

Table 3. *Geometry of the possible hydrogen bonds, distances in (Å) and angles in (°) with e.s.d.'s in parentheses*

D—H...A	D...A	H...A	D—H...A
N1—H1...Cl(A ¹)	3.14 (1)	2.16 (10)	166 (4)
N3—H3...O(1 ^b)	2.78 (1)	1.77 (10)	174 (6)
N4—H4...Cl(1 ^b)	3.12 (1)	2.11 (3)	167 (4)
N5—H52...N(5 ^{cd})	3.48 (1)	2.57 (3)	147 (6)
N7—H71...O(2 ^g)	3.01 (2)	2.05 (19)	164 (11)
N7—H72...Cl(B ^g)	3.31 (2)	2.64 (6)	122 (8)
O1—H101...Cl(1 ^h)	3.22 (1)	2.24 (2)	170 (4)
O1—H201...Cl(B ^{hi})	3.00 (1)	2.33 (6)	130 (5)
O1—H201...Cl(B ^{mi})	3.27 (1)	2.49 (7)	143 (5)

Symmetry code: (i) $+x, +y, +z - 1$; (ii) $+x - \frac{1}{2}, -y, +z - \frac{1}{2}$; (iii) $-x + 1, -y, -z - 1$; (iv) $-x + \frac{1}{2}, +y, -z + \frac{1}{2}$; (v) $+x - \frac{1}{2}, -y + 1, +z - \frac{1}{2}$; (vi) $1 - x, 1 - y, 1 - z$; (vii) $-x, 1 - y, 1 - z$; (viii) $x - \frac{1}{2}, -y, z + \frac{1}{2}$.

The authors are grateful to Dr C. R. Saha and Dr N. K. Roy of the Indian Institute of Technology, Kharagpur, for providing crystals and helpful discussions. They are grateful to Mr S. Chaudhury of RSIC, Bose Institute, for collecting data on the

Enraf-Nonius CAD-4 system. They are also grateful to a referee for various helpful suggestions.

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Acta Cryst. (1990). **C46**, 2068–2070

Structure of Bis- μ -(2-quinolinecarboxylato-*O,O,O'*)bis[triaqua-(2-quinolinecarboxylato-*N,O*)(2-quinolinecarboxylato-*O*)neodymium(III)] Trihydrate

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(Received 13 August 1988; accepted 9 February 1990)

Abstract. $[\{\text{Nd}(\text{C}_{10}\text{H}_6\text{NO}_2)_2(\text{H}_2\text{O})_3\}_2(\mu\text{-C}_{10}\text{H}_6\text{NO}_2)_2] \cdot 3\text{H}_2\text{O}$, $M_r = 1483.6$, triclinic, $P\bar{1}$, $a = 15.760$ (9), $b = 8.178$ (6), $c = 24.153$ (19) Å, $\alpha = 92.54$ (6), $\beta = 99.19$ (6), $\gamma = 109.40$ (6)°, $V = 2883$ (4) Å³ [reduced cell: $a = 8.178$ (6), $b = 15.154$ (12), $c = 24.153$ (19) Å, $\alpha = 79.05$ (7), $\beta = 87.46$ (6), $\gamma = 78.80$ (6)°], $Z = 2$, $D_m = 1.70$, $D_x = 1.709$ (2) Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 1.88$ mm⁻¹, $F(000) = 1488$, $T = 302$ (1) K, final $R = 0.047$ for 5110 reflections. The title compound is a dimer; the two Nd ions are bridged by two carboxyl groups. Each Nd ion is surrounded by one N atom, five carboxylic oxygens and three water molecules. Very short Nd—O (carboxyl) bonds [2.320 (7) and 2.325 (7) Å] were found.

Introduction. This work is part of our study on the structures and properties of complexes containing lanthanide–nitrogen bonds.

Experimental. The title compound was prepared by mixing aqueous solutions of NdCl₃ and 2-quinolinecarboxylic (quinaldic) acid, and then adding a dilute solution of *N*-2-hydroxyethylpiperazine-*N'*-ethanesulfonic acid (HEPES). After a few hours tiny violet plates were formed. Two specimens (0.3 × 0.4 × 0.5 mm and 0.3 × 0.3 × 0.4 mm) were cut from larger crystals. D_m by flotation in C₂H₄Br₂/CHCl₃. Oscillation and Weissenberg photographs showed no symmetry, thus indicating the triclinic system. The structure was successfully refined in space group $P\bar{1}$. Syntex P2₁ diffractometer, Mo $K\alpha$ radiation for lattice parameters (14 reflections, $21 < 2\theta < 26^\circ$), variable $\theta/2\theta$ scan, $4 < 2\theta < 45^\circ$, two standards every 100 reflections, maximum variation from means 7.1%, 4541 and 1281 intensities respectively measured from the two specimens, 166 common ones used for determination of the scale ratio between the two sets, $R_{\text{int}} = 0.028$, after averaging 5110 unique reflec-

tions with $I > 3\sigma(I)$, index range $h\ 0 \rightarrow 15$, $k\ -8 \rightarrow 7$, $l\ -25 \rightarrow 25$, no correction for absorption or extinction. Structure was solved with locally modified *XTL/XTLE* programs (Syntex, 1976), and refined with *SHELX76* (Sheldrick, 1976). 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 subsequent difference syntheses; C-bonded hydrogens were placed geometrically, water hydrogens from difference syntheses. Final full-matrix least-squares refinement based on F (non-H atoms anisotropic, C-bonded hydrogens with fixed positional parameters and common temperature factor, O-bonded hydrogens with common temperature factor and constrained positional parameters, the constraint refined as an additional parameter), $R = 0.047$, $wR = 0.044$, maximum $\Delta/\sigma = 0.32$, $\Delta\rho$ between -1.16 and $2.38\ e\ \text{\AA}^{-3}$, the highest peaks around Nd atoms, $w = 1/\sigma^2(F)$.

Discussion. Final atomic parameters are given in Table 1, and the geometry of the coordination environment of the Nd ions is shown in Table 2, together with average bond lengths for the quinaldate residues.* The structure consists of the neutral dimer, bis- μ -(2-quinolinecarboxylato)-bis-[triaquadi(2-quinolinecarboxylato)neodymium(III)], and water of hydration. The *ORTEP* view (Johnson, 1976) of the complex molecule is given in Fig. 1. The Nd1—Nd2 distance is $4.461(1)\ \text{\AA}$. The coordination environments of both metal ions are essentially the same. In each half of the dimer the three quinaldate moieties display different modes of coordination to Nd. The *A* (or *F*) moiety is involved in a bidentate carboxyl bridge, in which the two O atoms chelate the metal atom with an additional bond from one of the oxygens to the other metal atom. The *B* (or *D*) moiety is bonded through its nitrogen and one of its oxygens. The *C* (or *E*) moiety is bonded through one of its oxygens only. The distances Nd—N are longer than usually observed (Sinha, 1976), perhaps due to steric interactions within the complex molecule. The same reason may bring about variation of the Nd—O (water) distances. The steric interactions and the mode of coordination (Đào, 1987) may explain the Nd—O(carboxylic) bond length variation. The Nd1—O1C and Nd2—O1E distances are about

Table 1. Final atomic coordinates and equivalent isotropic thermal U factors

$$U_{eq} = \frac{1}{3} \sum U_{ij} a_i^* a_j^* a_i a_j$$

	x	y	z	$U_{eq} (\text{\AA}^2)$
Nd1	0.69083 (4)	0.08803 (5)	0.80462 (2)	0.0277 (3)
Nd2	0.89530 (4)	-0.03637 (5)	0.71833 (2)	0.279 (3)
O1A	0.8537 (6)	0.1408 (7)	0.8097 (3)	0.046 (3)
O2A	0.9877 (5)	0.0981 (8)	0.8121 (2)	0.040 (3)
N4	0.9030 (6)	0.2427 (8)	0.9250 (3)	0.033 (4)
C1A	0.9315 (9)	0.1388 (10)	0.8358 (4)	0.034 (5)
C2A	0.9554 (8)	0.1822 (10)	0.9004 (4)	0.034 (4)
C3A	1.0347 (7)	0.1562 (11)	0.9289 (4)	0.036 (4)
C4A	1.0550 (7)	0.1930 (12)	0.9864 (4)	0.041 (5)
C5A	1.0008 (8)	0.2547 (11)	1.0144 (4)	0.038 (5)
C6A	1.0167 (8)	0.2887 (13)	1.0740 (4)	0.049 (5)
C7A	0.9617 (10)	0.3455 (13)	1.0994 (4)	0.058 (6)
C8A	0.8845 (9)	0.3705 (13)	1.0679 (5)	0.059 (6)
C9A	0.8656 (7)	0.3389 (12)	1.0096 (4)	0.046 (5)
C10A	0.9229 (7)	0.2774 (10)	0.9832 (4)	0.032 (4)
O1B	0.7244 (4)	-0.1621 (7)	0.8390 (2)	0.037 (3)
O2B	0.7442 (5)	-0.3411 (8)	0.9019 (3)	0.061 (4)
NB	0.6687 (5)	0.0130 (8)	0.9142 (3)	0.034 (3)
C1B	0.7228 (7)	-0.2167 (11)	0.8876 (4)	0.038 (5)
C2B	0.6939 (6)	-0.1173 (10)	0.9302 (3)	0.029 (4)
C3B	0.6926 (7)	-0.1719 (12)	0.9852 (4)	0.042 (5)
C4B	0.6641 (8)	-0.0847 (13)	1.0231 (4)	0.050 (5)
C5B	0.6355 (7)	0.0537 (11)	1.0081 (4)	0.038 (4)
C6B	0.6030 (8)	0.1467 (15)	1.0449 (4)	0.056 (5)
C7B	0.5748 (8)	0.2763 (15)	1.0282 (4)	0.058 (6)
C8B	0.5763 (8)	0.3233 (12)	0.9736 (4)	0.051 (5)
C9B	0.6086 (7)	0.2378 (11)	0.9361 (4)	0.041 (5)
C10B	0.6376 (6)	0.0996 (11)	0.9525 (3)	0.034 (4)
O1C	0.5449 (5)	-0.1072 (8)	0.8040 (3)	0.042 (3)
O2C	0.4355 (5)	-0.3563 (8)	0.7658 (3)	0.061 (4)
NC	0.4169 (5)	0.0406 (9)	0.8137 (3)	0.023 (3)
C1C	0.4619 (8)	-0.2043 (12)	0.7883 (4)	0.033 (5)
C2C	0.3886 (7)	-0.1331 (11)	0.7990 (3)	0.030 (5)
C3C	0.2979 (8)	-0.2445 (11)	0.7931 (4)	0.032 (4)
C4C	0.2338 (8)	-0.1771 (12)	0.8038 (3)	0.040 (5)
C5C	0.2583 (8)	0.0031 (12)	0.8205 (4)	0.038 (5)
C6C	0.1962 (8)	0.0853 (14)	0.8311 (4)	0.049 (5)
C7C	0.2249 (9)	0.2598 (15)	0.8468 (4)	0.048 (6)
C8C	0.3171 (9)	0.3609 (12)	0.8516 (4)	0.044 (5)
C9C	0.3793 (8)	0.2890 (12)	0.8410 (4)	0.043 (5)
C10C	0.3526 (8)	0.1060 (12)	0.8244 (3)	0.030 (4)
O1D	0.8552 (5)	0.2063 (7)	0.6841 (2)	0.039 (3)
O2D	0.8242 (5)	0.3779 (9)	0.6221 (3)	0.061 (4)
ND	0.8787 (5)	0.0020 (9)	0.6015 (3)	0.035 (3)
C1D	0.8420 (7)	0.2491 (11)	0.6349 (4)	0.037 (5)
C2D	0.8497 (7)	0.1290 (11)	0.5874 (4)	0.037 (4)
C3D	0.8282 (8)	0.1618 (12)	0.5314 (4)	0.054 (5)
C4D	0.8356 (8)	0.0569 (13)	0.4891 (4)	0.058 (6)
C5D	0.8701 (8)	-0.0763 (12)	0.5021 (4)	0.050 (5)
C6D	0.8852 (9)	-0.1852 (14)	0.4602 (4)	0.059 (6)
C7D	0.9172 (9)	-0.3109 (15)	0.4747 (5)	0.065 (6)
C8D	0.9404 (8)	-0.3367 (12)	0.5321 (5)	0.059 (6)
C9D	0.9271 (7)	-0.2332 (11)	0.5725 (4)	0.042 (5)
C10D	0.8926 (7)	-0.1023 (11)	0.5593 (3)	0.033 (4)
O1E	1.0334 (5)	0.1499 (8)	0.7003 (3)	0.042 (3)
O2E	1.1392 (5)	0.4087 (8)	0.7245 (4)	0.074 (4)
NE	1.1627 (6)	0.0131 (9)	0.6818 (3)	0.035 (4)
C1E	1.1144 (8)	0.2528 (13)	0.7079 (4)	0.036 (5)
C2E	1.1887 (8)	0.1831 (11)	0.6964 (3)	0.031 (5)
C3E	1.2777 (8)	0.2943 (12)	0.7015 (4)	0.035 (5)
C4E	1.3446 (7)	0.2323 (12)	0.6912 (4)	0.039 (5)
C5E	1.3204 (8)	0.0536 (13)	0.6735 (4)	0.038 (5)
C6E	1.3830 (8)	-0.0254 (15)	0.6626 (4)	0.055 (6)
C7E	1.3565 (9)	-0.1983 (17)	0.6468 (4)	0.055 (6)
C8E	1.2658 (11)	-0.3010 (14)	0.6411 (4)	0.055 (6)
C9E	1.1999 (9)	-0.2353 (12)	0.6525 (4)	0.051 (5)
C10E	1.2275 (9)	-0.0507 (12)	0.6699 (3)	0.035 (5)
O1F	0.7271 (5)	-0.0986 (7)	0.7167 (2)	0.041 (3)
O2F	0.6089 (5)	-0.0018 (9)	0.7030 (3)	0.052 (4)
NF	0.6608 (6)	-0.2695 (9)	0.6071 (3)	0.040 (4)
C1F	0.6568 (8)	-0.0718 (11)	0.6851 (4)	0.033 (5)
C2F	0.6397 (7)	-0.1364 (12)	0.6232 (4)	0.037 (4)
C3F	0.6006 (8)	-0.0395 (15)	0.5841 (4)	0.063 (6)
C4F	0.5856 (10)	-0.0939 (18)	0.5290 (5)	0.086 (8)
C5F	0.6048 (8)	-0.2407 (14)	0.5095 (4)	0.056 (5)
C6F	0.5903 (10)	-0.3029 (19)	0.4527 (4)	0.080 (7)
C7F	0.6128 (10)	-0.4424 (18)	0.4380 (4)	0.086 (8)
C8F	0.6503 (9)	-0.5257 (14)	0.4785 (5)	0.073 (6)
C9F	0.6657 (8)	-0.4693 (13)	0.5336 (4)	0.058 (6)
C10F	0.6418 (7)	-0.3265 (12)	0.5502 (4)	0.041 (5)
W1	0.5840 (4)	0.2454 (7)	0.7970 (3)	0.043 (3)
W2	0.7505 (5)	0.3339 (8)	0.7433 (2)	0.046 (3)

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and hydrogen-bond geometrical parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53045 (38 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1 (cont.)

	x	y	z	U_{eq} (Å ²)
W3	0.7706 (5)	0.3573 (7)	0.8658 (3)	0.041 (3)
W4	0.8496 (5)	-0.2558 (8)	0.7891 (3)	0.042 (3)
W5	1.0021 (5)	-0.1914 (7)	0.7180 (3)	0.042 (3)
W6	0.8088 (5)	-0.3284 (7)	0.6697 (2)	0.040 (3)
W7	0.0066 (5)	0.5096 (8)	0.7538 (3)	0.055 (3)
W8	0.4206 (5)	0.4503 (8)	0.2406 (3)	0.061 (3)
W9	0.5982 (6)	0.3703 (10)	0.6650 (3)	0.080 (4)

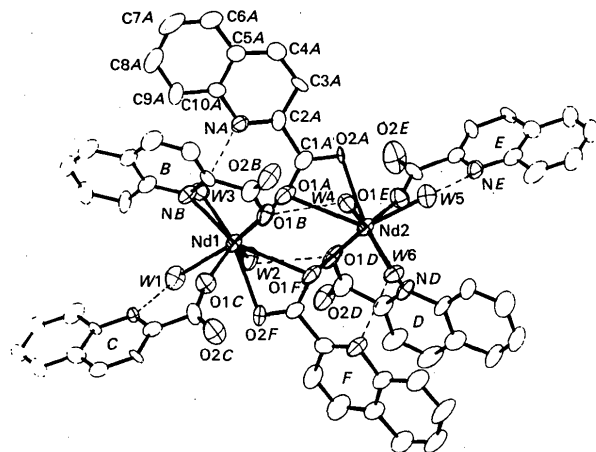


Fig. 1. Molecular diagram of the complex molecule. The numbering scheme of the ring atoms in the moieties A through F follows the pattern of that for the A moiety. The dashed lines represent the intramolecular hydrogen bonds.

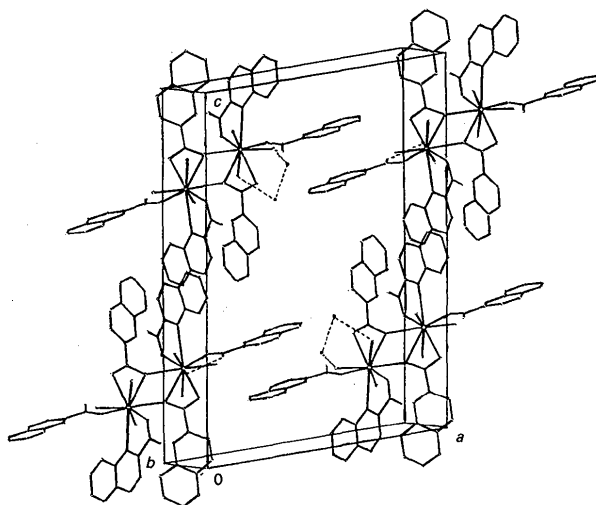


Fig. 2. View of the crystal structure. The dashed lines represent the intermolecular hydrogen bonds.

0.08 Å shorter than the values so far observed in Nd carboxylates (Sinha, 1976; Đào, 1987). The structure is held together by van der Waals interactions, and by a network of intermolecular hydrogen bonds. The crystal packing is shown in Fig. 2.

The author thanks Professor K. Bukietyńska for helpful discussion, and Dr T. Lis for advice and help

Table 2. Distances (Å) and angles (°) for the Nd coordination spheres, together with averaged bond lengths (Å) in the quinaldinate moieties

Nd1—O1A	2.439 (10)	Nd1—O1B	2.426 (6)	
—NB	2.793 (7)	—O1C	2.320 (7)	
—O1F	2.801 (6)	—O2F	2.535 (7)	
—W1	2.426 (6)	—W2	2.564 (6)	
—W3	2.428 (6)			
Nd2—O1A	2.866 (8)	Nd2—O2A	2.475 (5)	
—O1D	2.415 (6)	—ND	2.832 (7)	
—O1E	2.325 (7)	—O1F	2.521 (8)	
—W4	2.543 (7)	—W5	2.421 (8)	
—W6	2.453 (5)			
O1B—Nd1—O1A	71.4 (3)	NB—Nd1—O1B	61.6 (3)	
NB—Nd1—O1A	101.7 (3)	O1C—Nd1—O1B	78.5 (3)	
O1C—Nd1—O1A	148.8 (3)	O1C—Nd1—NB	69.7 (3)	
O1C—Nd1—NB	69.7 (3)	O1F—Nd1—O1B	70.4 (2)	
O1F—Nd1—O1A	66.9 (3)	O1F—Nd1—O1C	95.7 (3)	
O1F—Nd1—NB	131.5 (3)	O2F—Nd1—O1B	106.9 (3)	
O2F—Nd1—O1A	109.3 (3)	O2F—Nd1—O1C	71.7 (3)	
O2F—Nd1—NB	141.2 (3)			
O2F—Nd1—O1F	49.3 (3)	W1—Nd1—O1B	145.9 (3)	
W1—Nd1—O1A	140.1 (3)	W1—Nd1—O1C	71.1 (3)	
W1—Nd1—NB	92.9 (3)	W1—Nd1—O2F	78.2 (3)	
W1—Nd1—O1F	126.9 (3)	W2—Nd1—O1B	140.1 (3)	
W2—Nd1—O1A	72.7 (3)	W2—Nd1—O1C	131.8 (3)	
W2—Nd1—NB	144.3 (3)	W2—Nd1—O2F	69.6 (3)	
W2—Nd1—O1F	80.0 (2)			
W2—Nd1—W1	73.9 (3)	W3—Nd1—O1B	113.9 (3)	
W3—Nd1—O1A	74.0 (3)	W3—Nd1—O1C	127.5 (3)	
W3—Nd1—NB	73.1 (3)	W3—Nd1—O2F	137.4 (3)	
W3—Nd1—O1F	136.9 (3)			
W3—Nd1—W1	75.2 (3)			
W3—Nd1—W2	71.4 (3)			
O2A—Nd2—O1A	49.0 (3)	O1D—Nd2—O2A	100.4 (3)	
O1D—Nd2—O1A	71.5 (3)	ND—Nd2—O2A	143.4 (3)	
ND—Nd2—O1A	132.3 (3)	O1E—Nd2—O2A	74.8 (3)	
ND—Nd2—O1D	61.2 (3)	O1E—Nd2—ND	70.5 (3)	
O1E—Nd2—O1A	105.9 (3)	O1F—Nd2—O2A	111.4 (3)	
O1E—Nd2—O1D	77.4 (3)	O1F—Nd2—ND	93.1 (3)	
O1F—Nd2—O1A	64.9 (3)	W4—Nd2—O2A	72.0 (3)	
O1F—Nd2—O1D	71.1 (3)	W4—Nd2—ND	143.4 (3)	
O1F—Nd2—O1E	148.5 (3)	W4—Nd2—O1F	73.6 (3)	
W4—Nd2—O1A	73.2 (3)	W5—Nd2—O2A	84.7 (3)	
W4—Nd2—O1D	137.9 (3)	W5—Nd2—ND	94.2 (3)	
W4—Nd2—O1E	135.0 (3)	W5—Nd2—O1F	139.5 (3)	
W5—Nd2—O1A	130.6 (3)	W6—Nd2—O2A	138.6 (3)	
W5—Nd2—O1D	144.7 (3)	W6—Nd2—ND	74.1 (3)	
W5—Nd2—O1E	70.3 (3)	W6—Nd2—O1F	71.1 (3)	
W5—Nd2—W4	77.0 (3)			
W6—Nd2—O1A	128.3 (3)			
W6—Nd2—O1D	118.1 (3)			
W6—Nd2—O1E	125.8 (3)			
W6—Nd2—W4	69.4 (3)			
W6—Nd2—W5	72.9 (3)			
	Average	n	Min. value	Max. value
C—C*	1.388 (31)	54	1.324 (18)	1.451 (15)
C—C†	1.517 (15)	6	1.499 (13)	1.542 (13)
C—N	1.344 (37)	12	1.297 (15)	1.390 (11)
C—O	1.253 (35)	12	1.206 (14)	1.328 (14)

* Bonds within the aromatic rings.

† C(carboxyl)—C(ring) bonds.

in performing the measurements. This work was supported by the Polish Academy of Sciences (project CPBP 01.12).

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