# The Crystal and Molecular Structures of Two Hydrates of Ammonium Diaquapentanitratolanthanate(III)

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The crystal structures of ammonium diaquapentanitratolanthanate(III) dihydrate $(NH_4)_2[La(NO_3)_5-(H_2O)_2] \cdot 2H_2O$ (*1*) and ammonium diaquapentanitratolanthanate(III) monohydrate $(NH_4)_2[La(NO_3)_5(H_2O)_2] \cdot H_2O$ (*2*) have been determined from single crystal X-ray diffraction data. The compounds crystallize in the monoclinic space group $C2/c$ (No. 15) with four formula units in the cell of dimensions $a = 11.152(5)$, $b = 8.966(4)$ $c = 17.881(6)$ Å, $\beta = 101.6(4)°$ and $a = 10.969(10)$, $b = 9.012(5)$, $c = 17.439(10)$ Å, $\beta = 100.1(1)°$ for *1* and *2*, respectively. Least-squares refinement with anisotropic thermal parameters for all nonhydrogen atoms yielded the final $R$-values of 0.065 and 0.041 for *1* and *2*, respectively. The number of reflections used in the refinements was 2389 (*1*) and 1866 (*2*). The surroundings of the lanthanum atom are identical in the two compounds; there are five symmetrically bonded nitrate groups and two water molecules forming a distorted icosahedron. The La—O(nitrate) distances range from 2.66 to 2.73 in *1* and from 2.68 to 2.72 Å in *2* while the corresponding La—O(water) distances are 2.59 and 2.54 Å. The only significant structural difference between the two complexes is in the three-dimensional framework where one water molecule is lacking in compound *2*.

In contrast to the well—characterized dodecanitrato hydrates, *eg.* $Mg_3Ce_2(NO_3)_{12} \cdot 24H_2O$,[1] the structural information on solid lanthanoid pentanitrato hydrates is scarce. Only very recently was a representative of the latter series, *viz.* $K_2La(NO_3)_5 \cdot 2H_2O$, studied by X-ray single crystal methods.[2] There are, however, several examples of anhydrous pentanitrato species whose structures are known.[3-7] The coordination numbers are generally high, as in the case of simple nitrate hydrates, being twelve

for $K_2[La(NO_3)_5] \cdot 2H_2O$ and ten for the other structures with the exception of scandium.[2-7]

In continuation of our investigation into the structures of inorganic nitrato complexes of the lanthanoids,[2,8] we are now reporting the structures of two closely related lanthanum pentanitrato complexes $(NH_4)_2[La(NO_3)_5(H_2O)_2] \cdot nH_2O$ where $n$ is 1 and 2.

## EXPERIMENTAL

*Preparation.* The compounds were crystallized at room temperature from an aqueous solution containing lanthanum and ammonium ions in molar ratio 1:2 and a slight excess of nitric acid. According to chemical analyses the predominant product under these conditions was $(NH_4) \cdot La(NO_3)_5 \cdot 4H_2O$. The crystals with lower water content, *i.e.* 3 mol of water, obviously crystallize under nearly the same conditions as some of them were detected among the tetrahydrate crystals when carrying out unit cell determinations by single crystal diffractometry.

*Data collection.* The unit cell dimensions were obtained by least-squares refinements of setting angles for 25 reflections measured with an automated four-circle diffractometer. Several crystals were measured but the unit cell data given in Table 1 refer to crystals used in the intensity data collection with the same diffractometer. The monoclinic space group $C2/c$ (No. 15) was chosen for both of the compounds on the basis of the systematic absences in the intensity data and corroborated by the structure determination. Net intensities were corrected for Lorentz and polarization effects but no absorption correction was applied.

*Structure determination and refinement.* A three-dimensional Patterson synthesis using the data for

† Deceased.

*Table 1.* Details of the data collection.

|  | 1 | 2 |
|---|---|---|
| **(a) Crystal data** | | |
| Crystal system | monoclinic | monoclinic |
| Space group | $C2/c$ | $C2/c$ |
| $a$, Å | 11.152(5) | 10.969(10) |
| $b$, Å | 8.966(4) | 9.012(5) |
| $c$, Å | 17.881(6) | 17.439(10) |
| $\beta$, deg | 101.6(4) | 100.1(9) |
| $V$ | 1751.4 | 1697.1 |
| $Z$ | 4 | 4 |
| Molwt | 556.9 | 538.9 |
| $D_x$(calc, g cm$^{-3}$ | 2.10 | 2.11 |
| $\mu$(Mo$K_\alpha$), cm$^{-1}$ | 25.4 | 26.3 |
| **(b) Intensity measurements** | | |
| Radiation | Mo$K_\alpha$ | Mo$K_\alpha$ |
| Monochromator | Highly oriented graphite | Highly oriented graphite |
| Reflections measured | $\pm h$, $+k$, $+l$ with $h+k=2n$ | $\pm h$, $+k$, $+l$ with $h+k=2n$ |
| No. of collected data | 2782 | 2028 |
| $2\theta$ range, deg | 5−60 | 5−55 |
| Scan speed, deg min$^{-1}$ | 3 | 2 |
| Scan range, deg | $(2\theta \mathrm{Mo}K_\alpha-0.75)-$ $(2\theta \mathrm{Mo}K_\alpha+0.75)$ | $(2\theta \mathrm{Mo}K_\alpha-1)-$ $(2\theta \mathrm{Mo}K_\alpha+1)$ |
| Background measurement | At beginning and end of the $2\theta$, each for one half of the total scan time. | |
| Standards | 3 reflections after each batch of 43 data; no decrease of the intensity was observed | |
| No. observed unique data with $\sigma(I_{net})/I_{net} \leq 0.33$ | 2389 | 1866 |

compound *2* showed the La atoms of the unit cell in the special position *4e* of the space group $C2/c$. The coordinate of the La atom was refined to an $R$-value of 0.27 ($R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$). The subsequent electron density maps gave the positions of all remaining nonhydrogen atoms in the unit cell. Full-matrix least-squares refinement with an overall scale factor and isotropic thermal factors gave an $R$-value of 0.084; anisotropic thermal parameters were then introduced whereupon the $R$-value dropped to 0.041.

The unit cell of compound *1* is 54 Å$^3$ larger by volume than that of compound *2*. This corresponds very closely to the space needed for one water molecule per formula unit. The coordinates from compound *2* were refined using data for compound *1*; an isotropic refinement resulted in an $R$-value of 0.122. With anisotropic thermal parameters the $R$-value dropped to 0.0651. Unit weights were used in all calculations and the largest shift to standard deviation in coordinates was 0.3 in the last

cycle for both structures.

In an attempt to locate the hydrogen atoms, difference Fourier syntheses were calculated but the maps only had peaks up to 2.0 Å around the La atoms. The final coordinates and thermal parameters are listed in Table 2. The programs used in the structural analysis were SHELX and PLUTO. The analytical scattering factors of Cromer and Mann for the neutral atoms were used.[9] The listings of the structure factors are available request from B. Eriksson.

## DESCRIPTION AND DISCUSSION OF THE STRUCTURES

In both compounds the lanthanum ion is twelve-coordinated by five bidentate nitrate groups and two water molecules thus forming the diaqua-pentanitratolanthanate(III) anion [La(NO$_3$)$_5$-

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

| Atom | x | y | z | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|------|---|---|---|----------|----------|----------|----------|----------|----------|
| Compound 1, $(NH_4)_2[La(NO_3)_5(H_2O_2)]\cdot 2H_2O$ | | | | | | | | | |
| La | 0 | 0.0567(1) | 0.25 | 145(3) | 191(3) | 327(3) | 0 | 88(2) | 0 |
| O(11) | 0.0925(6) | -0.2222(8) | 0.2401(5) | 241(30) | 292(33) | 784(56) | 18(35) | 241(33) | 25(26) |
| O(12) | 0 | -0.4296(14) | 0.25 | 979(109) | 259(59) | 2356(215) | 0 | 1169(134) | 0 |
| O(21) | -0.0791(6) | 0.2519(8) | 0.1395(5) | 260(31) | 400(38) | 590(49) | -87(34) | 22(31) | 112(28) |
| O(22) | 0.1075(6) | 0.2925(8) | 0.1957(4) | 275(31) | 381(38) | 530(45) | 108(33) | -30(29) | -57(28) |
| O(23) | 0.0272(9) | 0.4213(12) | 0.0961(6) | 589(55) | 778(69) | 816(69) | 442(58) | -56(49) | -272(51) |
| O(31) | 0.0991(7) | -0.0017(11) | 0.1277(5) | 357(38) | 737(58) | 529(47) | -57(43) | 217(35) | -62(39) |
| O(32) | -0.0852(6) | -0.0864(9) | 0.1174(4) | 315(33) | 520(45) | 501(43) | -127(36) | 165(31) | -51(32) |
| O(33) | 0.0235(11) | -0.1495(18) | 0.0350(7) | 873(8) | 1801(144) | 941(87) | 871(94) | 455(72) | -24(88) |
| N(1) | 0 | -0.2959(12) | 0.25 | 266(48) | 413(48) | 267(50) | 0 | 139(44) | 0 |
| N(2) | 0.0186(7) | 0.3244(10) | 0.1426(5) | 312(38) | 348(42) | 536(53) | 100(40) | 34(36) | -99(34) |
| N(3) | 0.0144(9) | -0.0781(14) | 0.0912(5) | 384(46) | 840(79) | 423(49) | 219(53) | 178(39) | -51(50) |
| O(1) | 0.2364(5) | 0.0542(7) | 0.2914(4) | 176(25) | 337(32) | 481(37) | 60(30) | 102(24) | -4(24) |
| O(2) | 0.2962(9) | -0.1157(14) | -0.0306(7) | 555(57) | 852(79) | 992(86) | 254(68) | -42(55) | -100(56) |
| NH₄ | 0.2757(11) | 0.1431(18) | 0.0573(8) | 772(76) | 1661(139) | 1014(93) | -308(94) | 485(71) | -585(87) |
| Compound 2, $(NH_4)_2[La(NO_3)_5(H_2O_2)]\cdot H_2O$ | | | | | | | | | |
| La | 0 | 0.0572(1) | 0.25 | 174(2) | 175(2) | 309(2) | 0 | 44(2) | 0 |
| O(11) | 0.0947(4) | -0.2195(5) | 0.2413(3) | 265(20) | 261(21) | 625(30) | -4(20) | 169(20) | 1(17) |
| O(12) | 0 | -0.4261(8) | 0.25 | 827(63) | 170(34) | 2023(121) | 0 | 828(74) | 0 |
| O(21) | -0.0789(4) | 0.2518(5) | 0.1362(3) | 258(20) | 372(24) | 507(27) | -51(21) | 1(18) | 74(18) |
| O(22) | 0.1067(4) | 0.2935(5) | 0.1945(3) | 332(22) | 291(22) | 524(27) | 110(20) | -75(19) | -55(18) |
| O(23) | 0.0310(5) | 0.4220(6) | 0.0921(3) | 597(33) | 522(33) | 570(32) | 255(27) | -16(26) | -157(27) |
| O(31) | 0.1106(5) | 0.0053(6) | 0.1264(3) | 528(30) | 491(30) | 532(30) | 39(25) | 188(24) | -6(25) |
| O(32) | -0.0728(5) | -0.0861(6) | 0.1131(3) | 476(27) | 444(29) | 500(28) | -55(23) | 119(23) | 14(22) |
| O(33) | 0.0466(7) | -0.1514(7) | 0.0330(3) | 1147(55) | 715(42) | 485(33) | 150(31) | 310(35) | -236(39) |
| N(1) | 0 | -0.2899(8) | 0.25 | 272(33) | 226(33) | 467(42) | 0 | 103(30) | 0 |
| N(2) | 0.0190(5) | 0.3246(6) | 0.1398(3) | 327(25) | 265(25) | 417(29) | 41(22) | 20(21) | -39(21) |
| N(3) | 0.0287(6) | -0.0789(7) | 0.0891(3) | 636(39) | 383(32) | 361(29) | -20(25) | 164(27) | -149(29) |
| O(1) | 0.2342(4) | 0.0546(5) | 0.2902(3) | 241(19) | 206(19) | 676(30) | 54(20) | 129(19) | -1(16) |
| O(2) | 0.2842(10) | -0.0984(14) | -0.0213(7) | 623(69) | 884(90) | 908(88) | 176(67) | -55(55) | -11(59) |
| NH₄ | 0.2924(9) | 0.1423(15) | 0.0566(6) | 772(61) | 1838(121) | 1080(78) | 621(81) | -144(54) | -656(73) |

[a] The form of the anisotropic thermal factor is $\exp[-2\pi^2(U_{11}h^2a^{*2}\cdots 2U_{23}klb^*c^*)]$.
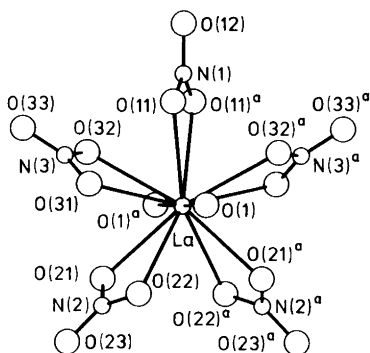
Fig. 1. A perspective view of the [La(NO$_3$)$_5$(H$_2$O)$_2$]$^{2-}$ complex with the atomic numbering system. The letter $a$ refers to the symmetry operation $-x$, $y$, $\frac{1}{2}-z$.



Fig. 2. A chain formed by ammonium ions and noncoordinated water molecules along the $y$-axis in compound 1. The solid lines indicate possible hydrogen bonds within the chain and to coordinated oxygen atoms (numbered ones).

(H$_2$O)$_2$]$^{2-}$. A perspective view of the complex, which has very similar geometry in both compounds, is depicted in Fig. 1 which also gives the numbering system.

As well as the ammonium ions two water molecules remain outside the coordination sphere of lanthanum in (NH$_4$)$_2$ [La(NO$_3$)$_5$(H$_2$O)$_2$] · 2H$_2$O (1) and one water molecule in (NH$_4$)$_2$[La(NO$_3$)$_5$-(H$_2$O)$_2$] · H$_2$O (2). The ammonium ions and non-coordinated water molecules are connected by hydrogen bonds in a chain-like structure along the $y$-axis. As the electron densities of an ammonium ion and a water molecule are very similar it is impossible to distinguish between them on the basis of electron density maps. However, the thermal parameters for these atoms in compound 1 indicate the given locations for the ammonium ion and the water molecule. Furthermore, a refinement of the
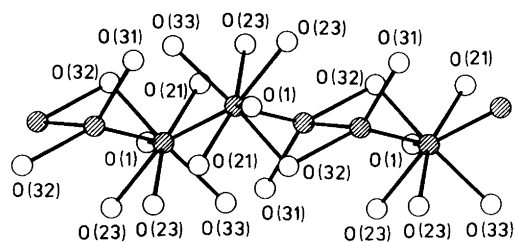
occupancy factors for both sites in compound 2 resulted in half occupancy for the water molecule (O(2)) and full occupancy for the ammonium site. Fig. 2 shows possible hydrogen bonds within the chain. Space group symmetry restricts the ammonium ions and water molecules to lie in the order H$_2$O$-$H$_2$O$-$NH$_4$$-$NH$_4$. It would be more favourable to place them in an alternating order: H$_2$O$-$NH$_4$$-$H$_2$O$-$NH$_4$, but the data is insufficient to prefer the later sequence. A stereoview showing the packing of the complexes in the unit cell of compound 1 is presented in Fig. 3.

In the dodecacoordinated lanthanoid nitrate structures Mg$_3$La$_2$(NO$_3$)$_{12}$ · 24H$_2$O[1] and K$_2$[La-(NO$_3$)$_5$(H$_2$O)$_2$] and in the present compounds La$-$O(nitrato) separations are similar. In both the ammonium compounds it is 2.70(2) Å while the corresponding distances for the magnesium and potassium compounds are 2.67(3) and 2.68(7) Å, respectively. The water oxygens may be at different distances, however, depending on the compound and
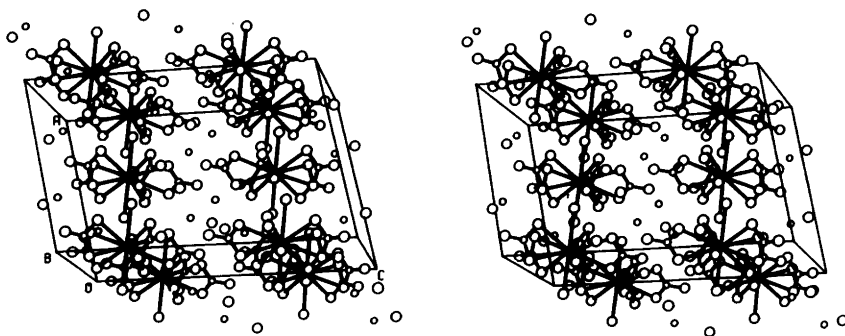


Fig. 3. A stereoview of the structure of (NH$_4$)$_2$[La(NO$_3$)$_5$(H$_2$O)$_2$] ·2H$_2$O (compound 1) showing the unit cell packing.
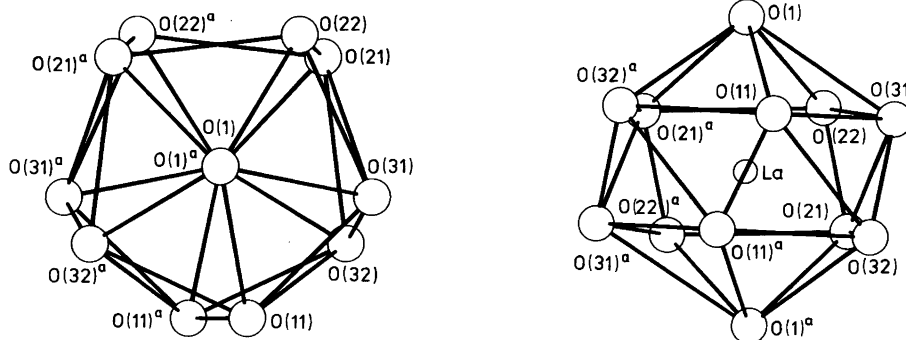
Fig. 4. Coordination polyhedron around the lanthanum atom. (a) A view along the "capping atoms" O(1) and O(1)$^a$. (b) A view perpendicular to that in (a). The letter $a$ refers to the symmetry operation $-x, y, \frac{1}{2}-z$.

its hydrogen bonding network. Thus, the La$-$O (water) distances are 2.59(1) and 2.54(1) Å in ammonium compounds $1$ and $2$ while in the potassium

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

|  | 1 | 2 |
|---|---|---|
| **Environment of lanthanum** | | |
| La$-$O(11)$^b$ ($\times 2$) | 2.731(7) | 2.716(6) |
| La$-$O(21)$^b$ ($\times 2$) | 2.663(8) | 2.675(5) |
| La$-$O(22)$^b$ ($\times 2$) | 2.713(8) | 2.690(6) |
| La$-$O(31)$^b$ ($\times 2$) | 2.703(8) | 2.693(6) |
| La$-$O(32)$^b$ ($\times 2$) | 2.705(8) | 2.709(6) |
| La$-$O(1)$^b$ ($\times 2$) | 2.594(6) | 2.542(6) |
| | | |
| O(11)$-$La$-$O(11)$^a$ | 46.7(3) | 46.7(2) |
| O(11)$-$La$-$O(31) | 63.0(3) | 64.2(2) |
| O(11)$-$La$-$O(32) | 63.2(3) | 63.6(2) |
| O(11)$-$La$-$O(32)$^a$ | 65.0(3) | 64.5(2) |
| O(11)$-$La$-$O(1) | 68.6(2) | 68.2(2) |
| O(21)$-$La$-$O(22) | 47.3(3) | 47.1(2) |
| O(21)$-$La$-$O(22)$^a$ | 69.4(3) | 69.1(2) |
| O(21)$-$La$-$O(31) | 69.6(3) | 69.7(2) |
| O(21)$-$La$-$O(32) | 69.7(3) | 69.7(2) |
| O(21)$-$La$-$O(1)$^a$ | 68.1(2) | 67.8(2) |
| O(22)$-$La$-$O(22)$^a$ | 77.2(3) | 75.3(3) |
| O(22)$-$La$-$O(31) | 65.0(3) | 64.2(2) |
| O(22)$-$La$-$O(1) | 67.1(3) | 67.9(2) |
| O(31)$-$La$-$O(32) | 47.2(3) | 46.9(2) |
| O(31)$-$La$-$O(1) | 70.8(3) | 69.1(2) |
| O(32)$-$La$-$O(1) | 65.5(3) | 68.0(2) |

**Symmetry code**

| None | $x, y, z$ |
|---|---|
| $(a)$ | $-x, y, \frac{1}{2}-z$ |
| $(b)$ | $x, y, z$ and $-x, y, \frac{1}{2}-z$ |

compound, which is also a pentanitrato complex, the corresponding distance is 2.70(1) Å.

The coordination polyhedron around the La atom can be described in both compounds as a slightly distorted icosahedron. This was also the case for the magnesium and potassium compounds. The pattern of the coordinated nitrate groups is, however, different from the potassium compound. In both cases the water molecules occupy *trans* positions of the capping atoms in the icosahedron. In the present complexes each of the five nitrate groups contributes one oxygen atom to each of the two five-membered rings in the icosahedron while in the potassium compound one of the nitrate groups belongs entirely to one of the rings. Fig. 4 shows the coordination polyhedron; distances and angles involved are listed in Tables 3 and 4.

The geometry of nitrate groups shows the expected trends.[2,8,10] Thus, the N$-$O distances range

*Table 4.* Least-squares plane. Atoms involved: O(32)$^a-$O(11)$-$O(31)$-$O(22)$-$O(21).$^a$

|  | 1 | 2 |
|---|---|---|
| **Angle between the planes (°)** | | |
| | 1.1(12)$^b$ | 1.3(5) |
| **Distances from the plane (Å)** | | |
| O(32) | 0.045(4) | $-0.003(3)$ |
| O(11) | 0.002(4) | 0.014(3) |
| O(31) | $-0.051(5)$ | $-0.019(3)$ |
| O(22) | 0.076(3) | 0.017(3) |
| O(21) | $-0.072(4)$ | $-0.008(3)$ |

$^a$Symmetry code $-x, y, \frac{1}{2}-z$. $^b$Estimated standard deviations are given in parentheses.

*Table 5.* Selected interatomic distances (Å) and angles (°) involving the nitrato groups.

|  | 1 | 2 |
|---|---|---|
| N(1)−O(11)[b] (×2) | 1.269(9) | 1.249(6) |
| N(1)−O(12) (×2) | 1.202(17) | 1.228(10) |
|  |  |  |
| O(11)−N(1)−O(11)[a] | 117.1(10) | 118.9(7) |
| O(11)−N(1)−O(12) | 121.5(5) | 120.5(4) |
|  |  |  |
| N(2)−O(21) | 1.262(11) | 1.251(7) |
| N(2)−O(22) | 1.264(11) | 1.262(7) |
| N(2)−O(23) | 1.225(14) | 1.233(8) |
|  |  |  |
| O(21)−N(2)−O(22) | 117.2(9) | 117.1(5) |
| O(21)−N(2)−O(23) | 121.5(9) | 122.2(5) |
| O(22)−N(2)−O(23) | 121.3(9) | 120.7(5) |
|  |  |  |
| N(3)−O(31) | 1.243(13) | 1.265(8) |
| N(3)−O(32) | 1.295(12) | 1.258(8) |
| N(3)−O(33) | 1.219(17) | 1.222(4) |
|  |  |  |
| O(31)−N(3)−O(32) | 117.3(10) | 116.8(6) |
| O(31)−N(3)−O(33) | 123.2(10) | 122.2(7) |
| O(32)−N(3)−O(33) | 119.4(10) | 121.0(7) |

[a,b] For symmetry code, see Table 3.

from 1.202 to 1.295 Å; the lowest values belonging to terminal bonds while the bonds involving chelating oxygens are lengthened relative to the regular nonbonded nitrate group. Likewise, the O−N−O interbond angles deviate as expected from 120° when the oxygen atoms are involved in bonding, *cf.* Table 5.

The investigated structures have different compositions but exhibit nevertheless a close structural relationship. The central lanthanum ion is in both cases coordinated similarly by five nitrato groups and two water molecules. The coordination geometry of the complex anion and crystal symmetry do not deviate from one structure to another. The only significant change is the contraction of the unit cell when there is one water molecule less. In both compounds the $[La(NO_3)_5(H_2O)_2]^{2-}$ complexes are joined by hydrogen bonds involving the coordinated water molecules in the $xy$-plane and this is in agreement with the unit cell contraction in the $z$-direction. Whether or not the removal of water is reversible and can be brought about by heating is currently under study by thermoanalytical methods.

REFERENCES

1. Zalkin, A., Forrester, J. D. and Templeton, D. H. *J. Chem. Phys. 39* (1963) 2881; Anderson, M. R., Jenkin, G. T. and White, J. W. *Acta Crystallogr. B 33* (1977) 3933.
2. Eriksson, B., Larsson, L. O., Niinistö, L. and Valkonen, J. *Acta Chem. Scand. A 34* (1980) 567.
3. Karaghouli, A. R. and Wood, J. S., *J. Chem. Soc. Dalton Trans.* (1973) 2318.
4. Toogood, G. E. and Chieh, C. *Can. J. Chem. 53* (1975) 831.
5. Addison, C. C., Greenwood, A. J., Haley, M. J. and Logan, N. *J. Chem. Soc. Chem. Commun.* (1978) 580.
6. Sherry, E. G. *J. Inorg. Nucl. Chem. 40* (1978) 257.
7. Bünzli, J.-C. G., Klein, B., Chapuis, G. and Schenk, K. J. *J. Inorg. Nucl. Chem. 42* (1980) 1307.
8. Eriksson, B., Larsson, L. O. and Niinistö, L. *J. Chem. Soc. Chem. Commun.* (1978) 1616; Eriksson, B., Larsson, L. O., Niinistö, L. and Valkonen, J. *Inorg. Chem. 19* (1980) 1207.
9. *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham 1974, Vol. 4, pp. 99−101.
10. Addison, C. C., Logan, N., Wallwork, S. C. and Garner, C. D. *Q. Rev. Chem. Soc. 25* (1971) 289.