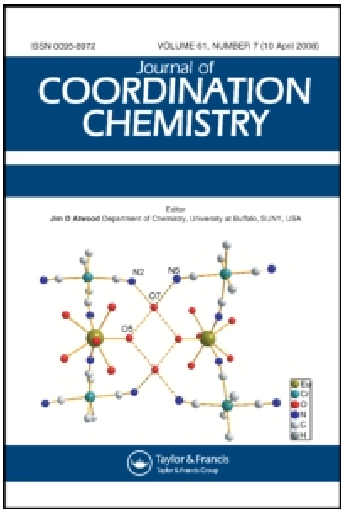

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THE CRYSTAL STRUCTURES OF TWO NEODYMIUM(III) COMPLEXES WITH PYRIDINE-2,6-DICARBOXYLIC ACID

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The structures of two complexes of neodymium(III) with pyridine-2,6-dicarboxylic acid of formula $(NH_4)_3[Nd(C_7H_3NO_4)_3]\cdot 7H_2O$ (**1**) and $(NH_4)[Nd_3(C_7H_3NO_4)_5\cdot 8H_2O]\cdot 5H_2O$ (**2**) have been determined by X-ray diffraction. Crystals of **1** are monoclinic, $P2_1/c$, a = 17.925(4), b = 10.198(2), c = 18.707(4) Å, β = 112.22(3)°, Z = 4. Crystals of **2** are monoclinic $C2/c$, a = 22.205(4), b = 13.774(3), c = 17.783(4) Å, β = 112.55(3)°, Z = 4. Both structures were solved by the heavy-atom method and refined to R = 0.032 for 7568 reflections (**1**) and 0.030 for 3267 reflections (**2**). The water molecules and NH_4^+ groups in both crystals participate in a network of hydrogen bonds.

Keywords: neodymium(III); pyridine complexes; X-ray structures

INTRODUCTION

Pyridine-2,6-dicarboxylate anion, because of the presence of five donor atoms in the molecule, has a great possibility of coordination with lanthanide ions. Among known lanthanide complexes with pyridine-2,6-dicarboxylic acid one can distinguish several groups of compounds. The first is a group of monomers in which the lanthanide(III) ions coordinate three ligands by the oxygen atoms of two carboxylate groups and the nitrogen atoms of the aromatic rings. When the carboxylate groups are deprotonated, a complex anion is formed and sodium [1,

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2] or ammonium [3] cations compensate the charge. When in pyridine-2,6-dicarboxylic acid only one carboxylate group is deprotonated, neutral *tris*(hydrogen-pyridine-2,6-dicarboxylato-O,N,O′)lanthanide(III)decahydrate complexes are formed. [4] In both cases the ratio Ln:L is 1:3 and the ligands coordinate to only one lanthanide(III) ion. Another group comprises polymeric complexes in which one [5, 6] or two [7] carboxylate groups of the pyridine-2,6-dicarboxylate ligand bridge lanthanide ions in a two- or three dimensional net. In the polymeric complexes the Ln:L relation is different from 1:3 and the ligands show different denticity. [5, 6] In the structures of polymeric complexes the presence of protonated carboxylate groups is also observed. [5] This paper presents two types of neodymium(III) and pyridine-2,6-dicarboxylic acid complexes.

EXPERIMENTAL

The compound $(NH_4)_3[Nd(C_7H_3NO_4)_3]\cdot 7H_2O$ (**1**) was obtained by recrystallization from an aqueous solution of the complex described previously, [8] and crystals of $(NH_4)[Nd_3(C_7H_3NO_4)_5\cdot 8H_2O]\cdot 5H_2O$ (**2**) were grown by slow evaporation of an aqueous (0.05 M) solution of $NdCl_3$ and the ammonium salt of pyridine-2,6-dicarboxylic acid (0.05 M) in a 3:5 ratio. Light violet crystals formed after a few days. The experimental percentage contents are Nd, 17.82; C, 30.45; H, 4.18; N, 10.55; O, 37.00; calculated are Nd, 17.60; C, 30.77; H, 4.30; N, 10.25; O, 37.08 for (**1**), and Nd, 28.42; C, 27.45; H, 2.89; N, 5.92; O, 35.32; Nd, 28.65; C, 27.83; H, 3.01; N, 5.56; O, 34.95 for (**2**), respectively. Experimental densities of crystals were measured by flotation in $CCl_4/C_2H_4Br_2$ mixture.

Thermal Measurements

The thermal stability of the complexes was examined by means of the TG, DTG and DTA technique. Measurements were made with an OD 102 derivatograph. Samples were heated at a rate of 10°C/min to 1000°C in a ceramic crucible in air using Al_2O_3 as reference material. The final product of thermal decomposition was identified by the Debye-Scherrer method using a DRON 2 diffractometer (Table I).

Spectroscopic Measurements

IR spectra were recorded in the solid state with a Specord M80 spectrophotometer in the range 4000-400cm^{-1} in KBr discs.

TABLE I Thermal decomposition data and selected IR bands for the complexes.

T*(°C)	Weight Loss (%)		T**(°C)	Weight Loss (%)		
Calc.	Found	Calc.	Found			
1	60-110	6.50	6.50	220-935	20.50	20.70
2	100-150	16.70	16.90	480-780	79.50	78.00
	ν N-H	ν_{as}COO	ν_{s}COOO	C-N	ν C-H	γC-H
1	2852; 2925	1580	1379	1274	1185; 1081	917-516
2	2855; 2924	1602; 1565	1400; 1377	1280	1194; 1081	924-584

*temperature range of loss of NH_3 (**1**) or NH_3 and water (**2**). **temperature range of decomposition to oxide.

X-ray Structure Determination

Preliminary Weissenberg photographs gave crystal systems, space groups and approximate unit cell dimensions. The crystals used had the following approximate dimensions: 0.25 × 0.25 × 0.30 mm for **1** and 0.12 × 0.12 × 0.18 mm for **2**. Intensity data were collected on a Kuma KM-4 computer-controlled κ-axis diffractometer with graphite-monochromated MoKα radiation at room temperature. The stability of intensities was monitored by measurement of three standards every 100 reflections. Crystallographic data and the refinement procedures are given in Table II. Intensities were corrected for Lorentz and polarisation effects but not for extinction or absorption. The structure was solved by the heavy-atom method using SHELXS-86 [9] and refined by full-matrix least-squares methods using the SHELXL-93 program. [10] H-Atoms of water molecules and ammonium groups were located from a difference Fourier map and refined. The other hydrogen atoms were placed in geometrically calculated positions with isotropic temperature factors taken as 1.2 U_{eq} of the neighbouring heavier atoms. Afterwards, their positional parameters were calculated in a riding mode with U_{iso} fixed. Several cycles of refinement of the coordinates and anisotropic thermal parameters for non-hydrogen atoms reduced the R value to 0.032 for **1** and to 0.030 for **2**. Scattering factors were those incorporated in SHELXL-93. Final parameters and their estimated standard deviations are listed in Tables III and IV.

RESULTS AND DISCUSSION

The compounds, crystallizing under different conditions, are light violet crystals of formulas $(NH_4)_3[NdL_3]\cdot 7H_2O$ (**1**) and $NH_4[NdL_3\cdot(NdL\cdot 4H_2O)_2]\cdot 5H_2O$ (**2**), where L is the pyridine-2,6-dicarboxylate(-2) anion. Both compounds are stable at room temperature, but when heated they decompose in a different way.

TABLE II Crystal data and summary of intensity collection and structure data.

	1	**2**
Formula	$C_{21}H_{35}N_6NdO_{19}$	$C_{35}H_{45}N_6Nd_3O_{33}$
Color	light violet	light violet
M_r	819.79	1510.49
Space group	$P2_1/c$	$C2/c$
Temp. °C	23	23
Cell constants	40 reflections, $18.9 < \theta < 38.6$	40 reflections, $23.5 < \theta < 38.6$
a, Å	17.925(4)	22.205(4)
b, Å	10.198(2)	13.774(3)
c, Å	18.707(4)	17.783(4)
β, °	112.22(3)	112.55(3)
Cell volume, Å^3	3165.7(12)	4947(2)
Z	4	4
F (000)	1660	2964
D_m, g cm^{-3}	1.72	2.031
D_c (flotation $CCl_4/C_2H_4Br_2$ g cm^{-3})	1.72	2.03
μ_{calc}, cm^{-1}	17.31	32.1
Crystal size, mm	0.25 × 0.25 × 0.30	0.12 × 0.12 × 0.18
Reflection measured	7771	3267
2θ range, deg	4.0-56.0	4.0-60.0
Range of h, k, l	$0 \rightarrow 23, 0 \rightarrow 13, -24 \rightarrow 22$	$-31 \rightarrow 28, 0 \rightarrow 18, 0 \rightarrow 24$
Criterion for observed reflections	$I > 2\sigma(I)$	
No. of observed reflections	7568	3267
425	358	
Weights[¶] (a, b, f)	0.0382, 4.9539, 1/3	0.0392, 1/3
GOF	1.071	1.051
$R = \Sigma(\lvert F_o\rvert - \lvert F_c\rvert)/\Sigma(\lvert F_o\rvert)$	0.0312	0.030
$R_w = \{\Sigma(wF_o^2 - F_o^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$	0.081	0.074

[¶] $w = 1/[\sigma^2(F_o^2) + (a{\cdot}P)^2 + b{\cdot}P]$ where $P = [f{\cdot}\mathrm{Max}$ of $(0$ or $F_o^2) + (1 - f)\,F_c^2]$.

TABLE III Final atomic coordinates and equivalent isotropic displacement parameters (Å^2) for non-hydrogen atoms with e.s.d. values in parentheses for compound **1**.

	x/a	*y/b*	*z/c*	U_{eq}
Nd	0.25338(1)	0.00246(2)	0.51104(1)	0.0232(1)
O(11)	0.1188(2)	0.0664(3)	0.4143(2)	0.039(1)
O(12)	−0.0121(2)	0.0348(3)	0.3522(2)	0.061(1)
O(13)	0.2773(2)	−0.1683(3)	0.6129(2)	0.037(1)
O(14)	0.2320(2)	−0.3057(3)	0.6799(2)	0.049(1)
O(21)	0.2297(2)	−0.1683(3)	0.4115(2)	0.037(1)
O(22)	0.2731(2)	−0.3016(3)	0.3419(2)	0.042(1)
O(23)	0.3877(2)	0.0667(3)	0.6098(2)	0.040(1)
O(24)	0.5210(2)	0.0453(3)	0.6671(2)	0.053(1)
O(31)	0.2855(2)	0.1109(2)	0.4082(2)	0.034(1)
O(32)	0.3067(2)	0.2858(3)	0.3486(2)	0.040(1)
O(33)	0.2215(2)	0.1135(2)	0.6135(2)	0.033(1)
O(34)	0.1988(2)	0.2913(3)	0.6709(2)	0.041(1)
O(1)	0.5009(3)	0.4893(4)	0.6536(3)	0.092(1)
O(2)	0.0615(2)	0.3164(4)	0.3361(3)	0.081(1)
O(3)	0.4044(2)	0.2959(4)	0.7028(2)	0.081(1)
O(4)	0.1227(3)	0.4702(4)	0.7496(3)	0.084(1)
O(5)	0.4341(2)	−0.2837(4)	0.7004(2)	0.080(1)
O(6)	−0.0400(4)	0.4166(5)	0.6425(3)	0.117(2)
O(7)	−0.1064(1)	0.2359(3)	0.2386(1)	0.034(1)
N(1)	0.3244(2)	−0.5009(3)	0.2637(2)	0.035(1)
N(2)	0.3121(2)	−0.5186(3)	0.7742(2)	0.034(1)
N(3)	−0.1450(2)	−0.0884(4)	0.2504(2)	0.046(1)
N(11)	0.1299(2)	−0.1238(3)	0.5124(2)	0.027(1)
N(21)	0.3779(2)	−0.1195(3)	0.5094(2)	0.028(1)
N(31)	0.2508(2)	0.2529(3)	0.5088(2)	0.025(1)
C(11)	0.0568(2)	−0.1013(4)	0.4583(2)	0.032(1)
C(12)	−0.0098(2)	−0.1739(5)	0.4545(2)	0.047(1)
C(13)	−0.0008(3)	−0.2726(5)	0.5089(3)	0.053(1)
C(14)	0.0745(2)	−0.2939(4)	0.5651(2)	0.041(1)
C(15)	0.1382(2)	−0.2166(3)	0.5652(2)	0.029(1)
C(16)	0.0530(2)	0.0073(4)	0.4031(2)	0.037(1)
C(17)	0.2224(2)	−0.2321(3)	0.6249(2)	0.030(1)
C(21)	0.3694(2)	−0.2103(4)	0.4557(2)	0.032(1)
C(22)	0.4334(3)	−0.2827(5)	0.4540(3)	0.051(1)
C(23)	0.5081(3)	−0.2615(7)	0.5104(3)	0.076(2)
C(24)	0.5173(2)	−0.1653(5)	0.5651(3)	0.060(1)
C(25)	0.4509(2)	−0.0951(4)	0.5620(2)	0.035(1)
C(26)	0.2839(2)	−0.2288(4)	0.3977(2)	0.030(1)
C(27)	0.4543(2)	0.0145(4)	0.6180(2)	0.036(1)
C(31)	0.2649(2)	0.3173(3)	0.4535(2)	0.029(1)
C(32)	0.2571(3)	0.4519(4)	0.4466(3)	0.051(1)
C(33)	0.2342(4)	0.5209(4)	0.4982(3)	0.065(2)
C(34)	0.2214(3)	0.4526(4)	0.5570(3)	0.048(1)
C(35)	0.2300(2)	0.3188(3)	0.5600(2)	0.028(1)
C(36)	0.2871(2)	0.2338(4)	0.3981(2)	0.029(1)
C(37)	0.2162(2)	0.2360(4)	0.6204(2)	0.029(1)

TABLE IV Final atomic coordinates and equivalent isotropic displacement parameters (Å^2) for non-hydrogen atoms with e.s.d. values in parentheses for compound **2**.§

	x/a	*y/b*	*z/c*	U_{eq}
Nd(1)	0.25634(2)	0.18589(3)	0.27559(2)	0.0210(1)
Nd(2)	0.0000	−0.01799(4)	0.2500	0.0165(1)
O(11)	0.2483(2)	0.3082(4)	0.3684(3)	0.034(1)
O(12)	0.2726(3)	0.3756(4)	0.4903(3)	0.044(1)
O(13)	0.3359(2)	0.0525(4)	0.3140(3)	0.031(1)
O(14)	0.4104(4)	−0.0412(6)	0.4048(4)	0.100(3)
O(21)	0.0821(2)	0.1112(4)	0.2702(3)	0.027(1)
O(22)	0.1371(2)	0.2133(4)	0.2252(3)	0.031(1)
O(23)	−0.0888(2)	−0.0629(4)	0.1119(3)	0.032(1)
O(24)	−0.1417(2)	−0.0523(4)	−0.0251(3)	0.035(1)
O(31)	0.0888(2)	−0.0990(4)	0.2221(3)	0.023(1)
O(32)	0.1432(2)	−0.2311(4)	0.2140(3)	0.036(1)
O(1)	0.2160(2)	0.0745(4)	0.3584(3)	0.033(1)
O(2)	0.1940(3)	0.0310(4)	0.1948(3)	0.043(1)
O(3)	0.2581(4)	0.1703(4)	0.1372(4)	0.063(2)
O(4)	0.2250(3)	0.3472(4)	0.1978(4)	0.042(1)
O(5)	0.0925(5)	0.4024(6)	0.2514(5)	0.089(3)
O(6)	0.3236(4)	0.0066(6)	0.1116(7)	0.105(4)
O(7)*	0.1915(8)	−0.1909(12)	0.4270(8)	0.121(9)
N(1)*	0.3684(13)	0.1350(11)	0.0198(16)	0.108(9)
N(11)	0.3383(3)	0.1752(4)	0.4262(4)	0.027(1)
N(21)	−0.0055(2)	0.0739(4)	0.1198(3)	0.019(1)
N(31)	0.0000	−0.2013(6)	0.2500	0.024(2)
C(11)	0.3353(3)	0.2416(5)	0.4818(4)	0.029(2)
C(12)	0.3792(4)	0.2359(6)	0.5648(4)	0.037(2)
C(13)	0.4259(4)	0.1659(6)	0.5894(5)	0.040(2)
C(14)	0.4290(4)	0.0967(7)	0.5342(5)	0.041(2)
C(15)	0.3824(3)	0.1045(6)	0.4519(5)	0.034(2)
C(16)	0.2816(3)	0.3137(5)	0.4440(4)	0.029(2)
C(17)	0.3765(4)	0.0327(6)	0.3852(5)	0.039(2)
C(21)	0.0390(3)	0.1422(5)	0.1275(4)	0.022(1)
C(22)	0.0387(4)	0.1956(5)	0.0614(4)	0.030(2)
C(23)	−0.0099(4)	0.1748(6)	−0.0158(5)	0.038(2)
C(24)	−0.0555(3)	0.1040(5)	−0.0250(4)	0.028(2)
C(25)	−0.0519(3)	0.0548(5)	0.0447(4)	0.022(1)
C(26)	0.0900(3)	0.1578(5)	0.2151(4)	0.025(2)
C(27)	−0.0986(3)	−0.0262(5)	0.0420(4)	0.024(1)
C(31)	0.0474(3)	−0.2520(5)	0.2385(4)	0.021(1)
C(32)	0.0490(4)	−0.3514(6)	0.2387(5)	0.039(2)
C(33)	0.0000	−0.4049(8)	0.2500	0.047(3)
C(36)	0.0983(3)	−0.1886(6)	0.2254(4)	0.022(1)

U_{eq} is defined as $U_{eq} = 1/3\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*a_ia_j$. *Occupancy factor O(7) and N(1) = 0.5.

Compound **1** at 60° loses three molecules of NH_3 and then through intermediate compounds decomposes to Nd_2O_3 at 935°. Polymeric compound **2** is stable up to about 100°C and then in one step loses NH_3 and all water, giving a stable compound, which decomposes at 480°C, forming Nd_2O_3 at about 780°C (Table I). Preliminary IR investigations showed that there are very strong hydrogen bonds in the range 2800-3500 cm^{-1} and bands 2852 and 2925 cm^{-1} for **1** and 2855 and 2924 cm^{-1} for **2** testify to the presence of N-H bonds in compounds. N_{as}COO at 1580cm^{-1} and ν_sCOO at 1379 cm^{-1} are not split in **1**, which may indicate the same character of the carboxylate group in the complex structure. In **2** these bands are split, ν_{as}COO at 1602 and 1565 cm^{-1} and ν_sCOO at 1400 and 1377 cm^{-1}, evidence that the carboxylate groups are not of equivalent character in the complex [11] (Table I).

The structures of two complexes of neodymium(III) with pyridine-2,6-dicarboxylic acid are illustrated in Figures 1 and 3. The compound triammonium-*tris*(pyridine-2,6-dicarboxylato-O,N,O′)neodymiate(III) heptahydrate (**1**) is a monomer. The Nd(III) cation coordinates the three organic anions through one of the two oxygen atoms of each carboxylate group and by the nitrogen atom of the pyridine ring. The charge of the created complex anion (−3) is compensated by the three ammonium cations. A previously published paper [4] shows the neodymium(III) complex with pyridine-2,6-dicarboxylic acid, *tris*(hydrogen-(pyridine-2,6-dicarboxylato-N,O,O′)neodymium(III) decahydrate also crystallizing in the monoclinic space group $P2_1/c$ with the same cell as ours, but the three pyridine-2,6-dicarboxylate anions are mono-protonated, so the complex is neutral. In this case, [4] the complex contains ten water molecules, three water molecules more than in our structure. Moreover, differences in the C-O of the carboxylate groups of ligands are not observed. This suggests that both carboxylate groups are probably deprotonated, and the composition of the cited complex [4] is the same as that stated in our paper. In the monomeric complex **1**, similar to the complexes of Tb(III), Dy(III), Yb(III) [2] and Ho(III), [3] the neodymium(III) ion is surrounded by nine donor atoms of organic ligands, six oxygen atoms from the carboxylic groups and three nitrogen atoms of the pyridine rings. The coordination polyhedron may be described as a slightly distorted tricapped trigonal prism with $\Delta = 0.061$ Å^2. The O(11), O(21), O(31) and O(33), O(13), O(23) atoms of the carboxylic groups form the bases of the trigonal prism and the nitrogen atoms N(11), N(21), N(31) cap the faces (Figure 2). Nd-O bond distances are 2.472(2)-2.505(3) Å and Nd-N in the range 2.554(3)-2.570(3) Å. These values are about 0.1 Å greater than those of the holmium(III) complex, [3] probably an account of the larger Nd(III) radius. In the coordinated pyridine-2,6-dicarboxylate anions, the aromatic ring of pyridine forms a quite planar system with the carboxylic groups with rotation angles of

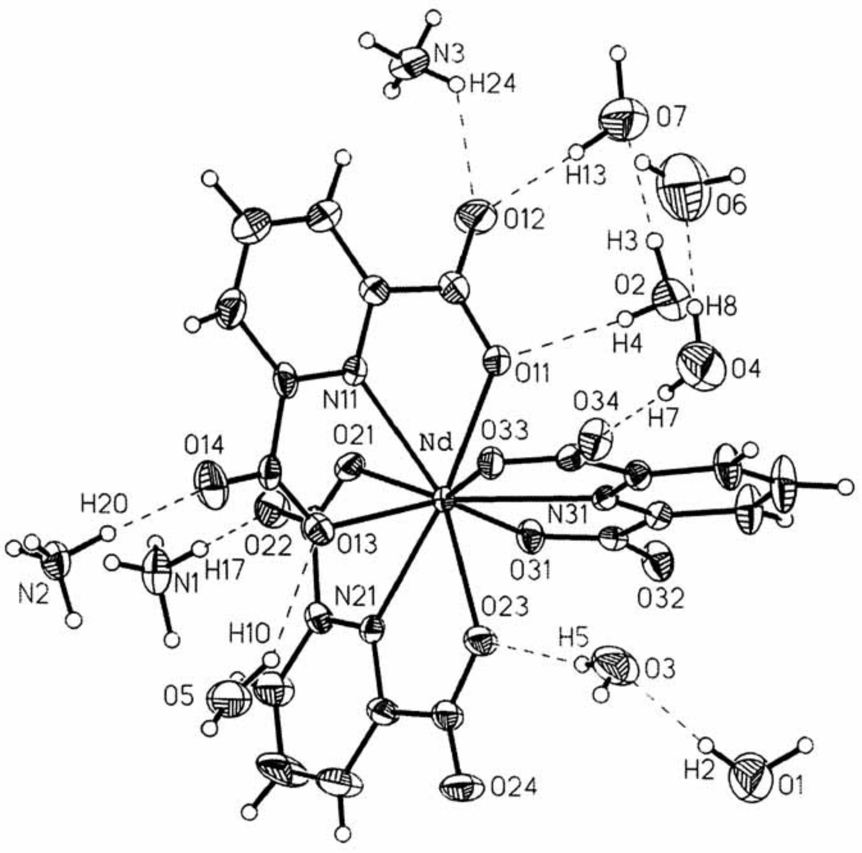

FIGURE 1 The molecular structure of triammonium*tris*(pyridine-2,6-dicarboxylato-O,N,O′)neodymiate(III) heptahydrate.

1.2(3), 8.8(3), 8.7(3), 3.4(3), 5.6(3) and 3.5(3)°. Each carboxylate group is monodentate with C-O 1.257(4) to 1.270(4) Å when the oxygen atom coordinates to a metal ion and 1.226(4) to 1.242(4) Å when oxygen does not coordinate. The O-C-O angles of the carboxylate groups are in the range 124.6(3)-126.0(4)° (Table V). The crystal structure of $(NH_4)_3[Nd(C_7H_3NO_4)_3]\cdot 7H_2O$ consists of, similar to the isomeric holmium(III) complex, [3] discrete units of *tris*(pyridine-2,6-dicarboxylato-O,N,O) neodymiate(III) anions and hydrogen bonded ammonium cations and water molecules. Each of the NH_4^+ ions acts as a proton donor for oxygen atoms of the carboxylate groups and water molecules. Each of the hydrogen atoms of seven water molecules is involved in hydrogen bonds with other water molecules and carboxylate oxygen atoms (Table VII).

In the polymeric complex ammonium*catena*(μ-pyridine-2,6-dicarboxylato-O,N,O,O′,O″)*bis*(μ-pyridine-2,6-dicarboxylato-O,N,O,O′)neodymiate(III)octaaqua*bis*(pyridine-2,6-dicarboxylato-O,N,O′)dineodymium(III) pentahydrate (**2**), the neodymium(III) ions are linked in chains by ligands in which the carboxylate groups of pyridine-2,6-dicarboxylate ligands play the bridging role. In the structure one can distinguish two different neodymium(III) environments and different denticity of ligands. As shown in Figure 3, Nd(1) coordinates one organic ligand by the nitrogen atom of the pyridine ring and by two oxygen atoms of two carboxylate groups of pyridine-2,6-dicarboxylate anions as well as two oxygen atoms from bridging carboxylate groups (O(22), O(32)^i). The coordination number of Nd(1) is brought to 9 by the four molecules of water. Nd(1)-O$_{carboxyl}$ bond distances are 2.416(5)-2.447(5) Å, Nd(1)-O$_{water}$ 2.487(6) to 2.623(5) Å and Nd(1)-N 2.541(6) Å. The coordination polyhedron may be described as a slightly distorted tricapped trigonal prism with $\Delta = 0.044$ Å^2. The O(3), O(13), O(32)^i and O(22), O(1), O(11) atoms form the bases of the trigonal

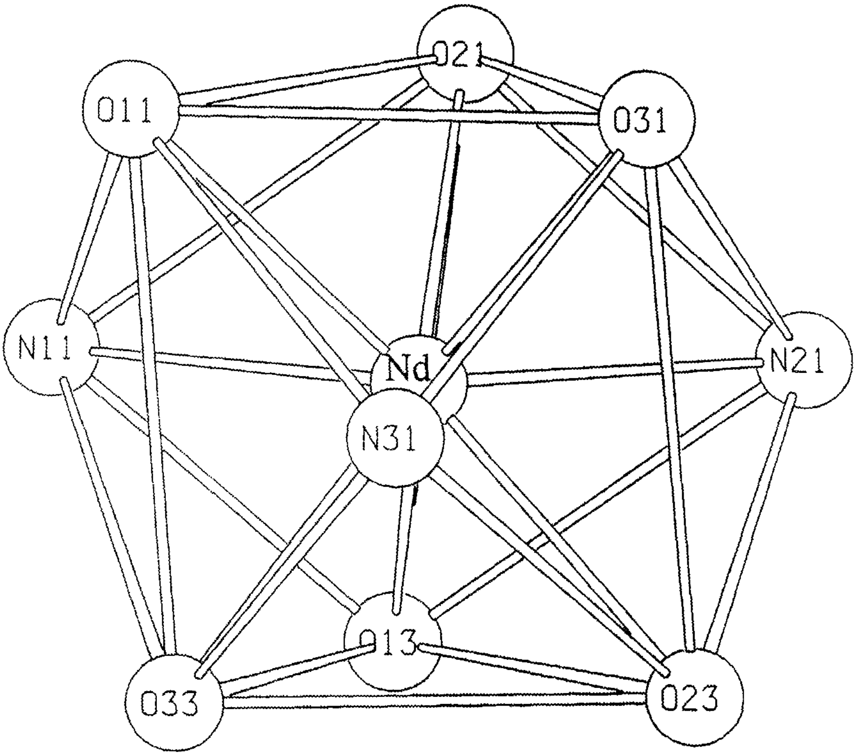

FIGURE 2 Coordination polyhedron around the neodymium(III) ion in $(NH_4)_3[NdL_3]7H_2O$.

prism and O(2), N(11), cap O(4) cap faces. The aromatic ring of the pyridine-2,6-dicarboxylate anion forms a planar system but the carboxylic groups O(11)-C(16)-O(12) and O(13)-C(17)-O(14) are rotated from the ring plane by 3.1(5) and 7.9(6)°, respectively. Nd(1) does not lie in the carboxylic planes lying 0.150(12) Å to 0.308(17) Å out of them.

The Nd(2) atom lies on the two-fold axis of symmetry. Nd(2) bonds to three pyridine-2,6-dicarboxylate anions in almost the same way as in the monomeric complex **1** achieving coordination number 9, but in this case some of the carboxylate groups of ligands have bidentate character, bridging four neighbouring neodymium Nd(1) ions in chains. The oxygen and nitrogen atoms around Nd(2) form a coordination polyhedron which can be represented as a distorted, tricapped trigonal prism (Figure 2) for which the value of Δ is 0.079 Å^2. The O(23), O(21)^{ii}, O(31)^{ii} and O(31), O(21), O(23)^{ii} atoms of the carboxylic groups

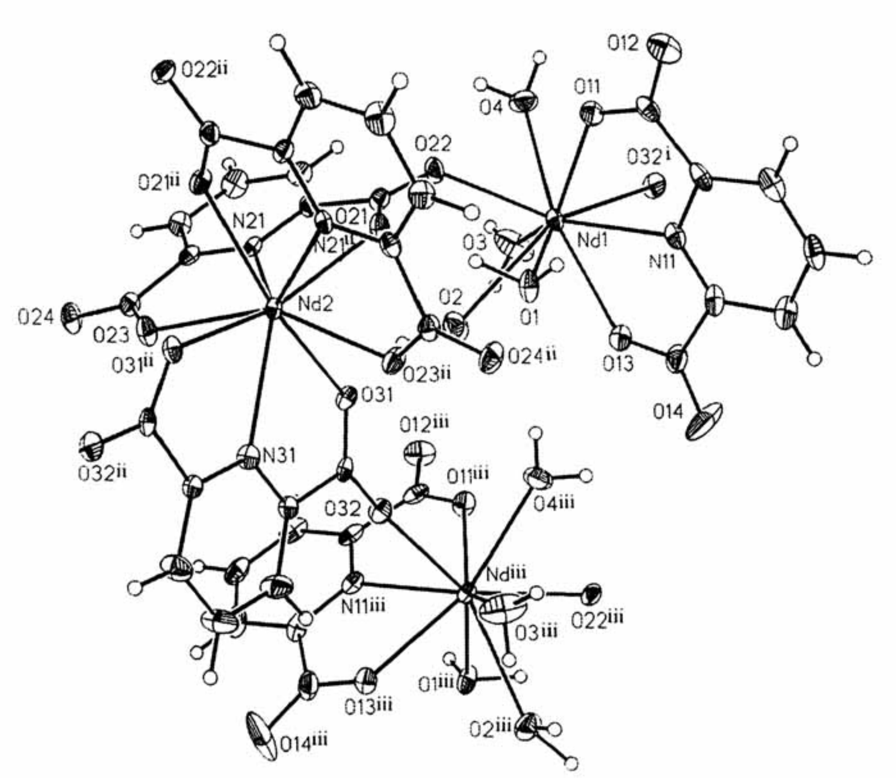

FIGURE 3 The molecular structure of ammonium*catena*(μ-pyridine-2,6-dicarboxylato-O,N,O,O′,O″)*bis*(μ-pyridine-2,6-dicarboxylato-O,N,O,O′)neodymiate(III) octaaquabis(pyridine-2,6-dicarboxylato-O,N,O′-dineodymium(III) pentahydrate. Symmetry code: i = 0.5 − *x*, 0.5 + *y*, 0.5 − *z*; ii = −*x*, *y*, 0.5 − *z*; iii = 0.5 − *x*, −0.5 + *y*, 0.5 − *z*.

TABLE V Selected bond lengths (Å) and angles (°) with esd's in parentheses for compound **1**.

Nd-O(31)	2.469(3)	Nd-O(23)	2.505(3)
Nd-O(21)	2.466(3)	Nd-N(31)	2.554(3)
Nd-O(33)	2.472(2)	Nd-N(11)	2.570(3)
Nd-O(13)	2.496(3)	Nd-N(21)	2.565(3)
Nd-O(11)	2.494(3)		
O(11)-C(16)	1.270(4)	O(12)-C(16)	1.226(4)
O(13)-C(17)	1.267(4)	O(14)-C(17)	1.232(4)
O(21)-C(26)	1.257(4)	O(22)-C(26)	1.235(4)
O(23)-C(27)	1.262(4)	O(24)-C(27)	1.242(4)
O(31)-C(36)	1.269(4)	O(32)-C(36)	1.227(4)
O(33)-C(37)	1.263(4)	O(34)-C(37)	1.237(4)
C(11)-C(16)	1.499(5)	O(12)-C(16)-O(11)	124.8(4)
C(15)-C(17)	1.508(5)	O(14)-C(17)-O(13)	126.0(4)
C(21)-C(26)	1.517(5)	O(22)-C(26)-O(21)	125.5(3)
C(25)-C(27)	1.518(5)	O(24)-C(27)-O(23)	125.8(4)
C(31)-C(36)	1.506(5)	O(32)-C(36)-O(31)	124.6(3)
C(35)-C(37)	1.504(5)	O(34)-C(37)-O(33)	125.4(4)
O(33)-Nd-O(11)	89.9(1)	O(13)-Nd-N(31)	135.0(1)
O(33)-Nd-O(21)	152.2(1)	O(13)-Nd-O(11)	125.2(1)
O(33)-Nd-N(11)	76.6(1)	O(13)-Nd-N(11)	62.8(1)
O(33)-Nd-O(13)	75.6(1)	O(23)-Nd-O(31)	90.9(1)
O(33)-Nd-N(21)	133.5(1)	O(23)-Nd-N(31)	75.9(1)
O(33)-Nd-O(23)	75.4(1)	O(23)-Nd-O(11)	149.6(1)
O(33)-Nd-O(31)	126.1(1)	O(23)-Nd-N(11)	135.6(1)
O(33)-Nd-N(31)	63.0(1)	O(23)-Nd-N(21)	62.5(1)
O(21)-Nd-O(13)	90.9(1)	O(31)-Nd-N(31)	62.1(1)
O(21)-Nd-N(21)	63.3(1)	O(31)-Nd-O(11)	76.3(1)
O(21)-Nd-O(23)	125.8(1)	O(31)-Nd-N(11)	133.5(1)
O(21)-Nd-O(31)	75.7(1)	O(31)-Nd-N(21)	75.4(1)
O(21)-Nd-N(31)	134.2(1)	N(31)-Nd-N(11)	119.4(1)
O(21)-Nd-O(11)	78.1(1)	N(31)-Nd-N(21)	119.7(1)
O(21)-Nd-N(11)	75.6(1)	N(31)-Nd-O(11)	73.7(1)
O(13)-Nd-N(21)	76.9(1)	O(11)-Nd-N(11)	62.5(1)
O(13)-Nd-O(23)	77.3(1)	O(11)-Nd-N(21)	136.5(1)
O(13)-Nd-O(31)	152.8(1)	N(11)-Nd-N(21)	121.0(1)

form the bases of a the trigonal prism and the nitrogen atoms N(21), N(21)^{ii}, N(31) cap faces. Nd(2)-O bond distances are 2.464(5)-2.506(5) Å and Nd(2)-N in the range 2.525(8)-2.597(5) Å. These values are in the same range as those for the Nd(1) ion. The aromatic ring of pyridine forms almost a planar system with the carboxylic groups with rotation angles of 2.7(5), 6.7(4)° and 27.1(4)° for ligand 3 (on the two-fold axis).

In this complex each pyridine-2,6-dicarboxylate ligand has a different character; tridentate by O(11), N(11), O(13) donor atoms, tetradentate by O(21),

TABLE VI Selected bond lengths (Å) and angles (°) with esd's in parentheses for compound **2**.

Nd(1)-O(11)	2.416(5)	Nd(2)-O(21)	2.464(5)
Nd(1)-O(13)	2.442(5)	Nd(2)-O(21)^{ii}	2.464(5)
Nd(1)-O(32)^{i}	2.445(5)	Nd(2)-O(31)	2.489(4)
Nd(1)-O(22)	2.447(5)	Nd(2)-O(31)^{ii}	2.489(4)
Nd(1)-N(11)	2.541(6)	Nd(2)-O(23)	2.506(5)
Nd(1)-O(1)	2.533(5)	Nd(2)-O(23)^{ii}	2.506(5)
Nd(1)-O(2)	2.623(5)	Nd(2)-N(31)	2.525(8)
Nd(1)-O(3)	2.487(6)	Nd(2)-N(21)^{ii}	2.597(5)
Nd(1)-O(4)	2.556(5)	Nd(2)-N(21)	2.597(5)
O(11)-C(16)	1.239(8)	O(12)-C(16)-O(11)	124.6(7)
O(12)-C(16)	1.257(8)	O(14)-C(17)-O(13)	124.8(8)
O(13)-C(17)	1.242(9)	O(22)-C(26)-O(21)	125.9(6)
O(14)-C(17)	1.228(10)	O(24)-C(27)-O(23)	125.4(7)
O(21)-C(26)	1.244(8)	O(32)-C(36)-O(31)	126.1(6)
O(22)-C(26)	1.246(8)		
O(23)-C(27)	1.274(8)		
O(24)-C(27)	1.233(8)		
O(31)-C(36)	1.249(8)		
O(32)-C(36)	1.242(8)		
O(11)-Nd(1)-O(32)^{i}	86.9(2)	O(23)-Nd(2)-O(31)^{ii}	73.6(2)
O(11)-Nd(1)-N(11)	62.9(2)	O(23)-Nd(2)-O(21)	123.7(2)
O(11)-Nd(1)-O(13)	125.7(2)	O(23)-Nd(2)-N(31)	75.7(1)
O(11)-Nd(1)-O(1)	83.2(2)	O(23)-Nd(2)-O(31)	93.5(2)
O(11)-Nd(1)-O(2)	140.3(2)	O(23)-Nd(2)-O(23)^{ii}	151.4(2)
O(11)-Nd(1)-O(22)	76.5(2)	O(23)-Nd(2)-N(21)^{ii}	136.1(4)
O(11)-Nd(1)-O(3)	140.6(2)	O(23)-Nd(2)-N(21)	211.3(2)
O(11)-Nd(1)-O(4)	71.5(2)	O(23)-Nd(2)-O(21)^{ii}	78.21(2)
O(32)^{i}-Nd(1)-N(11)	73.5(2)	O(31)^{ii}-Nd(2)-N(3)	63.4(1)
O(32)^{i}-Nd(1)-O(13)	78.4(2)	O(31)^{ii}-Nd(2)-O(31)	126.7(2)
O(32)^{i}-Nd(1)-O(1)	140.4(2)	O(31)^{ii}-Nd(2)-O(23)^{ii}	93.5(2)
O(32)^{i}-Nd(1)-O(2)	132.8(2)	O(31)^{ii}-Nd(2)-O(21)	153.4(2)
O(32)^{i}-Nd(1)-O(22)	140.4(2)	O(31)^{ii}-Nd(2)-N(21)^{ii}	77.8(2)
O(32)^{i}-Nd(1)-O(3)	74.1(2)	O(31)^{ii}-Nd(2)-N(21)	130.4(2)
O(32)^{i}-Nd(1)-O(14)	70.7(2)	O(31)^{ii}-Nd(2)-O(21)^{ii}	75.7(2)
N(11)-Nd(1)-O(13)	62.9(2)	N(31)-Nd(2)-O(31)	63.4(1)
N(11)-Nd(1)-O(1)	76.8(2)	N(31)-Nd(2)-O(23)^{ii}	75.7(1)
N(11)-Nd(1)-O(2)	120.9(2)	N(31)-Nd(2)-O(21)	136.2(1)
N(11)-Nd(1)-O(22)	125.9(2)	N(31)-Nd(2)-N(21)^{ii}	119.2(2)
N(11)-Nd(1)-O(4)	122.4(2)	N(31)-Nd(2)-N(21)	119.2(2)
N(11)-Nd(1)-O(3)	137.7(2)	N(31)-Nd(2)-O(21)^{ii}	136.2(1)
O(13)-Nd(1)-O(1)	76.8(2)	O(31)-Nd(2)-O(23)^{ii}	73.6(2)
O(13)-Nd(1)-O(2)	72.3(2)	O(31)-Nd(2)-O(21)	75.7(2)
O(13)-Nd(1)-O(22)	140.0(2)	O(31)-Nd(2)-N(21)^{ii}	130.4(2)
O(13)-Nd(1)-O(3)	84.5(2)	O(31)-Nd(2)-N(21)	77.8(2)
O(13)-Nd(1)-O(4)	143.9(2)	O(31)-Nd(2)-O(21)^{ii}	153.4(2)
O(1)-Nd(1)-O(2)	65.9(2)	O(23)^{ii}-Nd(2)-O(21)	78.6(2)
O(1)-Nd(1)-O(22)	73.5(2)	O(23)^{ii}-Nd(2)-N(21)^{ii}	61.3(2)
O(1)-Nd(1)-O(3)	132.6(2)	O(23)^{ii}-Nd(2)-N(21)	136.1(2)
O(1)-Nd(1)-O(4)	139.3(2)	O(23)^{ii}-Nd(2)-O(21)^{ii}	123.7(2)
O(2)-Nd(1)-O(22)	71.4(2)	O(21)-Nd(2)-N(21)^{ii}	76.1(2)
O(2)-Nd(1)-O(3)	67.0(2)	O(21)-Nd(2)-N(21)	62.4(2)
O(2)-Nd(1)-O(4)	116.6(2)	O(21)-Nd(2)-O(21)^{ii}	87.6(2)
O(22)-Nd(1)-O(3)	96.3(2)	N(21)^{ii}-Nd(2)-N(21)	121.6(2)
O(22)-Nd(1)-O(4)	70.0(2)	N(21)^{ii}-Nd(2)-O(21)^{ii}	62.4(2)
O(4)-Nd(1)-O(3)	69.7(2)	N(21)-Nd(2)-O(21)^{ii}	76.1(2)

Symmetry code: (i) $-x + 0.5, y + 0.5, -z + 0.5$; (ii) $-x, y, -z + 0.5$

TABLE VII Hydrogen bond lengths (Å) and angles (°) with esd's in parentheses for compound **1**.

D-H···A	D-H	H···A	D···A	∠D-H···A
O(1)-H(1)...O(5)^{i}	0.86	2.03	2.890(7)	174
O(1)-H(2)...O(3)	0.90	2.09	2.989(7)	172
O(2)-H(3)...O(7)	0.90	2.10	2.984(7)	167
O(2)-H(4)...O(11)	0.79	2.16	2.926(5)	163
O(3)-H(5)...O(23)	0.77	2.12	2.861(5)	162
O(3)-H(6)...O(5)^{ii}	1.00	1.91	2.891(6)	167
O(4)-H(7)...O(34)	1.09	1.89	2.980(6)	178
O(4)-H(8)...O(6)	0.90	2.01	2.898(8)	175
O(5)-H(9)...O(24)^{iii}	0.97	1.95	2.885(6)	162
O(5)-H(10)...O(13)	0.91	2.04	2.913(6)	160
O(6)-H(11)...O(2)^{iv}	0.92	1.90	2.799(7)	165
O(6)-H(12)...O(7)^{v}	0.78	2.18	2.947(7)	173
O(7)-H(13)...O(12)	1.03	1.99	2.977(6)	159
O(7)-H(14)...O(22)^{vi}	0.87	1.97	2.818(6)	165
N(1)-(15)...O(32)^{vii}	0.78	2.00	2.782(5)	176
N(1)-(16)...O(33)^{viii}	0.85	2.16	2.948(5)	154
N(1)-H(17)...O(22)	0.96	1.91	2.852(6)	166
N(1)-H(18)...O(1)^{ix}	1.08	1.93	2.924(7)	153
N(2)-H(19)...O(24)^{x}	1.03	1.83	2.846(6)	171
N(2)-H(20)...O(14)	0.94	1.90	2.823(6)	169
N(2)-H(21)...O(31)^{xi}	0.82	2.07	2.881(5)	173
N(3)-H(23)...O(2)^{xii}	0.86	1.91	2.764(7)	176
N(3)-H(24)...O(12)	1.02	1.75	2.730(7)	160
N(3)-H(26)...O(34)^{xiii}	0.87	2.05	2.906(6)	167

Symmetry code: (i) x, $1 + y$, z; (ii) $1 - x$, $0.5 + y$, $1.5 - z$; (iii) $1 - x$, $-0.5 + y$, $1.5 - z$: (iv) $-x$, $1 - y$, $1 - z$; (v) x, $0.5 - y$, $0.5 + z$; (vi) $-x$, $0.5 + y$, $0.5 - z$; (vii) x, $-1 + y$, z; (viii) x, $-0.5 - y$, $-0.5 + z$; (ix) $1 - x$, $-y$, $1 - z$; (x) $1 - x$, $-0.5 + y$, $1.5 - z$; (xi) x, $-0.5 - y$, $0.5 + z$; (xii) $-x$, $-0.5 + y$, $0.5 - z$; (xiii) $-x$, $-y$, $1 - z$.

O(22), N(21), O(23) and pentadentate by O(31), O(32), N(31), O(31)^{ii}, O(32)^{ii} atoms at Nd(2) ion. The monodentate carboxylate groups (O(11)-C(16)-O(12), O(13)-C(17)-O(14), O(23)-C(27)-O(24)) have O-C-O in the range 124.6(7)-125.4(7)° and bidentate-bridging groups (O(21)-C(26)-O(22), O(31)-C(36)-O(32)) have 125.9(6) and 126.1(6)°, respectively. C-O distances in both types of COO group are in the same range of 1.228(10)-1.274(8) Å (Table VI). In the crystal structure of **2**, water molecules are linked by hydrogen bonds, forming a considerably stable network. The two molecules of coordinated water (O1, O2) are proton donors to the oxygen atoms O(21), O(31) of carboxylate groups of the same molecule and to O(23) and O(12) at $-x$, $-y$, $-z$ and $0.5 - x$, $0.5 - y$, $1 - z$, respectively. The molecule of water of crystallization (O5) is hydrogen bonded with the carboxylate oxygen atom O(22) and with O(14) at $0.5 - x$, $0.5 + y$, $0.5 - z$ and the O6 with the innersphere O3 and carboxylate oxygen O(12) at $0.5 - x$, $-0.5 + y$, $0.5 - z$ (Table VIII).

TABLE VIII Hydrogen bond lengths (Å) and angles (°) with esd's in parentheses for compound **2**.

D-H···A	D-H	H···A	D···A	∠D-H···A
O(1)-H(1)···O(21)	1.04	1.75	2.772(7)	170
O(1)-H(1)···O(12)$^{\mathrm{i}}$	0.96	1.74	2.685(8)	169
O(2)-H(3)···O(23)$^{\mathrm{ii}}$	0.88	1.90	2.762(7)	167
O(2)-H(4)···O(31)	1.13	2.11	3.138(6)	149
O(4)-H(8)···O(14)$^{\mathrm{iii}}$	0.86	2.39	3.190(6)	156
O(5)-H(9)···O(22)	1.18	1.80	2.893(10)	151
O(5)-H(10)···O(14)$^{\mathrm{iii}}$	1.00	1.97	2.858(12)	146
O(6)-H(11)···O(3)	0.94	2.07	2.821(12)	135
O(6)-H(12)···O(12)$^{\mathrm{iv}}$	0.96	2.11	2.808(12)	128

Symmetry code: (i) $0.5 - x, 0.5 - y, 1 - z$; (ii) $-x, -y, -z$; (iii) $0.5 - x, 0.5 + y, 0.5 - z$; (iv) $0.5 - x, -0.5 + y, 0.5 - z$

Supplementary Material

Lists of H atom positions, thermal parameters and observed and calculated structure factors are available from the authors.

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