common eight-coordination geometries, the square antiprism and the dodecahedron, in fact provide the bases of the "idealized" ten-coordinate polyhedra,[1] one of the latter, the bicapped square antiprism, maintaining the full point symmetry D_{4d} of the parent polyhedron. The other two polyhedra considered are based on the dodecahedron. One has the additional ligands on one of the nonprincipal twofold axes and in the nomenclature of ref 1 is termed a bicapped dodecahedron of D_2 symmetry,[33] while the second has C_{2v} symmetry and has two of the trans B type positions of the original dodecahedron, each "divided" between two ligands. All three polyhedra are depicted in Figure 4.

Assuming equivalent metal–ligand distances, the bicapped square antiprism requires only one angular parameter to describe its shape. This is the angle of inclination, θ, of the metal–ligand bonds in the square-antiprismatic set (positions A) to the fourfold axis and is then defined as for eight-coordination.[32] In the bicapped dodecahedron (Figure 4(ii)) the two trapezoidal planes labeled BAAB are no longer constrained to be perpendicular as in the D_{2d} polyhedron, so that in addition to the angular parameters θ_A and θ_B, defined as for eight-coordination,[32] a third parameter θ_C defining the relative orientation of the two planes is also required. The bonds to ligand positions C are then inclined at $(90° - \theta_C/2)$ to either of the trapezoidal planes. The C_{2v} polyhedron (Figure 4(iii)) requires five angular parameters for its description, if different angles are introduced for the nonequivalent planes BAAB and B′A′A′B′. (Since B′ is not a ligand site but the midpoint of the edge *c*, the latter is not a real plane.) The angular parameters are then θ_A, θ_B, $\theta_{A'}$, and $\theta_{B'}$ defined as for the D_{2d} dodecahedron and θ_C which gives the angular separation of the C position ligands.

The calculations of the relative stabilities of the three polyhedra were carried out assuming the repulsive energy between the ligands U_R to arise solely from the Born term, *i.e.*

$$U_R = U_B = k \sum_{i \neq j} d_{ij}^{-n}$$

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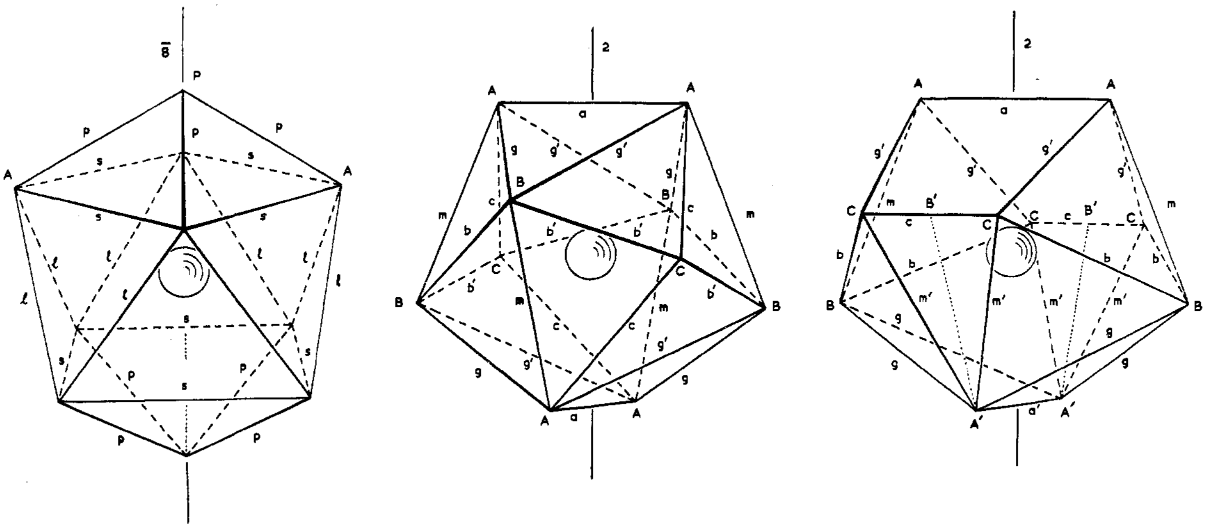
(30) G. H. Frost, F. A. Hart, C. Heath, and M. B. Hursthouse, *Chem. Commun.*, 1421 (1969).

(31) L. L. Merritt, Jr., and E. D. Schroeder, *Acta Crystallogr.*, **9**, 801 (1956).

(32) J. L. Hoard and J. V. Silverton, *Inorg. Chem.*, **2**, 235 (1963).

(33) The term "capped" usually refers to the placement of a ligand over a face of the polyhedron while in the present case the ninth and tenth ligands are located over an edge of type b, of the eight-coordination polyhedron, and on a C_2 axis.



(i) (ii) (iii)

Figure 4.—Framework diagrams of three idealized ten-coordination polyhedra: (i) the bicapped square antiprism (D_{4d}); (ii) the bicapped dodecahedron (D_2); (iii) the C_{2v} polyhedron based on a dodecahedron. The labeling of the polyhedron edges follows, as far as is possible, that for the parent eight-coordination polyhedra[32] and in (iii) the dotted lines A′B′ indicate the location of the original trapezoidal plane in the dodecahedron.

with the summation taken over all 45 ligand separations d_{ij}. Coulombic contributions and shielding by the central atom were neglected. The repulsive energy U_R can then be written as kYr^{-n} where r is the metal to ligand distance, n is the Born exponent, and Y is a geometrical factor involving the angular parameters described above. The preferred polyhedron of a given symmetry is that characterized by the minimum value of Y and the calculations involved the variation of the angular parameters for a given geometry, in sequence, in order to locate the minimum. The calculations were carried out for a variety of values of n.

As might be evident from an examination of the polyhedron geometries, the bicapped square antiprism is the most stable arrangement for all values of n, and for $n = 7$, which is that anticipated for neon-shell-like ligands,[34] the difference in repulsive energy between the D_{4d} and the C_{2v} and D_2 polyhedra amounts to *ca.* 7 kcal/mol for a metal–ligand distance of 2.50 Å, or to approximately 11% of the total repulsive energy (taking k to be 3400 kcal/(mol Å)).[32] The angles θ and θ_A, θ_B, and θ_C for the most favorable polyhedra of D_{4d} and D_2 symmetries are, with those for the eight-coordination geometries in parentheses, 64.8 (57.3) and 32.8 (35.2), 77.0 (73.5), and 60.0° (90.0°), respectively, while for the C_{2v} polyhedron, the five angles defining the most favorable arrangement are $\theta_A = 32.8$, $\theta_B = 65.8$, $\theta_{A'} = 34.9$, $\theta_{B'} = 77.8$, and $\theta_C = 63.8°$.

Despite the apparent preference for the D_{4d} polyhedron, only relatively small angle changes are needed to convert this into the D_2 or C_{2v} polyhedron and this point is masked by the conventional framework diagrams. For the $D_{4d} \rightarrow D_2$ rearrangement, the changes are identical in type with those needed to interconvert the parent eight-coordinate polyhedra.

The gold complex $Au[Au_{10}((C_6H_5)_3P)_7(SCN)_3]$ is the only ML_{10} species to have been structurally characterized,[9] but no assessment of the coordination polyhedron in terms of the models discussed above can be made from the published data. Two complexes containing bidentate ligands which achieve ten-coordination through polymer formation are uranium(IV) acetate, $U(CH_3COO)_4$,[35] and the thorium oxalate species $K_4Th(C_2O_4)_4 \cdot 4H_2O$.[12] The latter is pertinent to our present discussion, as the observed polyhedron dimensions correspond almost exactly with those predicted for the D_{4d} polyhedron having a ratio of metal–ligand distances to the axial (P) and A sites of 1.05. This value is very close to that determined experimentally and the additional stabilization achieved in the polyhedron with the relatively longer axial bonds is 4.5 kcal/mol. The calculated values, with observed values for the thorium complex in parentheses, are as follows: square edges, s, 3.13 Å (3.11 Å); pyramidal edges, p, 2.67 Å (2.67 Å); and equatorial edges, l, 2.74 Å (2.76 Å). A monomeric ten-coordinate complex of cerium, $Ce(NO_3)_4[(C_6H_5)_3PO]_2$, whose stoichiometry might be considered compatible with the D_{4d} polyhedron with the phosphine oxide ligands occupying the axial sites P and the four nitrates chelating edges of type l, only exhibits a slight resemblance to this geometry.[13] Although the phosphine oxides are trans, the O–Ce–O arrangement deviates considerably from linearity.

Two framework diagrams illustrating the coordination polyhedron in the lanthanum complex described here are given in Figure 5. For the discussion of the coordination geometry we assume C_2 point symmetry with atoms O(4) and O′(4) defining the polyhedron edge involving the disordered nitrate.

In terms of a D_{4d} description, atoms O(1) and O′(1) occupy the axial positions P, while N(1), N′(2), O(2), and O(4) define one set of square edges, s. However, this set of four atoms deviates appreciably from the coplanarity expected for this polyhedron. On the other hand, atoms O(2), N(1), N′(1), and O′(2) together with the lanthanum atom are almost coplanar

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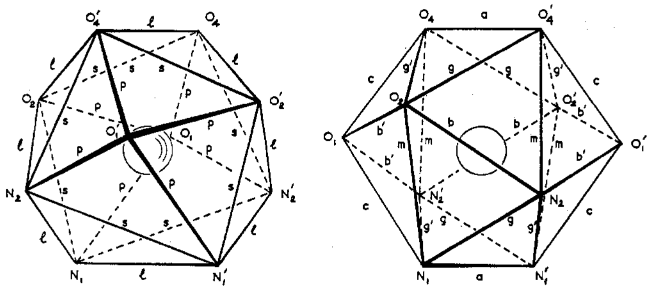

(i) (ii)

Figure 5.—Framework diagrams of the coordination polyhedron in $La(NO_3)_3(C_{10}H_8N_2)_2$ projected onto (001) and (100), respectively. In (i) the edges are labeled according to the D_{4d} geometry while those in (ii) are labeled according to the D_2 polyhedron.

and define one of the trapezoidal planes of a dodecahedral-based geometry. For the D_2 polyhedron, atoms O(4), O′(4), N(2), and N′(2) would define the second trapezoidal plane (although they are far from coplanarity) while O(1) and O′(1) occupy ligand sites C. The angle between the two trapezoidal planes, 1 and 3 in Table III(iii), is 65.2°. In terms of the nomenclature in Figure 4(ii), the bipyridyl ligands chelate edges of type g, nitrate group 2 chelates an edge of type a, and nitrate groups 1 chelate edges of type b′. In addition atoms O(1), O(2), and N′(2) and the metal atom are almost coplanar and this is anticipated for the D_2 geometry, the additional ligands being located on a C_2 axis.[33]

Alternatively, in terms of the C_{2v} polyhedron, atoms O(2), N(1), N′(1), and O′(2) define the trapezoidal plane BAAB (Figure 4(iii)) and the bipyridyl molecules chelate edges of type g′. Nitrate group 2 (atoms O(4) and O′(4)) then occupies sites A′ while groups 1 chelate edges of type b. However, although the plane through the lanthanum atom and O(4) and O′(4) (plane 2 in Table III(iii)) is approximately perpendicular to the trapezoidal plane as expected for the C_{2v} geometry, the four atoms occupying the C sites of the polyhedron, O(1), O′(1), N(2), and N′(2), are very far from being coplanar. On the basis of general shape criteria and reference to the polyhedron planes discussed above, we therefore prefer the description of the polyhedron in terms of the D_2 geometry. Reference to least-squares plane data has also enabled a more rigorous description of eight-coordination polyhedra to be made in several instances than that which is obtained from purely angle deviations.[36]

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CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, UNIVERSITY OF ILLINOIS AT CHICAGO CIRCLE,
CHICAGO, ILLINOIS 60680, AND HARVARD UNIVERSITY, CAMBRIDGE, MASSACHUSETTS 02138

Structural Studies on Clathro Chelate Complexes. II. Stereochemistry Intermediate between Octahedral and Trigonal Prismatic for d^6 Iron(II) in Crystalline $[\{FB(ONCHC_5H_3N)_3P\}Fe^{II+}][BF_4^-]\cdot CH_2Cl_2$

BY MELVYN ROWEN CHURCHILL* AND ARTHUR H. REIS, JR.

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[Fluoroborotris(2-aldoximo-6-pyridyl)phosphine]iron(II) tetrafluoroborate crystallizes from dichloromethane as the solvated species $[\{FB(ONCHC_5H_3N)_3P\}Fe^{II+}][BF_4^-]\cdot CH_2Cl_2$. Crystals belong to the centrosymmetric monoclinic space group $C2/c$ (C_{2h}^6; No. 15), unit cell parameters being $a = 19.847$ (20), $b = 10.514$ (15), $c = 24.193$ (43) Å, and $\beta = 105.08$ (8)°. Observed and calculated densities are 1.75 ± 0.01 and 1.77 g cm^{-3} (for $Z = 8$), respectively. A total of 2181 independent nonzero reflections were collected with a 0.01°-incrementing Supper-Pace diffractometer ($\sin \theta_{max} = 0.38$, Mo Kα radiation). The structure was solved by conventional Patterson, Fourier, and least-squares refinement techniques, the final discrepancy index being $R_F = 7.50\%$. The central iron(II) atom is coordinated to six nitrogen atoms with Fe–N(aldoximo) = 1.921 (7)–1.943 (8) Å and Fe–N(pyridyl) = 1.972 (7)–1.984 (8) Å. The cation is severely distorted from its possible (idealized) C_{3v} symmetry such that the triangle defined by the three pyridyl nitrogen atoms is rotated by approximately 21.7° relative to the triangle defined by the three aldoximo nitrogen atoms. The overall coordination geometry about iron is thus intermediate between trigonal prismatic and octahedral.

Introduction

Holm and his coworkers have reported[1,2] the synthesis of Fe(II), Co(II), Ni(II), and Zn(II) complexes of the bicyclic hexadentate encapsulation (or "clathro chelate") ligand $[FB(O\dot{N}CHC_5H_3\dot{N})_3P^-]$. We have previously[3,4] shown that the d^8 Ni(II) derivative adopts a configuration such that the metal's coordination environment approaches the ideal trigonal-prismatic case.

While the $[FB(ONCHC_5H_3N)_3P^-]$ ligand is designed especially to impose a trigonal-prismatic geometry upon a first-row transition metal, there are two main factors which may act to prevent this. (1) The metal atom may be smaller (or larger) than the cavity within

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* Address all correspondence to this author at the University of Illinois at Chicago Circle.

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