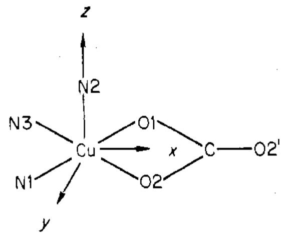
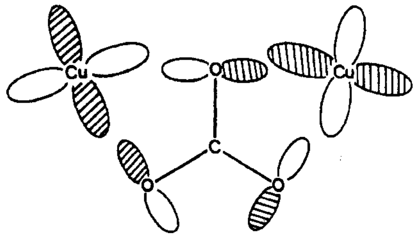


II

With these guidelines, and the geometry of the dimer, it is not a difficult task to sketch metal and carbonate orbitals which, upon overlap, would provide an effective route for strong exchange interaction (III).

It would be interesting, of course, to see if calculations of the type that were successful for the oxalate and squarate systems[9] are able not only to support the assignment above but also to give some quantitative interpretation of the observed diamagnetism resulting from exchange. Furthermore, the question as to whether consideration of the linear CuO1Cu



III

system is sufficient to account for the diamagnetism or whether symmetrical bridging via the entire carbonate anion is the essential structural parameter will require further theoretical inspection.

Acknowledgment. We wish to thank Professor Neil Curtis for the gift of the sample and for his continued interest in this work and the National Research Council of Canada for financial support.

Registry No. $[[Cu(L2)]_2CO_3](ClO_4)_2\cdot DMF$, 72784-64-6.

Supplementary Material Available: Listings of structure factor amplitudes and calculated hydrogen atom fractional coordinates (20 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Structural Chemistry,
Arrhenius Laboratory, University of Stockholm, Fack, S-10691 Stockholm, Sweden,
and the Department of Chemistry, Helsinki University of Technology, SF-02150 Espoo 15, Finland

Crystal and Molecular Structure of the Undecacoordinate Complex Pentaaquatris(nitrato)lanthanum(III) Hydrate

BIRGITTA ERIKSSON,*[1a] LARS OLOF LARSSON,[1a] LAURI NIINISTÖ,*[1b] and JUSSI VALKONEN[1b]

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The crystal and molecular structure of pentaaquatris(nitrato)lanthanum(III) hydrate, $[La(NO_3)_3(H_2O)_5]\cdot H_2O$, has been determined from 3102 reflections collected by counter methods. The complex crystallizes in the triclinic space group $P\bar{1}$ with two formula units in a cell of dimensions a = 8.933 (5) Å, b = 10.723 (4) Å, c = 6.664 (2) Å, α = 78.86 (3)°, β = 77.92 (4)°, and γ = 87.93 (4)°. The structure was solved by Patterson and Fourier techniques and refined by least-squares calculations to a final conventional R value of 0.038. The lanthanum atom is 11-coordinate, being bonded to three bidentate nitrate groups and five water molecules. The La–O(nitrate) and La–O(water) distances are in the ranges 2.617–2.875 and 2.526–2.668 Å, respectively. The N–O bond lengths vary between 1.219 and 1.280 Å; the shortest distances involve the noncoordinated oxygens. The sixth water molecule is outside the coordination sphere of lanthanum but participates in the network of hydrogen bonds.

Introduction

The geometries of high-coordination polyhedra with coordination numbers (CN) exceeding 9 have not been systematically analyzed, probably because of the relatively small number of structure determinations available. There exists thus a clear need for additional X-ray studies of reasonable accuracy. A high-coordination character is likely if the central ion is large, e.g., La^{3+} or Ce^{3+}, and the coordinating ligands are compact. The nitrate ion is a suitable ligand since, besides being relatively small, it often coordinates bidentately with a short bite. Accordingly an investigation into the nitrato complexes of trivalent lanthanum was initiated as part of a larger project concerning the structures of high-coordinate oxo complexes.[2-5]

The present paper describes the X-ray structural analysis of lanthanum nitrate hexahydrate, which is an 11-coordinate complex corresponding to the formula $[La(NO_3)_3(H_2O)_5]\cdot H_2O$.[4] According to the X-ray powder data, the cerium nitrate hexahydrate is isostructural, but the lanthanum and cerium compounds differ from the nitrate hexahydrates of the heavier lanthanoids;[6] a structural analysis carried out for the praseodymium compound has shown it to have a 10-coordinate structure $[Pr(NO_3)_3(H_2O)_4]\cdot 2H_2O$.[7]

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Table I. Details of Data Collection

(A) Crystal Parameters at 25 °C

cryst system	triclinic	V, Å^3	612.4
space group	$P\bar{1}$	Z	2
a, Å	8.933 (5)	mol wt	433.01
b, Å	10.723 (4)	d(obsd), g cm^{-3}	2.35 (2)
c, Å	6.664 (2)	d(calcd), g cm^{-3}	2.347
α, deg	78.86 (3)	abs coeff, cm^{-1}	34.9
β, deg	77.92 (4)		
γ, deg	87.91 (4)		

(B) Collection of Intensity Data

diffractometer	Syntex $P2_1$
radiation	Mo Kα = 0.710 69 Å
monochromator	highly oriented graphite
reflctns measd	$\pm h, \pm k, +l$
method	θ–2θ
2θ range, deg	5–60
scan speed, deg/min	1–3
scan range, deg	$(2\theta(\text{Mo K}\alpha_1) - 1.1)°$ – $(2\theta(\text{Mo K}\alpha_2) + 1.1)°$
bkgd measmt	at the beginning and end of the 2θ scan, each measurement for half of the total scan time
stds	3 reflections after each batch of 57; a linear decrease in intensity was corrected
no. of data collected	3613
no. of obsd unique data with $\sigma(I_{\text{net}})/I_{\text{net}} < 0.33^a$	3548

[a] $I_{\text{net}} = I_{\text{tot}} - I_{\text{back}}$; $\sigma(I_{\text{net}}) = (I_{\text{tot}} + I_{\text{back}})^{1/2}$; I_{tot} = counts for the total intensity; I_{back} = counts for the total background intensity.

Experimental Section

Well-formed crystals of $La(NO_3)_3 \cdot 6H_2O$ were produced at room temperature by dissolving La_2O_3 (99.9%; Kemira Oy, Finland) in aqueous nitric acid and recrystallizing twice. A crystal of approximate dimensions 0.3 × 0.3 × 0.4 mm was chosen for the X-ray diffraction study; the crystal had to be covered with several thin layers of shellac because of its instability in air. Unit cell dimensions were obtained from refinement of the angular settings for 25 reflections measured with a Syntex $P2_1$ diffractometer and were found to be in agreement with published data.[8] The intensity data were collected with the same diffractometer. Net intensities were corrected for Lorentz and polarization effects, and a linear correction was made to compensate for the intensity decay observed during the data collection; no correction was applied for the absorption effects. The crystal data and intensity measurements are summarized in Table I.

A three-dimensional Patterson synthesis gave the position of the La atom, and its coordinates were refined by a block-diagonal least-squares program to an R value of 0.26 ($R = (\sum||F_o| - |F_c||)/\sum|F_o|$). The remaining nonhydrogen atoms were found by successive structure factor and electron density calculations, whereafter the reflections with $F_o < 10.0$ were omitted in order to minimize computing costs. This reduced the total number of reflections to 3102 ($F(000) = 410.0$). After a preliminary isotropic refinement ($R = 0.076$), anisotropic vibrational parameters were introduced, the R value dropped to 0.038, and the "goodness-of-fit" parameter $= (\sum(\text{NO}(|F_o| - |F_c|)^2)/(\text{NO} - \text{NV}))^{1/2} = 2.20$. Unit weights were used during all calculations, which were performed on the IBM 370/165 computing system at the University of Stockholm.[9] The scattering factors for La^{3+}, O, and N were those of Cromer and Mann.[10]

After the refinement was completed, an attempt was made to locate the hydrogen atoms of the water molecules from a difference Fourier map. The only significant features, however, were several maxima of 0.5 Å^{-3} in the vicinity of La. The final atomic positional and thermal parameters are given in Table II.[11] Bond distances and angles are shown in Tables III and IV, respectively.

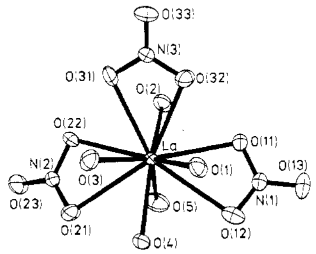

Figure 1. Perspective view of the $[La(NO_3)_3(H_2O)_5]$ complex with atomic numbering.

Description and Discussion of the Structure

The crystal structure of $La(NO_3)_3 \cdot 6H_2O$ is comprised of discrete pentaaquatris(nitrato)lanthanum(III) complexes and water of hydration which is associated with the complexes by a network of hydrogen bonds. A view of the $[La(NO_3)_3(H_2O)_5]$ complex is presented in Figure 1, which also shows the labeling of the atoms. A noteworthy feature of the complex is the 11-coordinate polyhedron around the central La atoms. Six of the coordination sites are occupied by three bidentate nitrate groups, and the remaining five ligands are water molecules.

No other lanthanum hydrate complex has been reported with CN = 11, but 11-coordination has been found in the thorium nitrates $Th(NO_3)_4 \cdot 5H_2O$[12] and $[Th(OH)(NO_3)_3(H_2O)_4]_2$[13] and recently also in the structure of a cerate(III) complex anion $[Ce(NO_3)_4(H_2O)_2(NC_5H_4 \cdot C_5H_4N)]$.[14] LaF_3 and CeF_3 are also reported to have an 11-fold coordination of fluorine atoms around the central lanthanoid;[15] two of the atoms are significantly more distant (>0.35 Å) than the others, however.

Coordination numbers 10 and 12 seem to be more favored and have been reported earlier in some La complexes. Thus, CN = 10 is reported in $La(NO_3)_3 \cdot 4(CH_3)_2SO$,[16] $La(NO_3)_3(C_{10}H_8N_2)_4$,[17] $La(OH_2)EDTA \cdot 3H_2O$,[18] $La_2(CO_3)_3 \cdot 8H_2O$,[19] and $[La(HEDTA)(H_2O)_2] \cdot 3H_2O$.[20] CN = 12 is found in $La_2Mg_3(NO_3)_{12} \cdot 24H_2O$[21] and for one of the two crystallographically different La^{3+} ions in the structure of $La_2(SO_4)_3 \cdot 9H_2O$.[22] In the complexes listed above the average La–O distance is 2.59 and 2.67 Å for CN = 10 and 12, respectively. In the present 11-coordinate complex, the average La–O distance is 2.66 Å.

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(8) *Natl. Bur. Stand.* (*U.S.*), *Monogr.* No. **25**, Section 8, 40 (1975).

(9) Programs utilized were the SHELX program package by G. M. Scheldrick and ORTEP II by C. K. Johnson.

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(11) For a listing of the observed and calculated structure factors, see the description of supplementary material at the end of the paper.

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Table II. Final Positional and Thermal[a] Parameters (×10⁴) with Estimated Standard Deviations in Parentheses

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
La	1974 (0)	2431 (0)	1493 (1)	133 (7)	124 (2)	182 (2)	−27 (1)	−8 (1)	−15 (1)
O(11)	1899 (7)	57 (6)	3420 (11)	250 (29)	239 (28)	537 (40)	21 (26)	41 (27)	33 (22)
O(12)	4241 (8)	528 (7)	1998 (13)	310 (35)	448 (40)	608 (47)	−18 (35)	23 (32)	−153 (29)
O(13)	6364 (9)	1407 (6)	6406 (14)	563 (48)	241 (33)	798 (59)	39 (35)	−131 (42)	123 (31)
O(21)	3253 (7)	4884 (6)	1298 (11)	226 (28)	325 (31)	485 (37)	−167 (27)	14 (25)	29 (23)
O(22)	859 (6)	4565 (5)	2691 (10)	219 (26)	217 (25)	438 (34)	−73 (23)	−28 (23)	−83 (20)
O(23)	8011 (7)	3765 (6)	6960 (11)	340 (32)	292 (31)	562 (41)	−264 (29)	−34 (29)	−44 (25)
O(31)	9078 (8)	3069 (6)	1134 (13)	402 (37)	173 (27)	725 (50)	41 (29)	−222 (34)	−89 (25)
O(32)	9579 (7)	1081 (6)	1201 (12)	242 (29)	334 (32)	627 (44)	−222 (31)	−109 (29)	45 (24)
O(33)	7262 (8)	1777 (8)	1212 (16)	224 (32)	518 (46)	1018 (70)	−78 (45)	−196 (39)	−87 (31)
O(1)	2591 (7)	1040 (6)	8506 (10)	356 (33)	289 (30)	389 (33)	−143 (25)	−20 (26)	−38 (24)
O(2)	146 (7)	2025 (6)	5116 (10)	283 (30)	291 (29)	337 (31)	−84 (24)	74 (24)	−55 (23)
O(3)	1760 (8)	3925 (6)	8081 (10)	373 (35)	372 (34)	317 (32)	34 (26)	−46 (26)	66 (27)
O(4)	4648 (7)	2995 (6)	9263 (11)	212 (28)	274 (29)	526 (40)	−70 (27)	64 (26)	−39 (22)
O(5)	3328 (8)	2659 (7)	4374 (10)	387 (35)	555 (42)	308 (32)	−51 (29)	−143 (27)	−139 (30)
O(6)	6038 (9)	4022 (8)	3766 (13)	476 (45)	592 (50)	558 (48)	53 (39)	−154 (37)	−88 (37)
N(1)	6715 (8)	300 (6)	6966 (6)	258 (32)	217 (30)	343 (35)	−46 (26)	−39 (27)	25 (24)
N(2)	7958 (7)	4746 (6)	7643 (10)	199 (28)	185 (27)	256 (30)	−68 (22)	−30 (23)	−8 (21)
N(3)	8602 (8)	1984 (7)	1176 (12)	221 (31)	216 (30)	415 (39)	−41 (28)	−85 (28)	−37 (24)

[a] The form of the anisotropic thermal factor is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

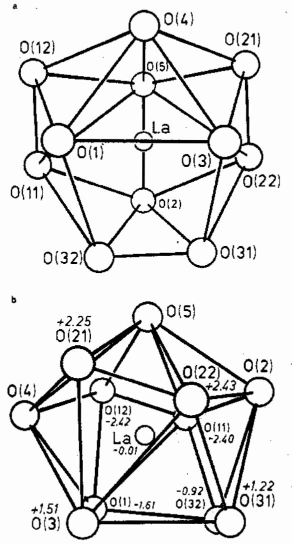

Figure 2. (a) Coordination around the lanthanum atom as viewed down the central points of O(1)–O(3) and O(2)–O(5). (b) Coordination polyhedron viewed perpendicular to the plane through atoms O(4), O(5), and O(2). The numbers represent the departures in angstrom units from the plane.

Table III. Bond Lengths (Å) with Estimated Standard Deviations in Parentheses

(A) Lanthanum Coordination Sphere

La–O(1)	2.668 (6)	La–O(11)	2.617 (6)
La–O(2)	2.585 (6)	La–O(12)	2.846 (7)
La–O(3)	2.554 (6)	La–O(21)	2.875 (6)
La–O(4)	2.560 (6)	La–O(22)	2.659 (6)
La–O(5)	2.526 (7)	La–O(31)	2.699 (6)
		La–O(32)	2.687 (6)

(B) Nitrate Groups

N(1)–O(11)	1.272 (9)	N(3)–O(31)	1.246 (9)
N(1)–O(12)	1.251 (10)	N(3)–O(32)	1.280 (8)
N(1)–O(13)	1.223 (10)	N(3)–O(33)	1.220 (10)
N(2)–O(21)	1.259 (9)		
N(2)–O(22)	1.268 (8)		
N(2)–O(23)	1.219 (9)		

The La–O(nitrate) bond lengths vary from 2.617 to 2.875 Å (Table III), but two of these distances, namely, La–O(12) and La–O(21) (2.846, 2.875 Å), are significantly longer than the others, as the average is 2.665 Å. This unsymmetrical binding of the nitrate groups is probably a result of the great number of coordinated water molecules. There is simply not space enough for all the oxygen atoms to be fitted around the La atom at the same distance.

Generally, the water oxygen atoms are found closer to the La atom than the nitrate oxygen atoms. The average La–O(water) distance is 2.579 Å, while the average La–O(nitrate) distance is 2.732 Å. According to Addison et al.,[23] a bidentate

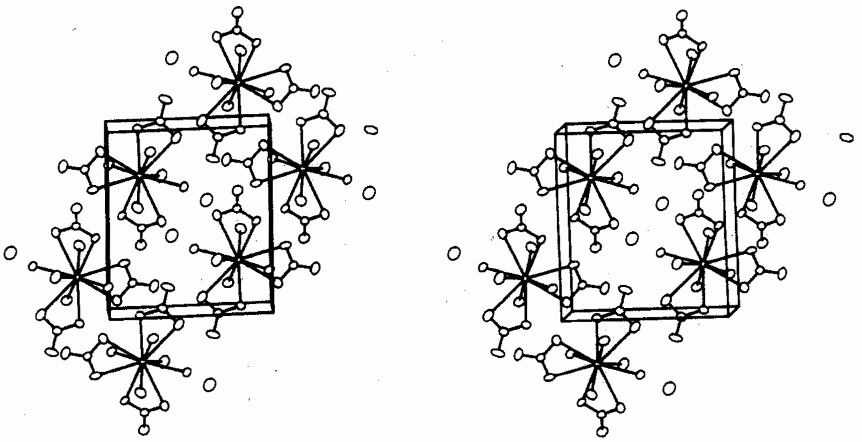

Figure 3. Stereoview of the structure showing the unit cell packing. With the origin in the upper right corner, a is horizontal, b is vertical, and c points into the paper.

Table IV. Angles (Deg) with Estimated Standard Deviations in Parentheses

(A) Lanthanum Coordination Sphere			
O(11)–La–O(12)	46.0 (2)	O(22)–La–O(3)	75.9 (2)
O(11)–La–O(32)	65.2 (2)	O(22)–La–O(5)	75.6 (2)
O(11)–La–O(1)	73.9 (2)	O(31)–La–O(32)	47.2 (2)
O(11)–La–O(2)	66.4 (2)	O(31)–La–O(2)	69.3 (2)
O(12)–La–O(1)	64.9 (2)	O(31)–La–O(3)	65.6 (2)
O(12)–La–O(4)	64.5 (2)	O(32)–La–O(1)	65.8 (2)
O(12)–La–O(5)	68.1 (2)	O(32)–La–O(2)	72.4 (2)
O(21)–La–O(22)	45.7 (2)	O(1)–La–O(3)	73.5 (2)
O(21)–La–O(3)	69.2 (2)	O(1)–La–O(4)	70.5 (2)
O(21)–La–O(4)	60.9 (2)	O(2)–La–O(5)	68.2 (2)
O(21)–La–O(5)	63.0 (2)	O(3)–La–O(4)	70.1 (2)
O(22)–La–O(31)	62.4 (2)	O(4)–La–O(5)	81.4 (2)
O(22)–La–O(2)	67.2 (2)		
(B) Nitrate Groups			
O(11)–N(1)–O(12)	116.3 (7)	O(21)–N(2)–O(22)	117.2 (6)
O(11)–N(1)–O(13)	121.0 (7)	O(21)–N(2)–O(23)	122.1 (6)
O(12)–N(1)–O(13)	122.7 (8)	O(22)–N(2)–O(23)	120.6 (6)
O(31)–N(3)–O(32)	117.2 (7)		
O(31)–N(3)–O(33)	122.0 (7)		
O(32)–N(3)–O(33)	120.8 (7)		

nitrate group is unsymmetrically bound to the coordinating atom if the distances between the central atom and the two oxygen atoms of the same nitrate group differ by more than 0.2 Å. In $La(NO_3)_3 \cdot 6H_2O$ the differences for nitrate 1 and nitrate 2 are 0.229 and 0.216 Å, respectively. The third nitrate group appears to be symmetrically bound to the La atom.

In a regular environment the nitrate group is planar, and the O–N–O interbond angles are equal to 120°. The average N–O distance is 1.245 ± 0.01 Å.[23] In a coordinated nitrate group the planarity is preserved, but the N–O bond lengths and O–N–O interbond angles are changed.[23] The investigated structure exhibits changes in bond lengths and angles like those in most other structures with coordinated bidentate nitrate groups.[23] As can be seen from Table III, in all three nitrate groups the terminal N–O bonds are shortened (average 1.221 Å) and the N–O bonds involving both chelating oxygen atoms are lengthened (average 1.263 Å) as compared with the bonds of a regular nitrate group. The O–N–O interbond angle involving both coordinated oxygen atoms is smaller than 120° (average 116.9°), and the other two angles are correspondingly larger (average 121.5°). There are no deviations from the planarity for either the symmetrically or the unsymmetrically bound nitrate groups; however, the maximum departure for the involved atoms is only 0.01 Å. The average of all O–N–O interbond angles is 120°, and the average N–O distance is 1.25 Å.

To derive a coordination polyhedron for a high-coordinated complex from an idealized polyhedron, it is desirable to have a complex with identical unidentate ligands. In the present complex the ligands are not identical and are furthermore both unidentate and bidentate. The resulting polyhedron (Figure 2a) has no imposed symmetry, but it appears from the figure and the bond distances that it comes close to possessing a mirror plane containing O(2), O(4), and O(5). Figure 2b is a view perpendicular to the plane, and the numbers represent the departures in angstrom units for the atoms. If one regards the nitrate groups as occupying only one coordination site, the reduced polyhedron comes very close to that of a D_{2d}-$\bar{4}2m$ dodecahedron with two mirror planes defined by the four-atom groups O(2)–O(4)–O(5)–O(3132) [O(3132) is the center of gravity for the two atoms] and O(1112)–O(2122)–O(1)–O(3), respectively. The angle between the least-squares planes is 88°, and the mean departures for the atoms involved are 0.06 and 0.09 Å, respectively.

It is relevant to note, however, that the coordination polyhedron in the structure of the tetrakis(nitrato)diaqua(4,4′-bipyridyl)cerate(III) anion has been described as a C_s octadecahedron.[14]

Figure 3 is a stereoview of the unit cell. As can be seen, there may exist a complicated three-dimensional network of hydrogen bonds holding the pentaaquatris(nitrato)lanthanum complexes and the water of hydration together in the crystal structure. For instance, the short contacts between the noncoordinated water oxygen O(6) and oxygens O(23) and O(5) (3.00 (1) and 2.79 (1) Å, respectively) as well as the corresponding angle 123.5° indicate possible hydrogen bonds.

Acknowledgment. The authors are indebted to Drs. D.-R. Svoronos and M. Quarton for helpful comments.

Registry No. $[La(NO_3)_3(H_2O)_5] \cdot H_2O$, 68811-97-2; lanthanum nitrate hexahydrate, 10277-43-7.

Supplementary Material Available: Listing of structure factor amplitudes (13 pages). Ordering information is given on any current masthead page.

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[23] C. C. Addison, N. Logan, S. C. Wallwork, and C. D. Garner, *Q. Rev., Chem. Soc.*, **25**, 289 (1971).