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Structure of Tetraaqua(2,6-pyridinedicarboxylato)neodymium Perchlorate

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Abstract. [Nd(C₇H₃NO₄)(H₂O)₄]ClO₄, $M_r = 480.9$, cubic, $Pa\bar{3}$, $a = 20.435(11)$ Å, $V = 8533(8)$ Å³, $Z = 24$, $D_m = 2.24$, $D_x = 2.246(2)$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 3.92$ mm⁻¹, $F(000) = 5592$, $T = 300(1)$ K, final $R = 0.0374$ for 2708 unique reflections. Each Nd ion is surrounded by one N and four carboxylic O atoms, and by four water molecules. Each dipicolinate anion is bonded to three different Nd cations.

Introduction. Previously, the structures of lanthanide tris(α, α' -dipicolinates) (Albertsson, 1970, 1972) and bis(α, α' -dipicolinates) (Guerriero, Casellato, Sitran, Vigato & Graziani, 1987) have been published. This work reports the structure of a mono(α, α' -dipicolinate)neodymium complex.

Experimental. The title compound was prepared by adding an aqueous solution of Nd(ClO₄)₃ with a slight excess of HClO₄ to an aqueous solution of sodium 2,6-pyridinedicarboxylate (α, α' -dipicolinate). After a few weeks pink–violet cubes with cut vertices were formed. A specimen $0.15 \times 0.35 \times 0.5$ mm was cut from a larger crystal. D_m was measured by flotation in C₂H₄Br₂/CHBr₃. Oscillation and Weissenberg photographs showed the cubic system and space group $Pa\bar{3}$. A Syntex P2₁ diffractometer with Mo $K\alpha$ radiation was used for data collection; variable $\omega/2\theta$ scan, $4 < 2\theta < 58^\circ$. Lattice parameters were determined using 15 reflections with $21 < 2\theta < 25^\circ$. Two standards measured every 50 reflections showed mean relative e.s.d. of 2.3%. 9073 intensities were measured, 6841 with $I \geq 3\sigma(I)$, of which 2708

were unique; $R_{\text{int}} = 0.035$; index range h 0→26, k 0→27, l 0→27. Absorption corrections, applied using the locally modified program *ABSORB* (Ugozzoli, 1987), were between 0.835 and 1.227. The structure was solved with *SHELXS86* (Sheldrick, 1986) and the *XTL/XTLE* suite of programs (Syntex, 1976), and refined with *SHELX76* (Sheldrick, 1976). Neutral-atom scattering factors were obtained from *International Tables for X-ray Crystallography* (1974, Vol. IV); real and imaginary components of anomalous dispersion were included for all non-H atoms. The Nd atom was located from a Patterson map and the remaining non-H atoms from subsequent difference syntheses; C-bonded H atoms and some disordered perchlorate O atoms were placed geometrically; water H atoms were located from difference syntheses (not all were found). Final full-matrix least-squares refinement was based on F {non-H non-disordered atoms anisotropic, H atoms and disordered atoms isotropic with constrained positional parameters and common temperature factors [the following quantities were constrained: Cl1—O n 1 and O n 1—O n' 1 ($n, n' = 1, 2, 3, 4$) distances, C—H and O—H bond distances, and the H—H distances within two of four water molecules; common temperature factors were set separately for C-bonded H atoms, for O-bonded H atoms, and for O11 and O41 atoms, except that O24 had its temperature factor set twice as large as that of C14]}. Refinement converged at $R = 0.0374$, $wR = 0.0304$ [$w = 1/\sigma^2(F)$], maximum shift/e.s.d. = 0.003; $\Delta\rho$ between -1.09 and 1.01 e Å⁻³ (highest peaks around the Cl atoms), for 240 parameters.

Table 1. Final atomic coordinates and equivalent isotropic thermal parameters (\AA^2)
$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U_{eq}
Nd	0.25768 (2)	0.35613 (2)	0.01998 (2)	0.0171 (1)
Cl1	0.5	0	0	0.0364 (7)
Cl2	0.2844 (1)	0.2844	0.2844	0.0529 (6)
Cl3	0.1279 (1)	0.1279	0.1279	0.0482 (5)
Cl4	0.0123 (2)	0.0123	0.0123	0.070 (3)*
O1	0.3555 (2)	0.3028 (2)	0.0646 (2)	0.028 (1)
O2	0.4231 (2)	0.2181 (2)	0.0801 (3)	0.032 (2)
O3	0.1233 (2)	0.2114 (2)	-0.0852 (2)	0.028 (2)
O4	0.1680 (2)	0.2971 (2)	-0.0338 (3)	0.031 (2)
O11	0.4827 (19)	0.0693 (8)	-0.0053 (20)	0.068 (6)†
O21	0.4901 (15)	-0.0320 (14)	-0.0624 (9)	0.043 (9)†
O31	0.4609 (14)	-0.0287 (14)	0.0519 (12)	0.052 (10)†
O41	0.5693 (8)	-0.0031 (21)	0.0173 (20)	0.068 (6)†
O12	0.3235 (4)	0.2547 (4)	0.2369 (4)	0.098 (4)
O22	0.3209 (5)	0.3209	0.3209	0.214 (8)
O13	0.1087 (4)	0.1648 (5)	0.0737 (4)	0.105 (4)
O23	0.1657 (5)	0.1657	0.1657	0.171 (6)
O14	0.0618 (6)	0.0433 (7)	-0.0281 (7)	0.069 (5)*
O24	-0.0288 (5)	-0.0288	-0.0288	0.141 (5)*
N	0.2694 (3)	0.2308 (3)	0.0045 (3)	0.023 (2)
C1	0.3706 (3)	0.2426 (3)	0.0599 (3)	0.026 (2)
C2	0.3221 (3)	0.1987 (3)	0.0270 (3)	0.024 (2)
C3	0.3288 (4)	0.1323 (4)	0.0228 (4)	0.041 (3)
C4	0.2801 (4)	0.0959 (4)	-0.0074 (5)	0.045 (3)
C5	0.2256 (4)	0.1287 (4)	-0.0314 (4)	0.033 (2)
C6	0.2216 (3)	0.1959 (3)	-0.0253 (3)	0.024 (2)
C7	0.1663 (3)	0.2369 (3)	-0.0502 (3)	0.024 (2)
OW1	0.3299 (3)	0.3285 (3)	-0.0743 (3)	0.036 (2)
OW2	0.3315 (3)	0.4522 (3)	0.0010 (3)	0.055 (2)
OW3	0.2049 (3)	0.2993 (3)	0.1146 (3)	0.050 (2)
OW4	0.1642 (3)	0.4247 (3)	0.0506 (3)	0.050 (2)

* Disordered, $\frac{1}{2}$ site occupancy, U_{iso} given.
 † Disordered, $\frac{1}{2}$ site occupancy, U_{iso} given.

Discussion. Final atomic parameters are given in Table 1;* the geometry of the coordination environment of the Nd ion is given in Table 2. The structure is composed of a three-dimensional polymeric cation with distinct hexameric rings built around $\bar{3}$ inversion axes centres [Wyckoff positions *a* and *b*; *International Tables for X-ray Crystallography*, (1987, Vol. A)], and perchlorate anions. Two of these perchlorate anions are disordered [Cl1 is placed on a $\bar{3}$ axis, Wyckoff position *b*, the O atoms bonded to it being disordered and placed in general positions with $\frac{1}{2}$ site occupancy; Cl4 lies on a threefold axis 0.436 (4) \AA away from the inversion centre defined by Wyckoff position *a*, and with $\frac{1}{2}$ site occupancy (one of its O atoms, O24, also lies on the $\bar{3}$ axis)]. The other two perchlorate anions (Cl2 and Cl3) lie on a threefold axis, one of the four O atoms from each perchlorate ion (O22 and O23 respectively) also being located on the $\bar{3}$ axis. The dipicolinate anion acts as a chelating tridentate O_2N -donor ligand with respect to one Nd cation, and also utilizes its other

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and hydrogen-bond interactions have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55035 (20 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU0259]

Table 2. Distances (\AA) and angles ($^\circ$) for the Nd coordination sphere

Nd—O1	2.452 (4)	Nd—O2'	2.505 (5)
Nd—O3 ⁱⁱ	2.509 (4)	Nd—O4	2.454 (5)
Nd—N	2.591 (6)	Nd—OW1	2.492 (6)
Nd—OW2	2.506 (6)	Nd—OW3	2.500 (6)
Nd—OW4	2.451 (6)		
O2 ⁱ —Nd—O1	142.03 (15)	O3 ⁱⁱ —Nd—O2'	119.84 (15)
O3 ⁱⁱ —Nd—O1	72.21 (13)	O4—Nd—O2'	70.14 (16)
O4—Nd—O1	123.86 (15)	N—Nd—O2'	116.58 (18)
O4—Nd—O3 ⁱⁱ	143.12 (15)	N—Nd—O4	61.88 (18)
N—Nd—O1	62.04 (17)	N—Nd—O2'	116.58 (18)
N—Nd—O3 ⁱⁱ	123.51 (16)	N—Nd—O4	61.88 (18)
OW1—Nd—O1	72.80 (17)	OW1—Nd—O2'	72.41 (18)
OW1—Nd—O3 ⁱⁱ	127.59 (17)	OW1—Nd—O4	89.12 (18)
OW1—Nd—N	68.11 (20)	OW2—Nd—O2'	70.38 (18)
OW2—Nd—O1	85.13 (17)	OW2—Nd—O4	139.91 (18)
OW2—Nd—O3 ⁱⁱ	66.69 (17)	OW2—Nd—OW1	72.62 (20)
OW2—Nd—N	134.41 (19)	OW3—Nd—O2'	135.52 (18)
OW3—Nd—O1	81.84 (17)	OW3—Nd—O4	78.22 (18)
OW3—Nd—O3 ⁱⁱ	71.33 (17)	OW3—Nd—OW1	138.47 (20)
OW3—Nd—N	71.07 (20)	OW4—Nd—O2'	69.65 (18)
OW3—Nd—OW2	138.02 (20)	OW4—Nd—O4	79.22 (18)
OW4—Nd—O1	142.63 (17)	OW4—Nd—OW1	142.04 (20)
OW4—Nd—O3 ⁱⁱ	73.03 (17)	OW4—Nd—OW3	74.44 (20)
OW4—Nd—N	131.94 (20)		
OW4—Nd—OW2	93.47 (20)		

Symmetry code: (i) $-x, \frac{1}{2} - z, x - \frac{1}{2}$; (ii) $-\frac{1}{2} - y, \frac{1}{2} + z, x$.

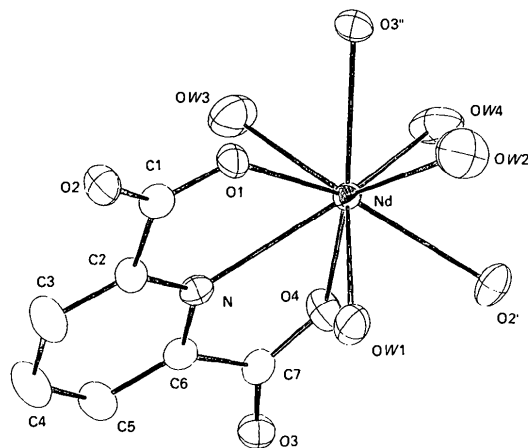


Fig. 1. Neodymium coordination. Symmetry codes are those from Table 2.

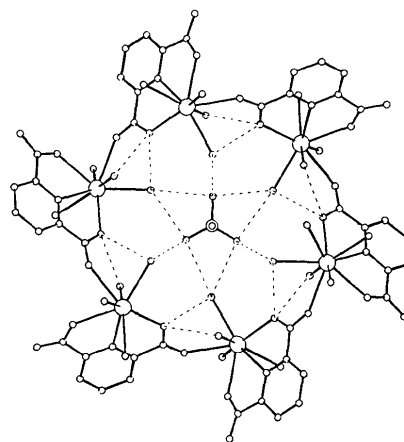


Fig. 2. Fragment of the polymeric cation, together with an accompanying perchlorate anion (that with the Cl4 atom). The dashed lines represent the hydrogen bonds.

two carboxylic O atoms to form bonds to two other Nd cations. Each metal ion is thereby involved in coordination to three dipicolinate anions and takes part in two hexameric rings. Each pair of connected hexamers has one Nd atom in common. The coordination figure of Nd may best be described as a tricapped trigonal prism with O1, OW2, OW1, and OW3, OW4, O4 defining the bases, and with O2, O3, N as the caps, $\Delta = 0.038 \text{ \AA}^2$ [$\Delta = \sum d_i^2/9$, where d_i is the distance between the real position of the i th atom and the relevant vertex in the ideal least-squares-fitted polyhedron (Drew, 1977)]. Two alternative descriptions in terms of a capped square antiprism are: (i) non-capped base O2, OW2, O3, OW4; capped base OW1, O1, OW3, O4; cap N; $\Delta = 0.067 \text{ \AA}^2$; and (ii) non-capped base O2, O4, N, OW1; capped base OW4, OW3, O1, OW2; cap O3; $\Delta = 0.078 \text{ \AA}^2$. An ORTEPII view (Johnson, 1976) of the Nd coordination is given in Fig. 1, and the hexameric fragment of the complex cation is presented in Fig. 2. The structure is held together by an elaborate network of

intermolecular hydrogen bonds, some of them disordered and bifurcated.

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Structure of Tetralithium 1,4,5,8-Naphthalenetetracarboxylate Dodecahydrate

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Abstract. $4\text{Li}^+ \cdot \text{C}_{14}\text{H}_4\text{O}_8^{4-} \cdot 12\text{H}_2\text{O}$, $M_r = 544.18$, triclinic, $P\bar{1}$, $a = 9.608$ (2), $b = 10.034$ (2), $c = 7.033$ (1) Å, $\alpha = 94.29$ (1), $\beta = 96.95$ (1), $\gamma = 64.52$ (1)°, $V = 607.4$ (2) Å³, $Z = 1$, $D_x = 1.49 \text{ g cm}^{-3}$, $\lambda(\text{Mo } K\alpha) = 0.71073 \text{ \AA}$, $\mu = 1.29 \text{ cm}^{-1}$, $T = 295 \text{ K}$, $F(000) = 284$, $R = 0.039$ for 2781 unique reflections having $I > \sigma_I$. The two inequivalent carboxyl groups adopt a non-planar arrangement with respect to the naphthalene core, making dihedral angles of 52.7 (1) and 54.6 (1)° with it. The Li⁺ ions are tetrahedrally coordinated by carboxyl and water O atoms. The Li—O distances are in the range 1.906 (3)–2.041 (3) Å, averaging 1.97 (4) Å; O—Li—O angles are 101.5 (1)–123.9 (1)°, averaging 109 (6)°. Each of the 12 inequivalent water H atoms is involved in hydrogen bonding. Of these bonds, 11 are typical two-centered hydrogen bonds with an average H···O (acceptor) distance of 1.92 (11) Å and

an average O—H···O (acceptor) angle of 172 (5)°. One water H atom is involved in a three-centered hydrogen bond with an average H···O (acceptor) distance of 2.61 (4) Å and an average O—H···O (acceptor) angle of 120 (3)°. Adjacent organic anions are separated by the Li⁺ ions and their coordination polyhedra, with the water molecules occupying positions above and below the naphthalene rings and participating in a three-dimensional hydrogen-bonded network.

Introduction. The structure determination of crystalline Group IA salts of 1,4,5,8-naphthalenetetracarboxylic acid is being undertaken as part of a continuing investigation of hydrogen bonding in organic solids. The effects of cation size on crystal structure and the attendant hydrogen-bond network, as well as on the conformation of the organic anion, are of particular interest. The structure of the tetrasodium salt has previously been reported (Fitzgerald,

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