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Structure of Tricaesium Diaquanonaazidedineodymate(III)

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(*Received* 19 *March* 1991; *accepted* 9 *July* 1991)

Abstract. $Cs_3[(H_2O)_2(N_3)_9Nd_2]$, $M_r = 1101.4$, triclinic, $P\bar{1}$, $a = 6.791$ (5), $b = 9.107$ (6), $c = 10.683$ (7) Å, $\alpha = 99.84$ (5), $\beta = 99.19$ (6), $\gamma = 110.56$ (6)°, $V = 592.0$ (9) Å^3, $Z = 1$, $D_m = 3.08$, $D_x = 3.089$ (4) Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 9.03$ mm^{-1}, $F(000) = 494$, $T = 302$ (1) K, final $R = 0.047$ for 1894 reflections. The Nd cations are eight coordinate (seven N atoms and a water molecule) and together with azide anions form a two-dimensional complex polymer network.

Introduction. Spectroscopic investigation of anhydrous complex caesium neodymium azides (Gatterer, Day, Fritzer & Sperka, 1988) indicated ninefold coordination of the Nd cation. Since, to the author's knowledge, no X-ray structure analysis of these systems has been reported, it was thought that it would be interesting to investigate the title complex which contains lanthanide–nitrogen bonds.

Experimental. The title compound was prepared by placing vessels containing an aqueous suspension of freshly precipitated $Nd(OH)_3$ with some Cs_2CO_3 added, together with a source of HN_3 ($NaN_3 + HClO_4$ in water), and a drying agent ($CaCl_2$) in a desiccator. After 2–3 weeks violet parallelepipeds, unstable in air, were formed. A crystal $0.4 \times 0.15 \times 0.25$ mm was cut from a larger one and placed in a capillary. D_m by flotation in $C_2H_4Br_2$/CH_2I_2. Oscillation and Weissenberg photographs indicated the triclinic system. Syntex $P2_1$ diffractometer, Mo $K\alpha$ radiation for lattice parameters (14 reflections, $16 < 2\theta < 28°$), variable $\theta/2\theta$ scan, $4 < 2\theta < 50°$, two standards every 50 reflections, final loss of intensity 26% after 57.5 h of irradiation, mean relative e.s.d. of the control reflections (after correcting for the decay) 3.3%, 2225 reflections measured out of which 2023 had $I \geq 3\sigma(I)$ and of which 1894 were unique, $R_{\text{int}} = 0.027$, index range h $0 \rightarrow 8$, k $-10 \rightarrow 10$, l $-12 \rightarrow 12$. Structure was solved with *SHELXS*86 (Sheldrick, 1986), and refined with *SHELX*76 (Sheldrick, 1976) in space group $P\bar{1}$. Neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV); real and imaginary components of anomalous dispersion included for all non-H atoms. The Nd atoms were located from a Patterson map; the remaining non-H atoms from a difference synthesis; one water H atom was found from a difference synthesis, the other was placed on the basis of assumed hydrogen-bond geometry. Absorption corrections computed after isotropic refinement with locally modified program *ABSORB* (Ugozzoli, 1987) were between 0.64 and 1.19. Final full-matrix least-squares refinement based on F (non-H atoms anisotropic, H atoms with common temperature factor and fixed positional parameters) gave $R = 0.0474$, $wR = 0.0497$, maximum $\Delta/\sigma < 0.001$, $\Delta\rho$ between -2.58 and 1.05 e Å^{-3}, highest peaks around Nd atoms, $w = 1/\sigma^2(F)$, number of parameters = 158.

Discussion. Final atomic parameters are given in Table 1 and the geometry of the Nd coordination in Table 2, together with average bond lengths for the azide anions.* An *ORTEP* view (Johnson, 1976) of the Nd coordination and crystal packing is shown in

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54464 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU0250]

0108-2701/92/010004-02$03.00

Table 1. *Final atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Nd	0.1969 (1)	0.21295 (7)	0.14334 (6)	0.0474 (2)
Cs1	0	0	0.5	0.0812 (6)
Cs2	0.1431 (2)	0.6694 (1)	0.23382 (8)	0.0660 (4)
N1	−0.1182 (17)	0.2776 (14)	0.0494 (11)	0.062 (5)
N2	−0.2837 (19)	0.2468 (12)	0.0842 (10)	0.060 (4)
N3	−0.4442 (17)	0.2218 (17)	0.1211 (12)	0.075 (6)
N4	0.3036 (18)	0.0727 (13)	0.3072 (10)	0.065 (5)
N5	0.4787 (20)	0.1208 (13)	0.3772 (11)	0.061 (5)
N6	0.6478 (20)	0.1631 (16)	0.4479 (12)	0.075 (5)
N7	0.4307 (21)	0.4578 (15)	0.3146 (12)	0.073 (5)
N8	0.6172 (20)	0.5364 (13)	0.3640 (10)	0.064 (5)
N9	0.7967 (22)	0.6120 (18)	0.4125 (12)	0.089 (6)
N10	0.1227 (17)	0.0550 (12)	−0.0886 (10)	0.058 (4)
N11	0.2419 (20)	0.1023 (12)	−0.1591 (11)	0.064 (4)
N12	0.3529 (25)	0.1472 (16)	−0.2263 (12)	0.087 (6)
N13	0.3290 (18)	0.4300 (13)	0.0168 (11)	0.062 (5)
N14	0.5	0.5	0	0.059 (7)
O*W*	0.0080 (15)	0.2714 (12)	0.3180 (9)	0.067 (4)

Table 2. *Distances* (Å) *and angles* (°) *for the* Nd *coordination sphere, together with averaged bond lengths in the azide ions*

Nd—N1	2.516 (12)	Nd—N3$^{\rm i}$	2.461 (13)
Nd—N4	2.496 (11)	Nd—N7	2.456 (13)
Nd—N10	2.517 (10)	Nd—N10$^{\rm ii}$	2.529 (11)
Nd—N13	2.568 (11)	Nd—O*w*	2.513 (10)

Bond	n	Mean	Min. value	Max. value
N—N	9	1.18 (2)	1.14 (2)	1.21 (2)

N3$^{\rm i}$—Nd—N1	144.2 (5)	N4—Nd—N3$^{\rm i}$	75.0 (5)
N4—Nd—N1	140.6 (4)	N7—Nd—N3$^{\rm i}$	79.8 (5)
N7—Nd—N1	104.0 (5)	N7—Nd—N4	83.2 (5)
N10—Nd—N1	82.6 (4)	N10—Nd—N3$^{\rm i}$	76.8 (5)
N10—Nd—N4	112.5 (4)	N10—Nd—N7	146.8 (5)
N10$^{\rm ii}$—Nd—N1	76.4 (4)	N10$^{\rm ii}$—Nd—N3$^{\rm i}$	120.3 (5)
N10$^{\rm ii}$—Nd—N4	76.8 (4)	N10$^{\rm ii}$—Nd—N7	145.7 (5)
N10$^{\rm ii}$—Nd—N10	67.5 (4)	N13—Nd—N1	71.4 (4)
N13—Nd—N4	146.1 (4)	N13—Nd—N3$^{\rm i}$	75.3 (5)
N13—Nd—N10	75.6 (4)	N13—Nd—N7	75.9 (5)
O*W*—Nd—N1	69.8 (4)	N13—Nd—N10$^{\rm ii}$	133.3 (4)
O*W*—Nd—N4	77.7 (4)	OW—Nd—N3$^{\rm i}$	139.8 (4)
O*W*—Nd—N10	141.8 (4)	OW—Nd—N7	68.2 (4)
O*W*—Nd—N13	117.2 (4)	OW—Nd—N10$^{\rm ii}$	80.4 (4)

Symmetry code: (i) $x + 1, y, z$; (ii) $-x, -y, -z$.

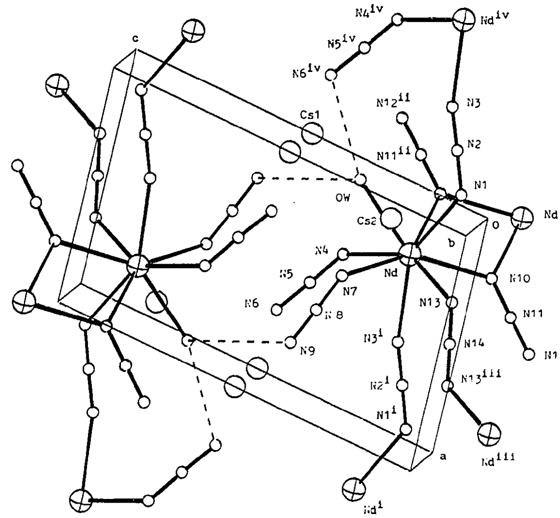

Fig. 1. Nd coordination and crystal packing. The dashed lines represent hydrogen bonds; the symmetry codes are the same as in Table 2, and also: (iii) $1 - x, 1 - y, -z$; (iv) $-1 + x, y, z$.

Fig. 1. The structure consists of Cs cations and two-dimensional polymeric complex anions parallel to the (001) plane. The polymeric net is formed by means of two kinds of azide bridges: longitudinal (Nd-N-N-N-Nd, in the case of N1—N2—N3 and N13—N14—N13′) and lateral, where one of the terminal azide N atoms bridges two Nd ions (the case of N10—N11—N12). Each of the two remaining azide ions (N4—N5—N6 and N7—N8—N9) is bonded to the metal through one of its terminal N atoms and forms a hydrogen bond with water through the other terminal N atom. The Nd—N bond lengths are significantly shorter than generally observed (*e.g.* Sinha, 1976; Starynowicz, 1991); the Nd—water distance is unexceptional; the shortest Nd—Nd separation is 4.197 (4) Å. The coordination of the metal may be best described as a slightly distorted square antiprism ($\Delta = 0.032$ Å^2, see Drew, 1977) with the bases defined by N1–N13–N7–O*W* and N10–N3–N4–N10$^{\rm ii}$. The best fitted dodecahedron had $\Delta = 0.086$ Å^2. The shortest Cs—N distances are between 3.13 and 3.26 Å. The structure is held together by electrostatic Cs–N interactions and by a network of intermolecular hydrogen bonds.

The author thanks Professor K. Bukietyńska for helpful discussion, and Professor T. Głowiak for advice and help in performing the measurements.

Note added in proof. Two structures of caesium lanthanide azides have recently been reported [Mautner, Krischner, Fritzer & Kratky (1989). *J. Mol. Struct.* **213**, 169–174; Mautner & Krischner (1990). *Monatsh. Chem.* **121**, 781–786]. I thank Dr Karl Gatterer for interesting discussion and information.

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