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# The Crystal Structure of the Complex $[Y(H_2O)_5(NO_3)_2]\ [Y(H_2O)_2(NO_3)_4]$*

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The title compound was prepared by thermal decomposition of crystals of $Y(H_2O)_4(NO_3)_3 \cdot 2H_2O$. The structure was solved by Patterson and Fourier methods and isotropically refined to $R=0.12$. The unit cell is orthorhombic; the space group is $C222_1$ The crystal contains two crystallographically and chemically different complex ions, with yttrium atoms as the center of the complexes. The coordination number of the ion $Y(H_2O)_2(NO_3)_4$ is 10, while the ion $Y(H_2O)_5(NO_3)_2$ has coordination number 9.

## INTRODUCTION

The coordination chemistry of rare earths has been studied comparatively little till recent years[1]. For this reason we have undertaken a program of systematic study of rare earth hydrate nitrates which aims to solve the structures of $Ce(H_2O)_5(NO_3)_3H_2O$ [2], $Y(H_2O)_4(NO_3)_32H_2O$ [3], $Ce(H_2O)_4(NO_3)_3$ [4]. The following structures have already been reported in the literature: $La(NO_3)(H_2O)_5H_2O$ [5], $Y(NO_3)_3(H_2O)_4H_2O$ [6] and $Pr(NO_3)_3(H_2O)_42H_2O$ [7]. Here we report the structural determination of a novel yttrium compound with the aim of contributing to a better understanding of the coordination chemistry of solid rare earth complexes.

## EXPERIMENTAL

The title compound was prepared by thermal decomposition of crystals of $Y(H_2O)_4(NO_3)_3\ 2H_2O$, which were subjected to thermal gravimetry (TG) and differential thermal analysis (DTA). The results of (TG) and (DTA) showed a phase transition at 361 K, accompanied by a weigth loss. Afterwards the crystals were kept at 361 K for seven days. Specimens of the title compound, suitable for X-ray analysis, were obtained from the melt. The crystals were transparent, rather hygroscopic and had to be sealed into Lindemann capillary tubes.

### *Crystal Data*

Approximate cell parameters were determined from oscillation photographs and accurate unit cell parameters were determined by a least-squares treatment of 15 reflections measured on a Synthex $P\bar{1}$ diffractometer. The unit cell is orthorhombic with $a = 0.9274(6)$ nm, $b = 1.1001(4)$ nm, $c = 2.0055(9)$ nm, $V = 2.046(2)$ nm$^3$. $D_x = 2.193$ Mg m$^{-3}$ for $Z = 4$. The extinctions indicated the space group $C222_1$, (No. 20).

* Dedicated to Professor D. Grdenić on occasion of his 65th birthday.

*Intensity data, Structure Determination and Refinement*

The intensity data were collected on a Syntex $P\bar{1}$ diffractometer using a ω-scan procedure, with graphite monochromated $MoK_\alpha$ radiation. Reflections up to $2\Theta = 50^\circ$ were collected and 660 with $I > 3\sigma(I)$ were accepted for structure solution and refinement. The intensity data were corrected for Lorentz and polarization, but not for absorption.

The structure determination was carried out by the standard heavy atom method. We started with the assumption that the unit cell contained eight symmetrically equivalent yttrium atoms, but this assumption did not lead to the solution. Only the hypothesis of two symmetrically independent yttrium atoms allowed the interpretation of the Patterson map. The other non hydrogen atoms were found by successive structure factor and electron density calculations. The structure was refined by the use of a block-diagonal least-squares procedure[8]. Because of the lack of measured reflections, only yttrium atoms were refined anisotropically, while the remaining atoms were refined isotropically.*

The last cycle converged to $R = 0.12$. The final values of the atomic positional and thermal parameters, with estimated standard deviations, are given in Table I.

TABLE I

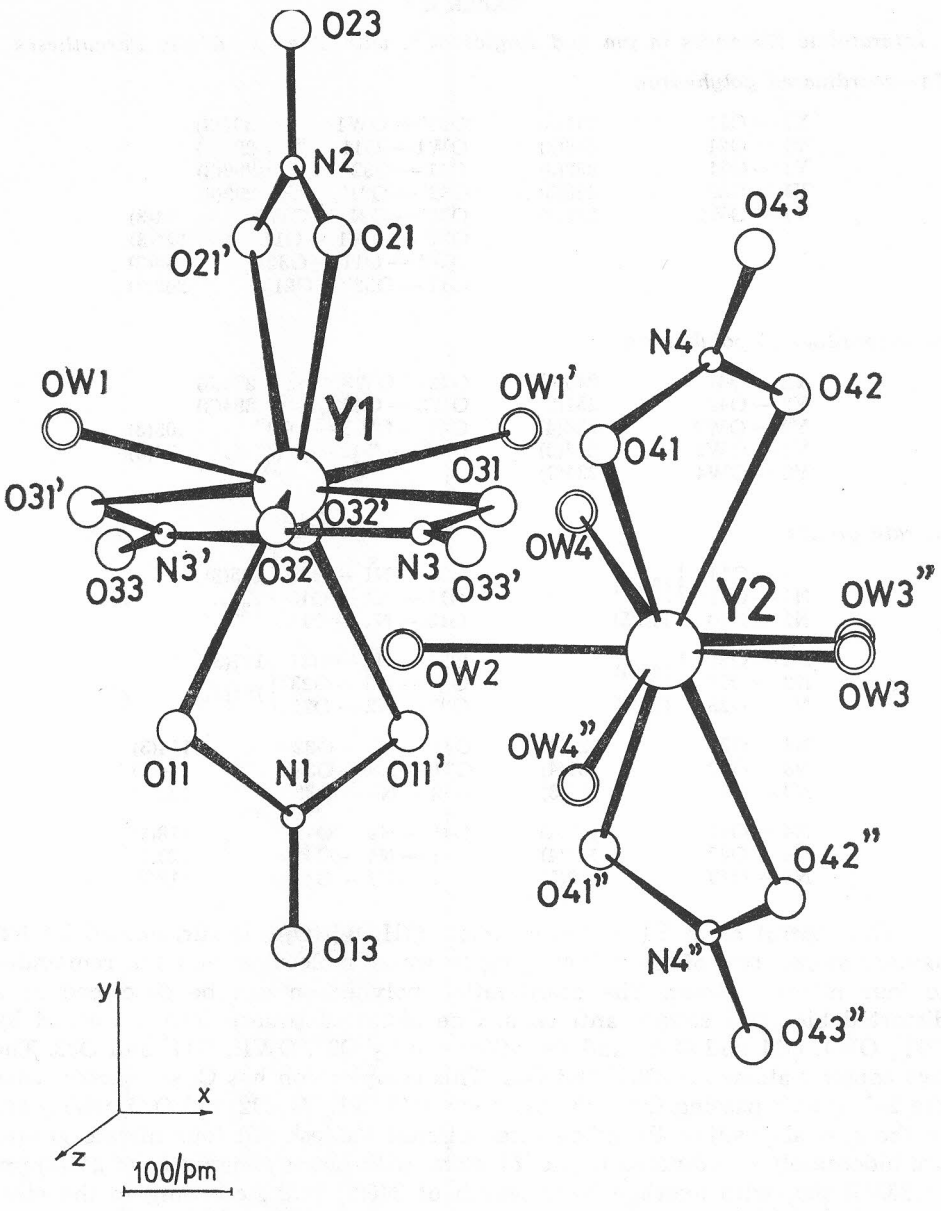
*Fractional Coordinates and Isotropic Thermal Parameters with e.s.d.'s in Parentheses*

| ATOM | $x$ | $y$ | $z$ | $B/10^4$ pm$^2$ |
|---|---|---|---|---|
| Y1 | 0.000 | 0.129(4) | 0.250 | $B_{eq} = 1.9(3)$ |
| Y2 | 0.364(5) | 0.000 | 0.000 | $B_{eq} = 2.3(3)$ |
| O11 | 0.387(4) | 0.433(3) | 0.262(2) | 4.3(7) |
| O13 | 0.500 | 0.261(4) | 0.250 | 2.7(7) |
| O21 | 0.039(3) | 0.330(2) | 0.300(1) | 1.8(5) |
| O23 | 0.500 | 0.005(5) | 0.250 | 5.5(9) |
| O31 | 0.199(4) | 0.112(3) | 0.335(2) | 3.8(6) |
| O32 | 0.487(4) | 0.595(3) | 0.371(1) | 3.6(6) |
| O33 | 0.173(3) | 0.080(3) | 0.438(1) | 3.0(6) |
| O41 | 0.202(4) | 0.338(3) | 0.574(1) | 3.2(6) |
| O42 | 0.017(3) | 0.297(2) | 0.512(1) | 2.6(5) |
| O43 | 0.053(4) | 0.180(4) | 0.597(2) | 4.9(8) |
| N1 | 0.000 | 0.136(4) | 0.750 | 2.1(7) |
| N2 | 0.000 | 0.389(4) | 0.250 | 2.1(8) |
| N3 | 0.126(3) | 0.092(3) | 0.383(1) | 1.1(5) |
| N4 | 0.093(4) | 0.269(3) | 0.560(2) | 3.1(7) |
| OW1 | 0.277(3) | 0.677(3) | 0.293(2) | 3.3(6) |
| OW2 | 0.109(5) | 0.000 | 0.000 | 3.6(8) |
| OW3 | 0.548(4) | —0.004(4) | 0.081(2) | 5.3(8) |
| OW4 | 0.224(3) | 0.390(3) | 0.408(1) | 2.7(5) |

## DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The crystal structure consists of two types of complex yttrium ions: Y1 is the central atom of the negatively charged complex ion diaquatetranitratoyttrium(III), $Y(H_2O)_2(NO_3)_4$, while Y2 is the central atom of the positively charged complex ion pentaaquadinitratoyttrium(III), $Y(H_2O)_5(NO_3)_2$, (Figure 1). Neither of these two types of ions has been reported till now[1-7]. The unit cell contains four ions of each kind.

* List of structure factors are available from the autors on request.




' : $\bar{x}$, y, $\frac{1}{2}$ - z

" : x, $\bar{y}$, $\bar{z}$

Figure 1. Projection of the two complex ion along 001 with the atomic numbering scheme

TABLE II

*Interatomic Distances in pm and Angles in °, with Their e.s.d.'s in Parentheses*

*Ten-coordinated polyhedron*

| | | | |
|---|---|---|---|
| Y1 — O11 | 241(3) | O21′ — OW1 | 304(3) |
| Y1 — O21 | 246(2) | OW1 — O11 | 294(3) |
| Y1 — O31 | 252(3) | O11 — O32′ | 296(3) |
| Y1 — O32 | 246(3) | O32′ — O21′ | 299(3) |
| Y1 — OW1 | 231(3) | O32′ — O21′ — OW1 | 84(3) |
| | | O21′ — OW1 — O11 | 104(3) |
| | | OW1 — O11 — O32′ | 54(3) |
| | | O11 — O32′ — O21′ | 202(3) |

*Nine-coordinated polyhedron*

| | | | |
|---|---|---|---|
| Y2 — O41 | 240(3) | O42 — OW3 | 274(3) |
| Y2 — O42 | 251(2) | OW3 — O42″ | 294(3) |
| Y2 — OW2 | 236(4) | O42 — OW3 — O42″ | 105(3) |
| Y2 — OW3 | 236(3) | OW3 — O42 — OW″ | 70(3) |
| Y2 — OW4 | 234(3) | | |

*Nitrate groups*

| | | | |
|---|---|---|---|
| N1 — O11 } | 132(5) | O11 — N1 — O11′ | 105(3) |
| N1 — O11′ } | | O11 — N1 — O13 } | 125(4) |
| N1 — O13 | 113(5) | O13 — N1 — O11′ } | |
| N2 — O21 } | 125(4) | O21 — N2 — O21′ | 117(3) |
| N2 — O21′ } | | O21 — N2 — O23 } | 121(4) |
| N2 — O23 | 127(7) | O23 — N2 — O21′ } | |
| N3 — O31 | 120(4) | O31 — N3 — O32 | 114(3) |
| N3 — O32 | 131(4) | O31 — N3 — O33′ | 124(3) |
| N3 — O33′ | 119(3) | O32 — N3 — O33′ | 122(3) |
| N4 — O41 | 130(4) | O41 — N4 — O42 | 118(3) |
| N4 — O42 | 123(4) | O41 — N4 — O43 | 123(3) |
| N4 — O43 | 128(5) | O43 — N4 — O42 | 118(3) |

The central atom Y1 of the complex $Y(H_2O)_2(NO_3)_4$, is surrounded by ten oxygen atoms, two of them belonging to water molecules, and the remainder to four nitrate groups. The coordination polyhedron can be described as a distorted bicapped square antiprism. One distorted square face is formed by O21′, OW1, O11 and O32′, and the other one by O21, OW1′, O11′ and O32. The two capping atoms are O31′ and O31. This complex ion has $C_2$ symmetry, with the 2-fold axis passing through the atoms O13, N1, Y1, N2 and O23, which are in the special position 4b in the International Tables[9]. All four nitrate groups are bidentately coordinated to the Y1 atom, with bonds ranging from 241(3) pm to 252(3) pm, with average bond length of 246(3) pm. According to the classification by Addison et al[10], one can conclude that all four nitrate groups are symmetrically bidentately coordinated to the central atom.

The central atom Y2 of the complex $Y(H_2O)_5(NO_3)_2$ is surrounded by nine oxygen atoms, five of them belonging to water molecules and the remainder to the nitrate groups. The coordination polyhedron can be described as a distorted monocapped square antiprism. One distorted square face is formed by O41″, OW4, O41, OW4″, and atom OW2 as a cap, while the other face is formed by O42″, OW3, O42, OW3″. This complex ion also has $C_2$ symmetry,

with the 2-fold axis passing through atoms 0W2 and Y2 which are in the special position 4a[9]. Both nitrate groups have symmetrically bidentate bonds to the central atom Y2, with an average bond length 246(3) pm.

The nitrate groups are distorted from their ideal geometry. All four oxygen atoms from water molecules have shorter bonds to the corresponding central atom of the complex than any oxygen atom from the nitrate groups, as is usual in hydrate nitrates[1–7].

The crystal as a whole can be considered to be made up from two types of layers. One type consists of $Y(H_2O)_5(NO_3)_2$ ions, while the other consists of $Y(H_2O)_2(NO_3)_4$ ions. Both types of layers are perpendicular to the same direction, which corresponds to the crystallographic c-axis. The layers alternate and the distance between the centres of neighbouring layers is one quarter of a *c* period, ($c/4 = 501.4$ pm).

Because of the absence of bridging nitrate groups, the ions in the structure are bonded only by hydrogen and ionic bonds. Hydrogen atoms from water molecules could not be localized.

REFERENCES


1. *Structural Aspects of Some Rare Earth Nitrate Hydrates in the Solid State,* B. Eriksson, *Chem. Comm.* (1982) No. 3, Department of Structural Chemistry Arrhenius Laboratory, University of Stockholm, Stockholm 1982.
2. N. Milinski, B. Ribár, and M. Satarić, *Cryst. Struct. Comm.* **9** (1980) 473.
3. B. Ribár, N. Milinski, Ž. Budovalčev, and I. Krstanović, *Cryst. Struct. Comm.* **9** (1980) 203.
4. N. Milinski, P. Radivojević, B. Ribár, and S. Đurić, *Cryst. Struct. Comm.* **11** (1982) 1241.
5. B. Eriksson, L. O. Larsson, L. Niinistö, and J. Valkonen, *Inorg. Chem.* **19** No. 5 (1980) 1207.
6. B. Eriksson, L. O. Larsson, L. Niinistö, adn J. Valkonen, *Acta Chem. Scand.* **A34** (1980) 567.
7. C. C. Fuller and R. A. Jacobson, *Cryst. Struct. Comm.* **5** (1976) 349.
8. V. Albano, A. Domenicano, and A. Vaciago, *Full and Block-Diagonal Matrix Least-Squares Refinement for IBM 7040 Computer* (adapted for the Varian 73 Computer by Gy. Argay), Centro di Studio per la Strutturistica Chemica dell CNR, Roma, 1966.
9. *International Tables for X-ray Crystallography,* Vol. **I**, 15, Birmingham: Kynoch Press, 1952.
10. C. C. Addison, N. Lagan, S. C. Wallwork, and C. D. Garner, *Quart. Rev. Chem. Soc.* **25** (1971) 289.


## SAŽETAK

### Kristalna struktura kompleksa $[Y(H_2O)_2(NO_3)_4][Y(H_2O)_5(N_3)_2]$

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Kristal je dobijen termičkom dekompozicijom kristala $Y(H_2O)_4(NO_3)_3 \cdot 2H_2O$. Struktura je određena standardnom Pattersonovom i Fourierovom metodom i izotropno utačnjena metodom najmanjih kvadrata do faktora $R = 0.12$. Kristal je rompski, prostorna grupa $C222_1$. Kristal sadrži dva kristalografski i hemijski različita kompleksna jona, sa atomima itrijuma kao centrima kompleksa. Koordinacioni broj jednog atoma itrijuma jest 10 a drugoga 9.