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Structure of Tripotassium Aquabis(nitrilotriacetato)neodymate(III) Pentahydrate

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Abstract. $K_3[Nd(C_6H_6NO_6)_2H_2O].5H_2O$, $M_r = 745·9$, monoclinic, $C2/c$, $a = 15·43$ (3), $b = 12·93$ (2), $c = 26·14$ (3) Å, $\beta = 96·58$ (15)°, $V = 5181$ (15) Å^3, $Z = 8$, $D_m = 1·93$, $D_x = 1·912$ (6) Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 2·57$ mm^{-1}, $F(000) = 2968$, $T = 302$ (2) K, final $R = 0·039$ for 5044 reflections. The Nd ion is nine-coordinate (seven O and two N atoms), forming an approximate tricapped trigonal prism. The analogous compounds of Eu and Ho are probably isomorphic.

Introduction. It is known from spectroscopic investigations (Bukietyńska & Mondry, 1985, 1987) that nitrilotriacetic acid (NTA) may form at least two different complexes with a lanthanide ion, depending on stoichiometry. The 1:1 complexes for light (Pr–Tb) and heavy (Dy–Lu) lanthanides have been described previously (Martin & Jacobson, 1972*a*,*b*). They display certain features common in the complexes of rare earths with aminopolycarboxylic acids (Sinha, 1976; Fuller, Molzahn & Jacobson, 1978; Nesterova, Porai-Koshits, Mitrofanova & Filippova, 1980): (*a*) the metal–nitrogen distance is 0·2–0·3 Å longer than the shortest metal–carboxylic oxygen bond; (*b*) waters or hydroxyl groups are often more remote than carboxyl oxygens; (*c*) the metal–carboxylic oxygen distance may be increased if the carboxyl group is involved in bridge formation [this is not limited to aminopolycarboxylates only (Đào, 1987)]. The present work aims to determine the structures of the lanthanide–NTA 1:2 complexes.

Experimental. The title compound was prepared by addition of NTA to a suspension of freshly precipitated $Nd_2(CO_3)_3$ in a hot aqueous solution of K_2CO_3. The resulting solution was allowed to evaporate at ambient temperature, until large well-formed pink parallelepipeds were formed. Anal.: calc.: Nd 19·3, K 15·7, C 19·3, N 3·8, H 3·2, water of coordination and crystallization 14·5%; found: Nd 18·7, K 17·2, C 17·3, N 3·7, H 3·2, water (thermogravimetrically) 14·4%. A parallelepiped 0·2 × 0·2 × 0·15 mm was cut from a larger crystal, D_m by flotation in $C_2H_4Br_2/CHCl_3$. Systematic absences indicated two possible space groups, Cc or $C2/c$, of which the latter was successfully attempted. Syntex $P2_1$ diffractometer, Mo $K\alpha$ radiation for lattice parameters (15 reflections, $19 < 2\theta < 24°$), variable $\theta/2\theta$ scan, $4 < 2\theta < 60°$, three standards every 100 reflections, mean variance 6·0%, 7780 intensities measured, index range h 0→20, k 0→18, l −36→36, no corrections for absorption or extinction. 5247 reflections with $I > 3\sigma(I)$ were averaged to 5050 unique reflections, $R(F^2)$ and $wR(F^2)$ were 0·0220 and 0·0201 respectively. Most calculations were performed with locally modified *XTL/XTLE* programs (Syntex, 1976). Neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974), real and imaginary components of anomalous dispersion included for all non-H atoms. The Nd atom was located from a Patterson map, the remaining non-H atoms from subsequent difference syntheses; C-bonded hydrogens placed geometrically, water hydrogens from difference syntheses, not all of them found. During structure solution it was necessary to interchange the positions of K4 and O*W*6 because of an abnormally large temperature factor for K4. The occupancy factor of K4 in its new position was set to 0·5 in accordance with stoichiometry, O*W*7 was also found to be disordered with site occupancy 0·5. Final full-matrix least-squares refinement based on F (non-H atoms anisotropic, except O*W*7 isotropic, hydrogens with fixed parameters), $R = 0·039$, $wR = 0·045$, $S = 2·47$, $\Delta\rho$ between −0·63 and 1·30 e Å^{-3}, the highest peaks around Nd and K atoms, $w = 1/\sigma^2(F)$. Oscillation and Weissenberg photographs, as well as the infrared spectra, suggest isomorphism of the analogous compounds of Eu and Ho.

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Discussion. Final atomic parameters are given in Table 1,* and the geometry of the neodymium coordination sphere is shown in Table 2, together with averaged bond lengths and angles for the NTA residues. The structure consists of aquabis(nitrilotriacetato)neodymate anions, potassium cations and water of hydration. The coordination environment of Nd^{3+} consists of six carboxylic oxygens, a water and two nitrogens, which form a distorted tricapped trigonal prism. The parameter Δ is 0·026 Å², where Δ is defined as $\sum d_i^2/9$, $i = 1,9$, d_i being the distance between the real position of the ith atom (vertex), and the relevant one in the ideal least-squares-fitted polyhedron (Drew, 1977). The caps are formed by N1, N2 and O*W*1, and the two bases by O1, O4, O5 and O2, O3, O6 respectively. The best alternative description of the coordination polyhedron is as a monocapped square antiprism with N1 as the cap, O1, O2, O3, O4 as the capped base, and O5, O6, N2 and O*W*1 as the non-capped one; in this case $\Delta = 0{\cdot}066$ Å². The *ORTEP* view (Johnson, 1976) of the complex anion is given in Fig. 1. The distances Nd—O and Nd—N follow the usual pattern observed in compounds of this kind. The mean Nd—N distance, 2·69 (1) Å, is 0·25 (2) Å greater than the average length of the Nd—O(carboxylic) bond, 2·44 (2) Å. The latter bonds show little variation due to the absence of carboxyl bridges. The Nd—O*W*1 distance is greater than Nd—O(carboxyl). The C—C, C—O and C—N bond lengths are within the normal ranges. There are

Table 1. *Final atomic coordinates and equivalent isotropic thermal parameters*

$$B_{eq} = \tfrac{1}{3}(B_{11} + B_{22} + B_{33}).$$

	x	*y*	*z*	B_{eq}(Å²)
Nd	0·17735 (2)	0·04352 (2)	0·35315 (1)	1·75 (1)
K1	0·3968 (1)	0·0382 (2)	0·05547 (6)	3·9 (2)
K2	0·1837 (2)	0·2686 (2)	0·16222 (7)	4·8 (2)
K3	0	0·2101 (2)	0·25	3·6 (2)
K4*	0·4139 (3)	−0·0174 (4)	0·2381 (2)	6·6 (5)
N1	0·0621 (3)	−0·0281 (4)	0·4149 (2)	2·3 (4)
N2	0·2997 (4)	0·1874 (4)	0·3799 (2)	2·5 (4)
O1	0·0221 (3)	0·0546 (4)	0·3207 (2)	2·4 (3)
O2	0·2423 (3)	−0·0052 (4)	0·4388 (2)	3·3 (4)
O3	0·1666 (3)	−0·1439 (4)	0·3563 (2)	3·6 (4)
O4	0·1297 (3)	0·1906 (4)	0·4009 (2)	3·0 (4)
O5	0·1732 (3)	0·1869 (4)	0·2936 (2)	3·2 (4)
O6	0·3274 (3)	−0·0026 (4)	0·3389 (2)	2·9 (4)
O7	−0·1181 (3)	0·0702 (4)	0·3312 (2)	3·2 (4)
O8	0·2330 (4)	−0·0908 (5)	0·5111 (3)	5·7 (6)
O9	0·1198 (4)	−0·2908 (4)	0·3869 (3)	5·8 (6)
O10	0·1503 (4)	0·3331 (4)	0·4479 (3)	4·4 (5)
O11	0·2234 (5)	0·3300 (5)	0·2624 (3)	6·4 (6)
O12	0·4678 (4)	0·0000 (4)	0·3685 (3)	4·7 (5)
O*W*1	0·1628 (3)	−0·0260 (4)	0·2626 (2)	3·3 (4)
O*W*2	−0·0087 (4)	0·3020 (5)	0·3423 (3)	5·4 (5)
O*W*3	0·1651 (4)	0·2614 (5)	0·0556 (3)	5·3 (5)
O*W*4	0·4932 (5)	0·1555 (7)	−0·0103 (3)	8·3 (8)
O*W*5	0·2994 (6)	0·0376 (9)	0·1520 (5)	13·6 (14)
O*W*6	0·5	0·3527 (7)	0·25	10·3 (15)
O*W*7*	0·5018 (12)	0·1550 (14)	0·2207 (7)	10·2 (5)†
C1	−0·0199 (4)	0·0310 (5)	0·4050 (3)	2·5 (4)
C2	0·1020 (5)	−0·0176 (6)	0·4683 (3)	3·2 (5)
C3	0·0435 (4)	−0·1379 (5)	0·4016 (3)	3·0 (5)
C4	−0·0408 (4)	0·0530 (5)	0·3478 (2)	2·2 (4)
C5	0·2003 (4)	−0·0392 (6)	0·4736 (3)	3·1 (5)
C6	0·1167 (5)	−0·1956 (5)	0·3814 (3)	2·8 (5)
C7	0·2738 (5)	0·2535 (6)	0·4211 (3)	3·7 (6)
C8	0·3097 (5)	0·2511 (6)	0·3334 (3)	3·8 (6)
C9	0·3812 (4)	0·1333 (5)	0·3961 (3)	3·0 (5)
C10	0·1767 (5)	0·2611 (5)	0·4230 (3)	2·8 (5)
C11	0·2291 (5)	0·2568 (6)	0·2939 (3)	3·4 (6)
C12	0·3939 (4)	0·0373 (6)	0·3650 (3)	3·0 (5)

* Disordered, occupancy factor 0·5.
† O*W*7 refined isotropically, B_{iso} given.

Table 2. *Distances* (Å) *and angles* (°) *for the neodymium coordination sphere, together with averaged bond lengths and angles in the NTA moieties*

Nd—N1	2·698 (5)	Nd—N2	2·685 (5)
Nd—O1	2·451 (4)	Nd—O2	2·427 (4)
Nd—O3	2·431 (4)	Nd—O4	2·434 (4)
Nd—O5	2·416 (4)	Nd—O6	2·459 (4)
Nd—O*W*1	2·517 (4)		
N1—Nd—N2	125·0 (2)	N1—Nd—O1	62·8 (2)
N1—Nd—O2	65·8 (2)	N1—Nd—O3	65·5 (2)
N1—Nd—O4	72·7 (2)	N1—Nd—O5	132·7 (2)
N1—Nd—O6	134·7 (2)	N1—Nd—O*W*1	116·5 (2)
N2—Nd—O1	132·8 (2)	N2—Nd—O2	74·7 (2)
N2—Nd—O3	136·9 (2)	N2—Nd—O4	69·5 (2)
N2—Nd—O5	66·6 (2)	N2—Nd—O6	62·0 (2)
N2—Nd—O*W*1	118·5 (2)	O1—Nd—O2	128·1 (2)
O1—Nd—O3	90·1 (2)	O1—Nd—O4	77·9 (2)
O1—Nd—O5	77·3 (2)	O1—Nd—O6	149·4 (2)
O1—Nd—O*W*1	73·6 (2)	O2—Nd—O3	74·5 (2)
O2—Nd—O4	81·2 (2)	O2—Nd—O5	140·4 (2)
O2—Nd—O6	77·3 (2)	O2—Nd—O*W*1	139·2 (2)
O3—Nd—O4	137·3 (2)	O3—Nd—O5	142·2 (2)
O3—Nd—O6	80·4 (2)	O3—Nd—O*W*1	71·2 (2)
O4—Nd—O5	75·2 (2)	O4—Nd—O6	127·7 (2)
O4—Nd—O*W*1	139·6 (2)	O5—Nd—O6	92·6 (2)
O5—Nd—O*W*1	71·1 (2)	O6—Nd—O*W*1	75·8 (2)

	n	Mean	Min. value	Max. value
C—N	6	1·472 (11)	1·458 (8)	1·491 (9)
C—C	6	1·515 (12)	1·498 (9)	1·533 (9)
C—O	12	1·250 (13)	1·232 (8)	1·274 (8)
C—N—C	6	110·4 (14)	108·4 (5)	112·2 (5)
N—C—C	6	113·3 (19)	110·5 (5)	115·3 (5)
C—C—O	12	117·7 (7)	116·7 (6)	118·7 (6)
O—C—O	6	124·5 (8)	123·1 (7)	125·4 (6)

n = number of bonds or angles.

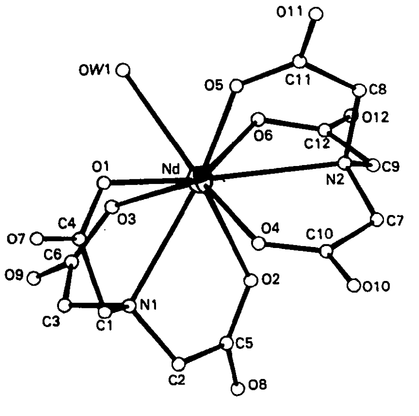

Fig. 1. Molecular diagram and the numbering scheme of the complex anion.

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* Lists of structure factors, anisotropic thermal parameters, hydrogen-bond distances and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43910 (34 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

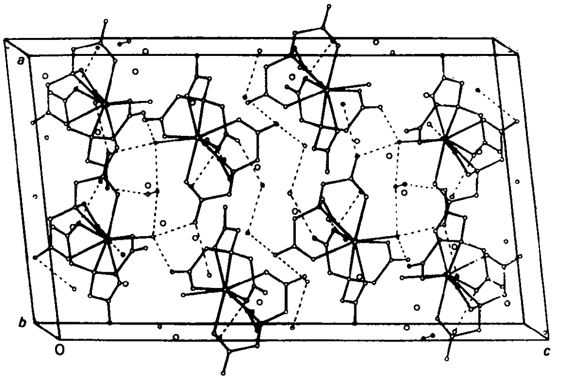

Fig. 2. View of the crystal structure. The dotted lines represent the hydrogen bonds.

four crystallographically independent potassium cations in the structure. K1, K2 and K3 ions are six coordinate (four carboxyl oxygens and two waters), the disordered K4 is five coordinate (two carboxyl oxygens and three waters). The whole structure is held together by a network of hydrogen bonds and K—O electrostatic interactions. The crystal packing is shown in Fig. 2.

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Structures of Tetrakis(1,2-dimethylimidazole)$M^{\rm II}$ Diperchlorates ($M^{\rm II}$ = Co, $\rm Zn_{0.98}Co_{0.02}$)

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Abstract. $[\rm Co(C_5H_8N_2)_4](ClO_4)_2$, $M_r = 642{\cdot}37$, trigonal, $P3_221$, $a = 12{\cdot}140\,(1)$, $c = 17{\cdot}399\,(2)$ Å, $V = 2220{\cdot}5\,(6)$ Å^3, $Z = 3$, $D_m = 1{\cdot}43\,(1)$, $D_x = 1{\cdot}442$ Mg m^{-3}, μ(Mo $K\alpha$, $\lambda = 0{\cdot}71073$ Å) = $0{\cdot}81$ mm^{-1}, $F(000) = 999$, $T = 297\,(1)$ K, $R(F) = 0{\cdot}054$ for 1967 reflections. $[\rm Co_{0.02}Zn_{0.98}(C_5H_8N_2)_4](ClO_4)_2$, $M_r = 648{\cdot}68$, trigonal, $P3_121$, $a = 12{\cdot}142\,(2)$, $c = 17{\cdot}420\,(1)$ Å, $V = 2224{\cdot}3\,(8)$ Å^3, $Z = 3$, $D_m = 1{\cdot}46\,(1)$, $D_x = 1{\cdot}453$ Mg m^{-3}, μ(Mo $K\alpha$, $\lambda = 0{\cdot}71073$ Å) = $1{\cdot}08$ mm^{-1}, $F(000) = 1008$, $T = 298\,(1)$ K, $R(F) = 0{\cdot}054$ for 1590 reflections. The structures are isomorphous and contain discrete pseudotetrahedral tetrakis(1,2-dimethylimidazole)$M^{\rm II}$ cations (site symmetry 2) separated by perchlorate anions. Corresponding Co—N [1·988 (3), 2·002 (3) Å] and Zn—N [1·983 (5), 2·015 (5) Å] distances are equal to each other and closely resemble those in other pseudotetrahedral Co$^{\rm II}$ and Zn$^{\rm II}$ complexes containing imidazole or substituted imidazole ligands.

Introduction. We have been interested in metal–imidazole complexes both intrinsically and as part of a long-range project involving structural and spectroscopic studies of compounds designed to model the active sites of copper-containing proteins, many of which are either known or thought to contain Cu$^{\rm II}$–imidazole bonding (Bernarducci, Bharadwaj, Krogh-Jespersen, Potenza & Schugar, 1983). Characterization of the active sites in these proteins is facilitated by spectroscopic studies in which Cu$^{\rm II}$ is substituted by

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