

The Crystal and Molecular Structure of Potassium Diaquapentanitratolanthanate(III)

BIRGITTA ERIKSSON,^a LARS OLOF LARSSON,^a LAURI NIINISTÖ^b and JUSSI VALKONEN^b

^a Department of Structural Chemistry, Arrhenius Laboratory, University of Stockholm, Fack, S-106 91 Stockholm, Sweden and ^b Department of Chemistry, Helsinki University of Technology, Otaniemi, SF-02150 Espoo 15, Finland

The structure of potassium diaquapentanitratolanthanate(III), $K_2[La(NO_3)_5(H_2O)_2]$, has been determined from single crystal X-ray diffraction data. The compound crystallizes in the orthorhombic space group *Fdd2* (No. 43), with eight formula units in a cell of dimensions $a=11.336(5)$, $b=21.621(11)$ and $c=12.355(9)$ Å. Least-squares refinement with anisotropic thermal parameters for all nonhydrogen atoms yielded a final *R*-value of 0.052 for 1406 observed reflections. The lanthanum atom is coordinated to five symmetrically bidentate nitrate groups and two water molecules forming a distorted icosahedron. The potassium atom is surrounded, in a distorted arrangement, by eight nitrate oxygen atoms within 3.1 Å (average 2.90(10) Å) and by one water molecule at 3.26 Å. The La–O(nitrate) distance varies from 2.595 to 2.791 Å and the La–O(water) distance is 2.697 Å. The N–O distances in the nitrate groups are in the range 1.225–1.292 Å; the shortest distances involve the noncoordinating oxygen atoms.

The trivalent lanthanoids are known to form two main series of double nitrate hydrates in aqueous solution, namely $M_2^III Ln_2(NO_3)_{12} \cdot 24H_2O$ ($Ln=La, Ce$) and $M_2^III Ln(NO_3)_5 \cdot nH_2O$. In the first series, $Mg_3Ce_2(NO_3)_{12} \cdot 24H_2O$ is widely applied in cryotechnics as a low temperature thermometer, and this is probably the reason why compounds of this type have been structurally well-characterized by both X-ray and neutron diffraction methods.^{1,2} For the second series, however, only the structure of an anhydrous potassium double nitrate $K_2Er(NO_3)_5$, grown from the molten salt, has been determined recently.³ In addition, the structure of $[(C_6H_5)_4As]_2[Eu(NO_3)_5]$ is known.⁴

We have previously reported the structure of $La(NO_3)_3 \cdot 6H_2O$, which is an 11-coordinate complex corresponding to the formula $[La(NO_3)_3(H_2O)_5] \cdot H_2O$.^{5,6} In double lanthanum nitrate hydrates high coordination numbers could be expected as well which can be seen from the structure of $Mg_3La_3(NO_3)_{12} \cdot 24H_2O$ where the lanthanoid ion has around it a twelvefold coordination of oxygen atoms.¹ The present paper describes the structure of $K_2La(NO_3)_5 \cdot 2H_2O$, which is a representative of the second main series of lanthanoid double nitrate hydrates.

EXPERIMENTAL

Preparation. The compound was crystallized at room temperature from an aqueous solution containing potassium and lanthanum nitrates in a ratio 2:1. The chemical analyses of the prismatic crystals gave for the K:La ratio a value of 2.0 but indicated between 1.5 and 2.0 water molecules per lanthanum atom. The former value of water content is in agreement with the formula given by Groth;⁷ the structure determination, however, corroborated the latter stoichiometry.

Data collection. The intensity data were collected on an automated Syntex P2₁ diffractometer using monochromated $MoK\alpha$ -radiation. The unit cell dimensions were obtained by least-squares refinements of setting angles for 25 reflections. The orthorhombic space group *Fdd2* (No. 43) was chosen on the basis of the systematic absences in the original intensity data; the structure determination confirmed the choice. The crystal data and intensity measurements are summarized in Table 1. The intensity data were corrected for Lorentz and

Table 1. Details of the data collection.

(a) Crystal data	
Crystal system	Orthorhombic
Space group	<i>Fdd2</i> (No. 43)
<i>a</i> , Å	11.335(5)
<i>b</i> , Å	21.621(11)
<i>c</i> , Å	12.355(9)
<i>V</i> , Å ³	3028
<i>Z</i>	8
<i>M_r</i>	563.2
<i>d</i> (calc), g cm ⁻³	2.47
μ (MoK α), cm ⁻¹	34.80
Crystal size, mm	0.25 × 0.15 × 0.15
(b) Intensity measurements	
Radiation	MoK α = 0.71069 Å
Monochromator	Highly oriented graphite
Reflections measured	1592
2 θ range, deg	5–60
Scan speed, deg min ⁻¹	1–3
Scan range, deg	(2 θ MoK α –1) – (2 θ MoK α +1)
Background measurement	At beginning and end of the 2 θ , each for one half of the total scan time.
Standards	2 reflections after each batch of 60 data; no decrease of the intensity was observed.
No. of observed unique data with $\sigma(I_{\text{net}})/I_{\text{net}} \leq 0.33$	1406

polarization effects and an empirical absorption correction from ϕ -scan data was applied (minimum relative transmission value was 0.59).

Structure determination and refinement. From a three-dimensional Patterson syntheses the La atom was found to occupy the special position 8(a) on the twofold rotation axis. The origin was fixed by giving the *z*-coordinate of the La atom a value of zero. Full-matrix least-squares refinement with an overall scale factor and isotropic thermal parameters for the La atom resulted in $R=0.27$ ($R=(\sum||F_o|-|F_c||)/\sum|F_o|$). Possible starting parameters for the potassium atom were obtained from the electron density map and a least-squares refinement of the La and K atoms positions, using an overall scale factor and isotropic temperature factors, gave an *R*-value of 0.18. The subsequent electron density map gave the positions of all remaining non-hydrogen atoms in the unit cell. A refinement with anisotropic thermal parameters for the La atom and isotropic parameters for the remaining atoms resulted in an *R*-value of 0.060. As a final step anisotropic vibrational parameters were introduced for all atoms, whereupon the *R*-value dropped to 0.052. Unit weights were used in the refinement, and the ratio of largest shift to standard deviation in coordinates was 0.005 in the last cycle.

All atoms except lanthanum, one oxygen atom, O(32), and one nitrogen atom, N(3), are in general positions. The thermal parameters have normal values except for the nitrogen atom N(3) and the oxygen atom O(32) both located on the twofold axis. This anomaly is discussed below.

After the refinement was completed a difference Fourier synthesis was calculated in an attempt to locate the hydrogen atoms, but the map only had peaks up to $1.8 \text{ e } \text{Å}^{-3}$ around the La atom. The final coordinates and thermal parameters are listed in Table 2. All calculations were performed on the IBM 370/165 computing system at the University of Stockholm, and the programs used for the structural analysis were SHELX and PLUTO. The analytical scattering factors of Cromer and Mann for the neutral atoms La, K, O and N were used.⁸ A listing of structure factors is available on request from L.O. Larsson.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The crystal structure comprises discrete $[\text{La}(\text{NO}_3)_5(\text{H}_2\text{O})_2]^{2-}$ anions and K^+ cations. Fig. 1 shows a stereo view of the unit cell. The La atoms

Table 2. Final positional and thermal^a parameters ($\times 10^4$) with estimated standard deviations in parentheses.

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
La	0	0	0	166(3)	235(0)	190(2)	0	0	19(3)
O(11)	.1869(8)	.0484(4)	.0953(8)	290(40)	335(39)	356(42)	-72(35)	-52(37)	74(34)
O(12)	.2226(7)	-.0406(4)	.0185(8)	259(36)	350(39)	431(52)	-80(38)	-36(38)	44(32)
O(13)	.3687(8)	.0171(5)	.0767(9)	224(40)	597(61)	499(58)	-103(49)	-65(42)	20(41)
O(21)	.1400(7)	.0587(4)	-.1437(7)	245(38)	435(46)	307(40)	-110(36)	62(34)	-58(35)
O(22)	-.0468(8)	.0617(4)	-.1750(7)	236(38)	366(38)	271(37)	-85(31)	3(32)	-26(32)
O(23)	.0774(9)	.10251(5)	-.2923(7)	466(55)	435(48)	287(41)	-101(37)	-31(40)	-97(44)
O(31)	.0370(10)	-.0467(4)	.2078(8)	509(59)	292(40)	386(49)	-61(37)	-97(44)	125(42)
O(32)	0	0	.3598(10)	1472(198)	664(104)	82(43)	0	0	-286(119)
O(1)	-.0127(8)	.1235(4)	.0289(6)	327(43)	369(37)	256(36)	36(29)	-74(35)	-7(37)
K	.0581(2)	.1044(1)	.4818(2)	294(11)	346(11)	372(14)	-3(10)	-63(11)	21(10)
N(1)	.2627(8)	.0089(5)	.0638(8)	207(41)	336(47)	298(42)	-26(36)	-21(37)	41(36)
N(2)	.0577(9)	.0753(4)	-.2063(7)	276(45)	286(40)	168(33)	-44(31)	2(34)	-42(37)
N(3)	0	0	.2595(11)	599(101)	401(70)	119(46)	0	0	-63(64)

^a The form of the anisotropic thermal factor is $\exp [-2\pi^2(U_{11}h^2a^*2 + \dots + 2U_{23}klb^*c^*)]$.

are found in layers with $z=n/4$ ($n=0, 1, 2, 3$) parallel to the ab -plane.

The La atom is coordinated to twelve oxygen atoms; ten of these belong to five bidentate nitrate groups and two are water molecules. A view of the $[\text{La}(\text{NO}_3)_5(\text{H}_2\text{O})_2]^{2-}$ complex is shown in Fig. 2, which also gives the numbering system used to identify the atoms. Selected distances and angles are given in Table 3.

Twelve-coordination for lanthanum has been earlier reported in the structures of $\text{Mg}_3\text{La}_2(\text{NO}_3)_{12}\cdot 24\text{H}_2\text{O}^1$ and $\text{La}_2(\text{SO}_4)_3\cdot 9\text{H}_2\text{O}^9$. In these

structures the coordination polyhedra around the La atom consist only of nitrate and sulfate oxygen atoms, respectively, and the overall average of all La-O distances is 2.69 Å. In the investigated structure, the polyhedron around the La atom is formed by two kinds of ligands, bidentate nitrate groups and water molecules. Thus, in this case all water molecules have entered the inner coordination sphere of the lanthanoid ion. The coordinated nitrate and water oxygens are found at approximately the same distance from the La atom. The La-O(water) distance is 2.70(1) Å, while the

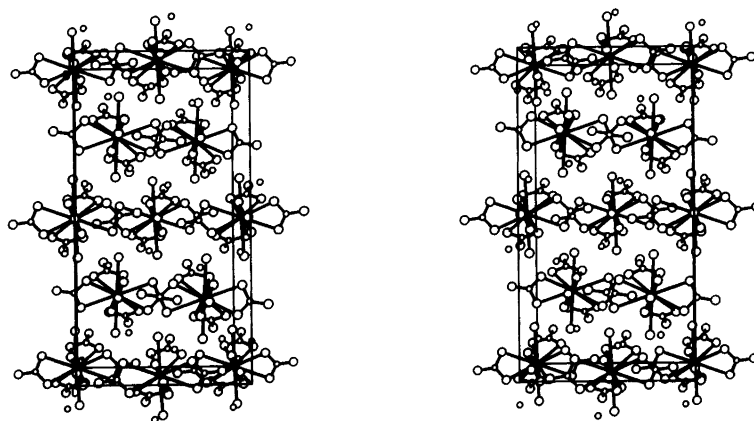


Fig. 1. A stereo view along the c -axis showing the unit cell packing. The front part of the unit cell is omitted for clarity.

Table 3. Selected interatomic distances (Å) and angles (°).

Environment of lanthanum

La—O(11) ^a (× 2)	2.641(9)
—O(12) ^a (× 2)	2.681(8)
—O(21) ^a (× 2)	2.698(9)
—O(22) ^a (× 2)	2.595(8)
—O(31) ^a (× 2)	2.791(10)
—O(1) ^a (× 2)	2.697(9)

O(11)—La—O(12)	48.5(3)
O(11)—La—O(21)	68.6(3)
O(11)—La—O(31)	67.2(3)
O(11)—La—O(1)	65.9(3)
O(12)—La—O(21)	69.9(3)
O(12)—La—O(22) ^b	73.1(3)
O(12)—La—O(31)	70.2(3)

O(12)—La—O(1) ^h	67.3(3)
O(21)—La—O(22)	48.0(3)
O(21)—La—O(22) ^h	64.7(3)
O(21)—La—O(1)	69.7(3)
O(22)—La—O(22) ^h	67.2(4)
O(22)—La—O(1)	65.8(3)
O(31)—La—O(31) ^h	46.1(4)
O(31)—La—O(1) ^h	60.8(3)

Environment of potassium

K—O(12) ^b	2.879(9)
—O(13) ^c	3.089(10)
—O(13) ^b	2.994(11)
—O(21) ^d	3.086(9)
—O(23) ^e	2.799(10)

K—O(23) ^d	2.792(11)
—O(31) ^f	2.783(10)
—O(32)	2.794(7)
—O(1) ^g	3.262(9)

Nitrate groups

N(1)—O(11)	1.272(13)
—O(12)	1.292(13)
—O(13)	1.225(13)

O(11)—N(1)—O(12)	116.9(9)
O(11)—N(1)—O(12)	121.7(10)
O(12)—N(1)—O(13)	121.5(10)

N(2)—O(21)	1.264(13)
—O(22)	1.280(13)
—O(23)	1.235(13)

O(21)—N(2)—O(22)	115.7(9)
O(21)—N(2)—O(23)	121.9(10)
O(22)—N(2)—O(23)	122.5(10)

N(3)—O(31) ^a (× 2)	1.267(12)
—O(32)	1.238(12)

O(31)—N(3)—O(31) ^h	119.3(7)
O(31)—N(3)—O(32)	120.3(7)

Symmetry code

none	x, y, z
(a)	x, y, z and $-x, -y, z$
(b)	$\frac{1}{2} - x, -y, \frac{1}{2} + z$
(c)	$x - \frac{1}{2}, y, \frac{1}{2} + z$
(d)	$x - \frac{1}{4}, -y, \frac{3}{4} + z$
(e)	$x, y, 1 + z$

(f)	$\frac{1}{4} - x, \frac{1}{4} + y, \frac{1}{4} + z$
(g)	$\frac{1}{4} + x, \frac{1}{4} - y, \frac{1}{4} + z$
(h)	$-x, -y, z$
(i)	$\frac{1}{4} - x, (\frac{3}{4} + y) - 1, (\frac{1}{4} + z) - 1$
(j)	$(\frac{3}{4} + x) - 1, \frac{1}{4} - y, (\frac{3}{4} + z) - 1$

average La—O(nitrate) separation is 2.68(7) Å.

The $[\text{La}(\text{NO}_3)_5(\text{H}_2\text{O})_2]^{2-}$ complex has no direct contact with adjacent La-complexes, but the three-dimensional framework is formed by potassium ions and hydrogen bonds. A potassium ion binds to three

La-polyhedra. The nitrate oxygen atoms O(13), O(23) and O(32), which are not coordinated to the La atom, belong to the coordination sphere around K^+ . The geometrical environment of the K^+ ion consists of nine oxygen atoms (Table 3). Eight of

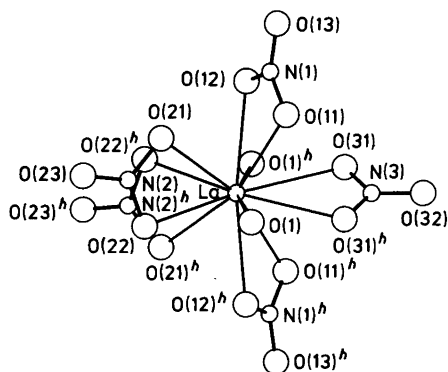


Fig. 2. A perspective view of the $[\text{La}(\text{NO}_3)_5(\text{H}_2\text{O})_2]^{2-}$ complex with the atomic numbering system. The letters refer to symmetry operations given in Table 3.

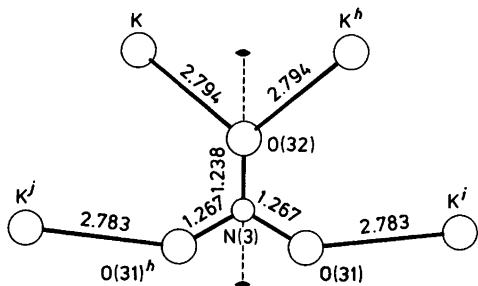


Fig. 3. Surroundings of the N(3) nitrate group. The distances are given in Å units; the esd's are less than 0.01 Å. The letters refer to symmetry operations given in Table 3.

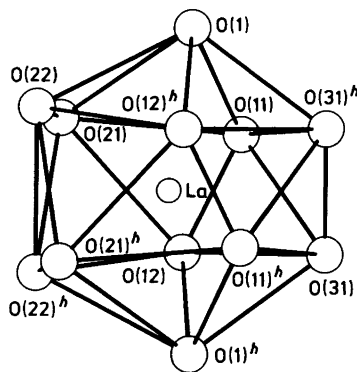
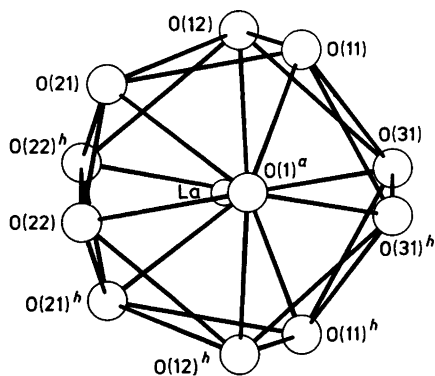


Fig. 4. Coordination polyhedron around the lanthanum atom. (a) A view along the "capping atoms" O(1) and O(1)^a. (b) A view perpendicular to that in (a). The letters refer to symmetry operations given in Table 3.

these atoms are nitrate oxygen atoms at distances 2.78–3.09 Å (average 2.90(10) Å, and one is a water molecule at 3.26 Å from the K^+ ion. The arrangement is very irregular.

The dimensions of the nitrate groups are in agreement with those found in related crystal structures. The N–O distances in the nitrate groups range from 1.225 to 1.292 Å. Such large variations are not unusual, and they can be correlated with the various aspects of the bonding network of the crystal structure. The O–N–O interbond angle involving the two coordinated oxygen atoms is smaller than 120° (average $117.3(1.8)^\circ$), and the other two angles are correspondingly larger (average $121.4(8)^\circ$). The angle involving the two coordinated oxygen atoms in nitrate(3) is slightly larger, $119.3(7)^\circ$, than the corresponding angles for the other two nitrate groups ($116.9(9)$ and $115.7(9)^\circ$, respectively (see Table 3), and this is probably a result of the surroundings of the three oxygen atoms in this nitrate group. All oxygen atoms are highly involved in interactions with four K^+ ions as can be seen in Fig. 3. O(32) is situated between and very close to two K^+ ions in a plane perpendicular to the c -axis. This may explain the high thermal parameters in the ab -plane for the O(32) atom. Another reason for the large thermal parameter value may be that the assumed symmetry is too high. However, the object of this investigation was the coordination around the La atom, and we have not considered it worthwhile to collect new data in order to attempt to refine the structure in a monoclinic space group.

The ideal geometry for a twelve coordination polyhedron is the icosahedron. In the investigated

structure large distortions are caused by the small bite of the nitrate groups as compared to other oxygen–oxygen distances in the polyhedron: 2.1 and 2.7 Å, respectively. Taking the water molecules as “capping atoms” in the icosahedron, three of the nitrate groups contribute one atom to each five-atom plane while N(2) nitrate groups fill the remaining positions in the planes as shown in Figs. 4a and 4b. The angle between the two five-atom planes is 8°, and the maximum departure of the involved atoms from the least-squares planes is 0.1 Å.

Acknowledgement. The authors are indebted to Ms. P. Riihonen, M.Sc., for experimental aid in the preparation and analysis of the crystals.

REFERENCES

1. Anderson, M. R., Jenkin, G. T. and White, J. W. *Acta Crystallogr. B* 33 (1977) 3933.
2. Zalkin, A., Forrester, J. D. and Templeton, D. H. *J. Chem. Phys.* 39 (1963) 2881.
3. Sherry, E. G. *J. Inorg. Nucl. Chem.* 40 (1978) 257.
4. Bünzli, J.-C. G., Klein, B., Chapuis, G. and Schenk, K. J. *J. Inorg. Nucl. Chem.* To be published.
5. Eriksson, B., Larsson, L. O. and Niinistö, L. *J. Chem. Soc. Chem. Commun.* 17 (1978) 616.
6. Eriksson, B., Larsson, L. O., Niinistö, L. and Valkonen, J. *Inorg. Chem.* 19 (1980) 1207.
7. Groth, P. *Chemische Krystallographie, Teil 2*, Engelmann, Leipzig 1908, p. 152.
8. *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham 1974, Vol. IV, pp. 99–101.
9. Hunt, J. E. B., Rundle, R. E. and Stosick, A. J. *Acta Crystallogr.* 7 (1954) 106; Dereigne, A. and Pannetier, G. *Bull. Soc. Chim. Fr.* (1968) 174; Sherry, E. G. *J. Solid State Chem.* 19 (1976) 271.

Received March 25, 1980.