SHORT-FORMAT PAPERS

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Reinvestigation of the Structure of [Y(H$_2$O)$_5$(NO$_3$)$_2$][Y(H$_2$O)$_2$(NO$_3$)$_4$]

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Abstract. Diyttrium hexanitrate heptahydrate, Y$_2$(NO$_3$)$_6$.7H$_2$O, M_r = 675.94, orthorhombic, $C222_1$, a = 9.295 (2), b = 11.029 (3), c = 20.010 (4) Å, V = 2051.3 (8) Å^3, Z = 4, D_x = 2.188 Mg m^{-3}, λ(Mo Kα) = 0.7107 Å, μ = 5.788 mm^{-1}, F(000) = 1336, T = 294 K. Least-squares refinement of 840 independent observed ($|F| > 3\sigma|F|$) reflections gave R = 0.058, wR = 0.053. This reinvestigation has resulted in a smaller R factor and smaller e.s.d.'s by a factor of two compared to those obtained previously by the refinement of 660 reflections by Radivojević, Milinski, Ribár & Lazar [*Croat. Chem. Acta* (1984), **57**, 451–455].

Experimental. The title compound was prepared by thermal decomposition of crystals of Y(NO$_3$).6H$_2$O (Merck Art. 12516) at 378 K. Differential thermal analysis showed two strong endothermic peaks at 361 and 378 K. At the first peak a complex of [Y(H$_2$O)$_5$(NO$_3$)$_2$][Y(H$_2$O)$_2$(NO$_3$)$_4$] (Radivojević, Milinski, Ribár & Lazar, 1984) arises and at the second one Y(NO$_3$)$_3$.3H$_2$O (Ribár, Radivojević, Argay & Kálmán 1988) is formed together with the crystals which have been analysed in our investigation. The structure of these crystals was solved and identified as the same complex of [Y(H$_2$O)$_5$(NO$_3$)$_2$][Y(H$_2$O)$_2$(NO$_3$)$_4$] which appears at the lower temperature (Radivojević, Milinski, Ribár & Lazar, 1984).

A transparent crystal with dimensions 0.42 × 0.33 × 0.17 mm was mounted on a Syntex $P2_1$ diffractometer equipped with graphite-monochromated Mo Kα radiation. Cell parameters were derived by least-squares fit for 25 centred reflections with 25 < 2θ < 29°. 2111 reflection intensities were measured to $2\theta_{max}$ = 55° and for $0 \le h \le 12$, $0 \le k \le 14$, $0 \le l \le 21$, with ω scans (scan speed minimum 6, maximum

60° min^{-1}, scan range 0.8°). Of 1045 unique reflections, 840 were taken as observed with $F > 3\sigma(F)$. Two standard reflections ($\overline{1}\overline{1}2$ and 0$\overline{4}$2) were verified every 100 reflections. No intensity variation was observed. The data were corrected for Lorentz and polarization effects and an empirical (ellipsoidal) absorption correction was applied (minimum and maximum transmission factors 0.427 and 0.736, respectively).

The structure was solved by direct methods using *SHEXTL* (Sheldrick, 1984). Full-matrix least-squares refinement with anisotropic thermal parameters for non-H atoms was carried out with *SHELX*76 (Sheldrick, 1976) by minimizing $\sum w(\Delta F)^2$

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* [Å$^2 \times 10^4$ *for* Y(1) *and* Y(2), Å$^2 \times 10^3$ *for* N *and* O *atoms*] *with e.s.d.'s in parentheses*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Y(1)	1357 (2)	0	5000	285 (4)
Y(2)	0	3708 (2)	2500	237 (4)
N(3)	867 (16)	−2334 (13)	4392 (7)	51 (4)
N(4)	1287 (13)	4053 (11)	3822 (6)	35 (3)
N(5)	0	6268 (16)	2500	42 (5)
N(6)	0	1064 (17)	2500	43 (5)
O(7)	1973 (13)	−1650 (10)	4265 (6)	53 (3)
O(8)	601 (17)	−3211 (12)	4039 (6)	82 (5)
O(9)	110 (13)	−1998 (11)	4875 (6)	64 (3)
O(10)	−93 (11)	4082 (9)	3703 (5)	50 (3)
O(11)	1726 (12)	4200 (12)	4383 (5)	55 (4)
O(12)	2024 (12)	3846 (13)	3333 (5)	57 (4)
O(14)	0	7428 (12)	2500	56 (5)
O(15)	1096 (12)	5699 (9)	2394 (8)	70 (4)
O(16)	389 (11)	1710 (9)	2998 (5)	40 (3)
O(17)	0	−20 (16)	2500	86 (7)
OW(1)	2253 (12)	−1108 (10)	5928 (5)	48 (3)
OW(2)	−497 (12)	−139 (15)	5800 (6)	77 (4)
OW(3)	2229 (10)	3205 (10)	2063 (5)	39 (3)
OW(4)	3895 (13)	0	5000	36 (3)

Table 2. *Interatomic distances* (Å) *and selected angles* (°) *with e.s.d.'s in parentheses*

Nine-coordinated polyhedron

Y(1)—O(7)	2.409 (11)		
Y(1)—O(9)	2.502 (12)		
Y(1)—OW(1)	2.374 (10)		
Y(1)—OW(2)	2.357 (12)		
Y(1)—OW(4)	2.359 (12)		

O(9)—Y(1)—O(7)	52.0 (4)
OW(1)—Y(1)—O(7)	90.3 (4)
OW(1)—Y(1)—O(9)	77.7 (4)
OW(2)—Y(1)—O(7)	122.6 (4)
OW(2)—Y(1)—O(9)	70.9 (4)
OW(2)—Y(1)—OW(1)	72.0 (4)
OW(4)—Y(1)—O(7)	76.2 (3)
OW(4)—Y(1)—O(9)	117.6 (3)
OW(4)—Y(1)—OW(1)	69.5 (3)
OW(4)—Y(1)—OW(2)	137.1 (4)

Ten-coordinated polyhedron

Y(2)—O(10)	2.444 (10)
Y(2)—O(12)	2.518 (11)
Y(2)—O(15)	2.430 (10)
Y(2)—O(16)	2.445 (10)
Y(2)—OW(3)	2.316 (10)

O(12)—Y(2)—O(10)	50.5 (4)
O(15)—Y(2)—O(10)	87.0 (4)
O(15)—Y(2)—O(12)	71.9 (4)
O(16)—Y(2)—O(10)	75.9 (3)
O(16)—Y(2)—O(12)	71.0 (4)
O(16)—Y(2)—O(15)	142.0 (4)
OW(3)—Y(2)—O(10)	116.4 (3)
OW(3)—Y(2)—O(12)	66.2 (4)
OW(3)—Y(2)—O(15)	79.0 (4)
OW(3)—Y(2)—O(16)	78.8 (3)

Nitrate group

N(3)—O(7)	1.300 (19)	O(7)—N(3)—O(9)	115.1 (13)
N(3)—O(8)	1.223 (19)	O(7)—N(3)—O(8)	120.4 (14)
N(3)—O(9)	1.252 (19)	O(8)—N(3)—O(9)	124.5 (15)
N(4)—O(10)	1.305 (16)	O(10)—N(4)—O(12)	114.3 (12)
N(4)—O(11)	1.205 (16)	O(11)—N(4)—O(12)	125.7 (13)
N(4)—O(12)	1.216 (16)	O(10)—N(4)—O(11)	120.0 (12)
N(5)—O(14)	1.279 (22)	O(15)—N(5)—O(15a)	118.0 (12)
N(5)—O(15)	1.215 (14) (× 2)	O(14)—N(5)—O(15)	121.1 (11)
		O(14)—N(5)—O(15a)	120.9 (11)
N(6)—O(16)	1.277 (14) (× 2)	O(16)—N(6)—O(16a)	112.3 (11)
N(6)—O(17)	1.196 (26)	O(16)—N(6)—O(17)	123.9 (11)
		O(17)—N(6)—O(16a)	123.8 (12)

where $w = [\sigma^2(F) + 0.001(F)^2]^{-1}$. Final $R = 0.058$, $wR = 0.053$ for 153 parameters refined and $S = 1.195$. The residual electron density in the final difference Fourier synthesis was $\Delta\rho_{max} = 0.76$, $\Delta\rho_{min} = -0.65 \, e \, Å^{-3}$ located near $OW(4)$. The average shift to e.s.d. ratio Δ/σ was ≤ 0.010. Atomic scattering factors were those of *SHELX*76. The refined atomic and isotropic thermal parameters are listed in Table 1.* Interatomic distances and bond angles for non-H atoms are presented in Table 2. The atom-labelling schemes of the two types of complex Y ions Y(1) (coordination nine) and Y(2) (coordination ten) are shown in Fig. 1. Fig. 2 represents the packing diagram of the complex Y ions which shows that Y(1) ions are packed in one plane normal to the *c* axis, while Y(2) ions pack into another plane parallel to the previous one, the two planes being stacked alternately along the *c* axis.

Related literature. The redetermination of the crystal structure was undertaken to enable a precise comparison between the structure of this compound and those of the other yttrium nitrates. Analysis of the structures of $Y(NO_3)_3.6H_2O$ [av. Y—O = 2.470 Å,

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55481 (7 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: KA1002]

$D_x = 2.062$ Mg m^{-3} (Ribár, Milinski, Budovalčev & Krstanović, 1980)], $Y(NO_3)_3.5H_2O$ [av. Y—O = 2.458 Å, $D_x = 2.076$ Mg m^{-3} (Eriksson, 1982)], $Y_2(NO_3)_6.7H_2O$ [av. Y—O = 2.418 Å, $D_x = 2.188$ Mg m^{-3} (present study)], $Y(NO_3)_3.3H_2O$ [av. Y—O = 2.396 Å, $D_x = 2.246$ Mg m^{-3} (Ribár, Radivojević, Argay & Kálmán, 1988)] and $Y(NO_3)_3.H_2O$ [av.
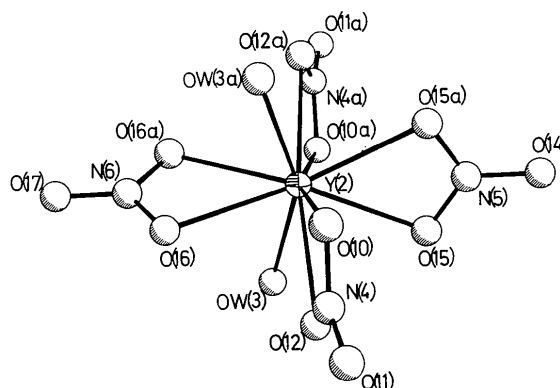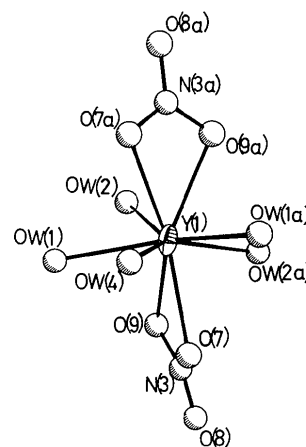
Fig. 1. Perspective views of (top) [Y(H₂O)₅(NO₃)₂] (symmetry code: (a) x, −y, 1 − z] and (bottom) [Y(H₂O)₃(NO₃)₄] [symmetry code: (a) −x, y, ½ − z], showing atomic numbering.
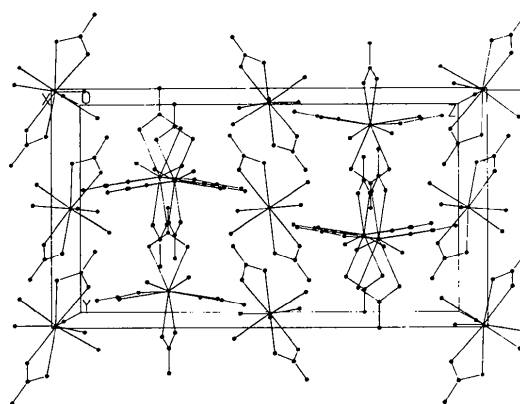
Fig. 2. Packing of the coordination polyhedra.

Y—O = 2.389 Å, D_x = 2.570 Mg m^{-3} (Ribár, Radivojević, Argay & Kálmán, 1990)], indicates the decrease of the average length of the Y—O bonds with the increase of the crystal density, which is directly related to the decrease of the number of water molecules.

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References

ERIKSSON, B. (1982). *Acta Chem. Scand. Ser. A*, **36**, 186–188.
RADIVOJEVIĆ, P., MILINSKI, N., RIBÁR, B. & LAZAR, D. (1984). *Croat. Chem. Acta*, **57**, 451–455.
RIBÁR, B., MILINSKI, N., BUDOVALČEV, Z. & KRSTANOVIĆ, I. (1980). *Cryst. Struct. Commun.* **9**, 203–206.
RIBÁR, B., RADIVOJEVIĆ, P., ARGAY, GY. & KÁLMÁN, A. (1988). *Acta Cryst.* C**44**, 595–597.
RIBÁR, B., RADIVOJEVIĆ, P., ARGAY, GY. & KÁLMÁN, A. (1990). *Acta Cryst.* C**46**, 525–527.
SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
SHELDRICK, G. M. (1984). *SHELXTL User's Manual*. Revision 4. Nicolet XRD Corporation, Madison, Wisconsin, USA.

Caesium Nitrate (II) at 296 K

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Abstract. CsNO$_3$(II), M_r = 194.91, trigonal, $P3_1$ (or its enantiomorph $P3_2$), a = 10.902 (2), c = 7.740 (2) Å, V = 796.7 (4) Å^3, Z = 9, D_x = 3.656 (2) g cm^{-3}, λ(Ag $K\alpha$) = 0.56087 Å, μ = 102.04 cm^{-1}, $F(000)$ = 774, R = 0.019 and wR = 0.027 for 1036 unique data with $I > 3\sigma(I)$. The structure is isomorphous to that of RbNO$_3$(IV). Regarding the Cs and N atoms alone, the structure is of a slightly distorted CsCl type with nine pseudocubes per unit cell. The nitrate groups form almost planar equilateral triangles. Each nitrate plane is essentially parallel to a pair of pseudocube faces and one of the N—O bonds is nearly parallel to a pseudocube cell edge.

Experimental. Single crystals of CsNO$_3$ were grown, by slow evaporation of an aqueous solution at 292 K, as hexagonal-shaped c-axis needles. A single crystal 0.18 mm across and 31 mm long was mounted on a glass fiber. An Enraf–Nonius CAD-4 diffractometer controlled by a PDP 11/34 computer under Enraf–Nonius software (Frenz, 1983), with graphite monochromator, was used to measure both unit-cell dimensions and integrated intensities. The former were determined from accurate measurement of the Bragg angles of 25 reflections with $10 < \theta <$ 20°. Data were collected by an ω–2θ scan technique, for $\Delta\omega$ = 0.6° + 0.45°tanθ. The maximum measurement time was 300 s. The integrated intensity of each reflection was measured for $2 < \theta < 22°$ (max. sinθ/λ

= 0.668 Å^{-1}) with indices in the range $-14 \le h \le$ 14, $-14 \le k \le 6$, $0 \le l \le 10$. Two standard reflections (060, 600) measured every 2 h showed no systematic variation of the intensities. Three other standard reflections ($10,\bar{8},\bar{1}$, 090, 900) measured every 300 reflections were used to control the orientation. 3353 reflections measured included 613 reflections which were considered unobserved, $I <$ $3\sigma_c(I)$, σ_c from counting statistics. The shape and dimensions of the crystal were used to calculate absorption corrections with maximum and minimum transmission values of 0.60 and 0.51, respectively. Lorentz and polarization corrections were made. Merging equivalent reflections [$R_{int}(F_o)$ = 0.027 for observed reflections and $R_{int}(F_o)$ = 0.041 for all reflections] resulted in 1036 reflections which were used to refine the structure. The room-temperature structure of RbNO$_3$(IV) (Pohl, Pohl & Adiwidjaja, 1992) with space group $P3_1$ was used as the initial model structure. The refinement converged rapidly using the programs *SHELX76* (Sheldrick, 1976) and *ORXFLS3* (Busing *et al.*, 1971). The origin was fixed by the Cs(2) atom. Scattering factors for Cs$^+$, N and O atoms and anomalous-dispersion terms for all atoms were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). In the final cycle all atoms were refined with anisotropic temperature factors and an isotropic extinction parameter (q = 0.03 × 10^4) was included. The function minimized was $\sum w(|F_o| - |F_c|)^2$ where weights w = 1/$\sigma^2(F)$ were