### Références

ANDERS, G. N. & KIERKEGAARD, P. (1968). Acta Chem. Scand. 22, 1466–1474

ARMSTRONG, R. D., BULMER, R. S. & DICKINSON, T. (1972). Fast Ion Transport in Solids, Belgirate Colloquium, édité par W. VAN GOOL, pp. 269–284. Amsterdam: North-Holland.

BEN AMARA, M., OLAZCUAGA, R., LE FLEM, G. & VLASSE, M. (1979). Acta Cryst. B35, 1567–1569.

BEN AMARA, M., VLASSE, M., OLAZCUAGA, R. & LE FLEM, G. (1979). Acta Cryst. B35, 50–52.

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). ORFLS. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.

GOODENOUGH, J. B., HONG, H. P. & KAFALAS, J. A. (1976). Mater. Res. Bull. 11, 203–220.

HAGENMULLER, P. & VAN GOOL, W. (1978). Rédacteurs, Solid Electrolytes. New York: Academic Press.

HOLT, E., DRAI, S., OLAZCUAGA, R. & VLASSE, M. (1977). Acta Cryst. B33, 95–98.

MCMASTER, W. H., KERR DEL GRANDE, N., MALLET, J. H. & HUBBEL, J. H. (1969). Compilation of X-ray Cross-Sections. Natl. Bur. Stand. US UCRL-50174, Sec. II, Rev. 1.

MAJLING, J. & HANIC, F. (1976). Chem. Zvesti, 30 (2), 145–152.

SAUBAT, B., VLASSE, M. & FOUASSIER, C. (1980). J. Solid State Chem. 34, 271–277.

# Tetraaquatrinitratoneodymium(III) Dihydrate, [Nd(NO3)3(H2O)4].2H2O

BY DEREK J. ROGERS, NICHOLAS J. TAYLOR AND GERALD E. TOOGOOD*

Department of Chemistry, University of Waterloo, 200 University Avenue West, Waterloo, Ontario, Canada N2L 3G1

**Abstract.** $M_r = 438.35$, triclinic, $P\bar{1}$, $a = 9.307$ (1), $b = 11.747$ (1), $c = 6.776$ (1) Å, $\alpha = 91.11$ (1), $\beta = 112.24$ (1), $\gamma = 109.15$ (1)°, $V = 639.0$ (2) Å³, $Z = 2$, $D_m = 2.27$, $D_x = 2.278$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 4.192$ mm⁻¹, $F(000) = 426$, $T = 298$ K. Final $R = 0.020$ (including H atoms) for 3311 observed reflections. Three symmetrically bidentate nitrates and four coordinated water molecules produce a formally ten-coordinate neodymium. However, the structure is best visualized as a tetragonal base–trigonal base seven-coordinate arrangement, with each nitrate considered as occupying only one coordination site. Two additional water molecules per unit are hydrogen-bonded, both inter- and intramolecularly, but are not directly coordinated to the metal. The overall arrangement is very nearly mirror-symmetrical.

**Introduction.** The structures of several hydrated lanthanoid nitrates have been published recently (Fuller & Jacobson, 1976; Ribár, Milinski & Budovalcev, 1980; Milinski, Ribár & Sataric, 1980), but in none of these studies have the positions of the H atoms been clearly established. This deficiency is even more marked in earlier studies involving film techniques (Rumanova, Volodina & Belov, 1965). To complement a Raman and IR spectroscopic investigation we have investigated the crystal and molecular structure of the title compound.

---

* To whom correspondence should be addressed.

**Experimental.** A crystal approximating a sphere of diameter 0.18 mm sealed in a quartz capillary. Syntex $P2_1$ diffractometer, graphite-monochromatized Mo $K\alpha$ radiation. Accurate cell constants from positions of 15 well distributed general reflections ($20 \leq 2\theta \leq 24°$). Data collected by $\theta$–$2\theta$ scan method using variable scan rates ($2.0$–$29.3°$ min⁻¹), scan width from $0.8°$ below $K\alpha_1$ to $0.8°$ above $K\alpha_2$; background counts at beginning and end of each scan for a total time equal to half the scan time. Two standard reflections (242 and 401) monitored every 100 measurements (only ±2% variation) and used to scale data to a common level. 3757 reflections ($3.2 \leq 2\theta \leq 60°$), $h: 0 \to 13$; $k: -16 \to 15$; $l: -9 \to 9$, 3311 with $I > 3\sigma(I)$ considered observed and used in structure determination and refinement. Data corrected for Lorentz and polarization effects and adjusted for the small spherical absorption effect ($\mu R = 0.38$) applied to $I_o$. Structure solved by Patterson and Fourier techniques and found to be isomorphous with praseodymium analogue. With all non-H atoms isotropic, structure refined on $F$ to $R = 0.062$; refinement with anisotropic temperature factors lowered $R$ to $0.025$. A difference Fourier synthesis clearly revealed positions of all water H atoms; these were included in the refinement which converged at $R = 0.020$, $R_w = 0.024$; the empirical weighting scheme $w^{-1} = 1.42 - 0.0315|F_o| + 0.00057|F_o|^2$ was utilized to give constant error throughout the various magnitudes of $F_o$. Programs described elsewhere (Taylor, Jacobson & Carty, 1975). Scattering factors for non-H atoms including cor-

rections for anomalous scattering of Nd from *International Tables for X-ray Crystallography* (1974), scattering factors for H those of Stewart, Davidson & Simpson (1965).

**Discussion.** Final positional parameters are listed in Table 1.* Bond lengths are shown in Table 2. All intra- and intermolecular H-atom contacts (2·9 Å) are shown in Table 3.

---

* Tables of structure factors, anisotropic thermal parameters, angles and OH bonds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38492 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final atomic coordinates (fractional,* $\times 10^4$, *for* H $\times 10^3$) *and isotropic thermal parameters* ($\times 10^4$, *for* H $\times 10^3$)

$$U_{eq} = (U_{11} U_{22} U_{33})^{1/3}.$$

| | $x$ | $y$ | $z$ | $U_{eq}$ or $U_{iso}$(Å$^2$) |
|---|---|---|---|---|
| Nd | 4013·0 (2) | 2251·1 (1) | 985·8 (2) | 269·2 (7) |
| O(1) | 4465 (4) | 416 (2) | 2302 (4) | 404 (12) |
| O(2) | 4422 (3) | 4322 (2) | 2455 (4) | 398 (12) |
| O(3) | 2323 (3) | 1765 (3) | 3103 (4) | 457 (13) |
| O(4) | 6030 (3) | 2790 (2) | 4724 (4) | 417 (12) |
| O(5) | 7785 (3) | 1383 (2) | 6859 (4) | 416 (12) |
| O(6) | 7975 (3) | 5146 (3) | 6748 (5) | 455 (13) |
| O(11) | 3124 (3) | 3289 (2) | −2436 (4) | 485 (13) |
| O(12) | 1349 (3) | 2718 (2) | −1002 (4) | 477 (14) |
| O(13) | 809 (3) | 3637 (3) | −3774 (5) | 550 (15) |
| O(21) | 3060 (3) | 702 (2) | −2469 (4) | 391 (11) |
| O(22) | 1231 (3) | 239 (3) | −1118 (4) | 493 (14) |
| O(23) | 805 (3) | −905 (2) | −3966 (4) | 469 (13) |
| O(31) | 6480 (3) | 2018 (2) | 467 (5) | 523 (14) |
| O(32) | 6539 (3) | 3853 (2) | 690 (5) | 554 (15) |
| O(33) | 8553 (3) | 3482 (3) | 280 (5) | 518 (15) |
| N(1) | 1722 (3) | 3229 (2) | −2450 (4) | 367 (13) |
| N(2) | 1670 (3) | −11 (2) | −2547 (4) | 354 (12) |
| N(3) | 7237 (3) | 3129 (3) | 493 (4) | 368 (13) |
| H(11) | 380 (7) | −11 (5) | 258 (8) | 70 (16) |
| H(12) | 498 (7) | 20 (5) | 228 (9) | 45 (16) |
| H(21) | 364 (6) | 441 (4) | 259 (8) | 65 (14) |
| H(22) | 502 (6) | 483 (4) | 247 (8) | 60 (13) |
| H(31) | 152 (7) | 137 (5) | 295 (9) | 76 (18) |
| H(32) | 266 (7) | 199 (5) | 434 (9) | 74 (15) |
| H(41) | 639 (4) | 238 (3) | 527 (6) | 32 (9) |
| H(42) | 653 (5) | 346 (4) | 523 (7) | 49 (11) |
| H(51) | 844 (6) | 175 (4) | 778 (8) | 59 (14) |
| H(52) | 830 (7) | 125 (5) | 632 (9) | 89 (18) |
| H(61) | 841 (7) | 556 (5) | 599 (9) | 82 (16) |
| H(62) | 864 (6) | 510 (4) | 765 (8) | 67 (15) |

Table 2. *Bond lengths* (Å)

| | | | | |
|---|---|---|---|---|
| Nd—O(1) | 2·450 (3) | | N(1)—O(11) | 1·280 (5) |
| Nd—O(2) | 2·462 (2) | | N(1)—O(12) | 1·260 (4) |
| Nd—O(3) | 2·451 (3) | | N(1)—O(13) | 1·210 (4) |
| Nd—O(4) | 2·429 (3) | | N(2)—O(21) | 1·270 (4) |
| Nd—O(11) | 2·621 (2) | | N(2)—O(22) | 1·249 (4) |
| Nd—O(12) | 2·580 (3) | | N(2)—O(23) | 1·223 (4) |
| Nd—O(21) | 2·605 (2) | | N(3)—O(31) | 1·259 (4) |
| Nd—O(22) | 2·718 (3) | | N(3)—O(32) | 1·260 (4) |
| Nd—O(31) | 2·547 (3) | | N(3)—O(33) | 1·223 (4) |
| Nd—O(32) | 2·565 (3) | | | |

Table 3. *Hydrogen bonds*

| O—H···O | O···O (Å) | O—H (Å) | H···O (Å) | O—H···O (°) |
|---|---|---|---|---|
| O(1)—H(11)···O(5)' | 2·687 (4) | 0·80 (6) | 1·88 (5) | 178 (2) |
| O(2)—H(21)···O(6)' | 2·734 (5) | 0·80 (6) | 1·94 (6) | 171 (2) |
| O(4)—H(41)···O(5) | 2·751 (4) | 0·71 (4) | 2·05 (4) | 171 (2) |
| O(4)—H(42)···O(6) | 2·739 (4) | 0·76 (4) | 1·98 (4) | 175 (2) |
| O(5)—H(52)···O(23)' | 2·876 (4) | 0·75 (7) | 2·14 (7) | 164 (2) |
| O(6)—H(61)···O(13)' | 2·857 (5) | 0·84 (6) | 2·03 (6) | 171 (2) |

Contacts (O···O) > 2·90 Å not listed.

In company with its praseodymium (Fuller & Jacobson, 1976) and yttrium (Ribár *et al.*, 1980) analogues, $Nd(NO_3)_3 6H_2O$ exists as $[M(NO_3)_3(H_2O)_4]$ units, with two additional water molecules per unit hydrogen-bonded both inter- and intramolecularly, but not directly coordinated to the metal. The molecule and its environment have approximate mirror-symmetry, the mirror passing through Nd, O(3), O(4), N(3) and O(33). Each $[Nd(NO_3)_3(H_2O)_4]$ unit is most easily visualized in terms of a seven-coordinate neodymium, with the nitrates considered as single entities as suggested previously in other structures by Bergman & Cotton (1966). Four O atoms from the water ligands and the three N atoms from the nitrate ligands are arranged in the tetragonal base–trigonal base mode shown in Fig. 1, and discussed as a possible geometry for heptacoordination by Muetterties & Wright (1967). An alternative description, involving a ten-coordinate geometry with bidentate nitrate ligands, in a distorted-bicapped-square-antiprism arrangement has been suggested for the analogous yttrium compound (Ribár *et al.*, 1980). Bond lengths and angles within the $[Nd(NO_3)_3(H_2O)_4]$ unit are generally unremarkable when compared with previously published data for nitratolanthanates if allowance is made for differences in the size of neodymium relative to other lanthanoids (*e.g.* Fuller & Jacobson, 1976; Ribár *et al.*, 1980; Toogood & Chieh, 1975; Chieh, Toogood, Boyle & Burgess, 1976). The bidentate nitrate ligands are symmetrically bonded according to the definition of Addison, Logan, Wallwork & Garner (1971) and the metal—oxygen (water ligand) bond lengths are significantly shorter than those to the nitrate O atoms.

With respect to the coordinated and crystallization water molecules we have been able to locate all H atoms and appropriate O—H and H···O separations are listed in Table 3 which also includes O···O distances and O—H···O angles. Most of the O—H···O
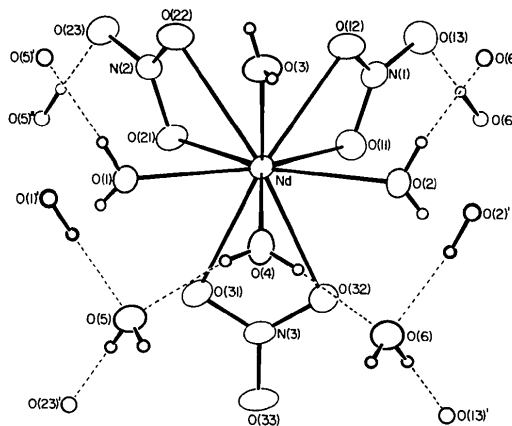


Fig. 1. *ORTEP* plot (Johnson, 1976) of $|Nd(NO_3)_3(H_2O)_4|.2H_2O$ showing atomic labelling and hydrogen-bonding scheme.

angles are close to 180° though packing restraints force some deviation from linearity. As the figure shows, each of these water molecules is involved in three hydrogen bonds (the fourth possible interaction, with an $O\cdots O$ separation of 2·9 Å, is deemed too weak to be included).

Even longer 'hydrogen bonds', both inter- and intramolecular, between coordinated waters and nitrate ligands, have been ignored in Table 3, although such interactions have been discussed by others (*e.g.* Burns, 1979) for $O\cdots O$ distances up to 2·95 Å.

The different water sites are reflected in different $\bar{v}$ values for their bending modes (Raman: 1650, 1634; IR: 1680 and 1640 cm$^{-1}$). As is often the case (*e.g.* Chakravorty, 1974) the O—H stretching absorptions are extremely broad (over 1000 cm$^{-1}$) with a vague maximum at about 2800 cm$^{-1}$. Metal–water vibrations occur at 320 (Raman), metal–nitrate vibrations at 225 and 200 cm$^{-1}$ (Raman).

**References**

ADDISON, C. C., LOGAN, N., WALLWORK, S. C. & GARNER, C. D. (1971). *Q. Rev. Chem. Soc.* **25**, 289–322.
BERGMAN, J. G. & COTTON, F. A. (1966). *Inorg. Chem.* **5**, 1208–1213.
BURNS, J. (1979). *Inorg. Chem.* **18**, 3044–3047.
CHAKRAVORTY, A. (1974). *Coord. Chem. Rev.* **13**, 1–46.
CHIEH, C., TOOGOOD, G. E., BOYLE, T. D. & BURGESS, C. M. (1976). *Acta Cryst.* B**32**, 1008–1011.
FULLER, C. C. & JACOBSON, R. A. (1976). *Cryst. Struct. Commun.* **5**, 349–352.
*International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
JOHNSON, C. K. (1976). *ORTEP*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.
MILINSKI, N., RIBÁR, B. & SATARIC, M. (1980). *Cryst. Struct. Commun.* **9**, 473–476.
MUETTERTIES, E. L. & WRIGHT, C. M. (1967). *Q. Rev. Chem. Soc.* **21**, 109–194.
RIBÁR, B., MILINSKI, N. & BUDOVALCEV, Z. (1980). *Cryst. Struct. Commun.* **9**, 203–206.
RUMANOVA, I. M., VOLODINA, G. F. & BELOV, N. V. (1965). *Sov. Phys. Crystallogr.* **9**, 545–550.
STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
TAYLOR, N. J., JACOBSON, S. E. & CARTY, A. J. (1975). *Inorg. Chem.* **14**, 2648–2653.
TOOGOOD, G. E. & CHIEH, C. (1975). *Can. J. Chem.* **53**, 831–835.

---

# Calcium Cesium Triazide Monohydrate, CaCs(N₃)₃.H₂O

BY H. KRISCHNER AND F. A. MAUTNER

*Institut für Physikalische und Theoretische Chemie, Abteilung für Strukturforschung, Technische Universität Graz, Rechbauerstrasse 12, A-8010 Graz, Austria*

AND CH. KRATKY

*Institut für Physikalische Chemie der Universität Graz, Heinrichstrasse 28, A-8010 Graz, Austria*

**Abstract.** $M_r = 317.06$, triclinic, $P\bar{1}$, $a = 6.846$ (1), $b = 7.557$ (1), $c = 8.810$ (1) Å, $\alpha = 71.59$ (1), $\beta = 82.80$ (1), $\gamma = 81.09$ (1)°, $V = 425.82$ Å$^3$, $Z = 2$, $D_x = 2.47$ Mg m$^{-3}$, $F(000) = 304.01$, Mo $K\alpha$, $\lambda = 0.71069$ Å (graphite monochromator), $\mu = 4.9$ mm$^{-1}$, $T = 298$ K. The crystal structure was solved by Patterson and Fourier methods and refined to $R = 0.034$ for 1475 independent counter reflections. Ca is seven-coordinated to six N atoms of azide groups and to one water molecule. The polyhedra around Ca are pentagonal bipyramids sharing one edge. Cs is nine-coordinated to eight azide groups and one water molecule. The mean N—N distance is 1.17 (2) Å.

**Introduction.** Crystal structures of several compounds between alkaline azides and alkaline-earth azides have been determined during the last few years (Krischner & Maier, 1980; Paar & Krischner, 1981). In the ternary system cesium azide/calcium azide/water, the title compound is formed at room temperature together with three other calcium cesium azide hydrates of different composition (Krischner & Hofer, 1983). Crystals are colorless and transparent. They dissolve readily in water, are stable for several days at room temperature and are not explosive.

**Experimental.** Crystal dimensions 0·25 × 0·25 × 0·30 mm, Stoe four-circle diffractometer. Cell dimensions from setting angles of 11 reflections with $2\theta \simeq 30°$. Intensity data: all reflections of one hemisphere with $2\theta \leq 50°$ (sin$\theta/\lambda \leq 0.595$ Å$^{-1}$), range of