

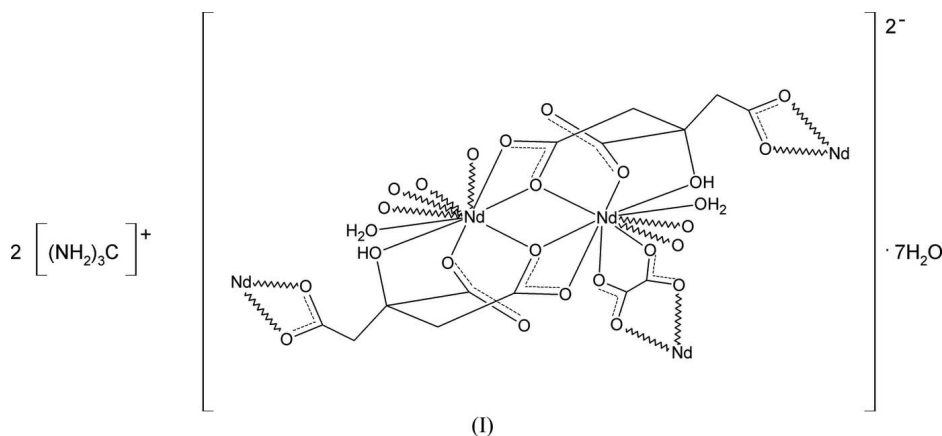
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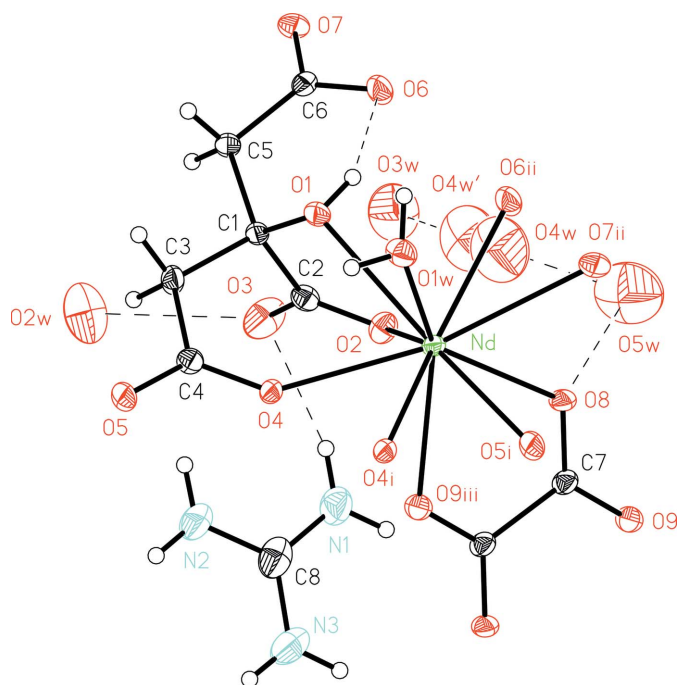
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Key indicatorsSingle-crystal X-ray study
 $T = 298$ K
Mean $\sigma(\text{C}-\text{C}) = 0.007$ Å
H-atom completeness 66%
Disorder in solvent or counterion
 R factor = 0.033
 wR factor = 0.074
Data-to-parameter ratio = 12.2For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.**Poly[bis(guanidinium) [diaquabis(μ_3 -hydrogen
citrate)- μ_2 -oxalato-dineodymium(III)]
heptahydrate]**The structure of the title compound, $[\text{C}(\text{NH}_2)_3]_2[\text{Nd}_2(\text{C}_6\text{H}_5\text{O}_7)_2(\text{C}_2\text{O}_4)(\text{H}_2\text{O})_2] \cdot 7\text{H}_2\text{O}$, contains anionic layers in which every Nd atom is linked to three other Nd atoms by citrate anions and to one Nd atom by the centrosymmetric oxalate anion. The Nd atoms are ten-coordinated; their coordination polyhedra form pairs sharing one edge owing to bridging by O atoms of carboxylate groups of citrate anions.

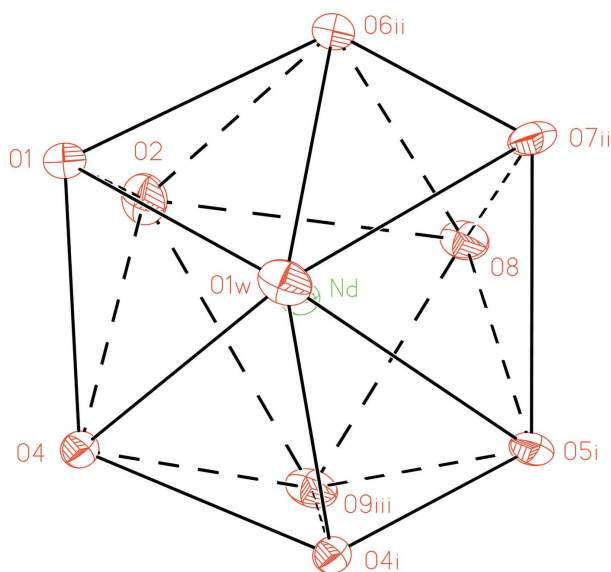
Received 21 April 2006

Accepted 21 June 2006

CommentThe knowledge of the structure of complexes of different metals with citric acid $[\text{H}_4\text{Cit}, \text{COH}(\text{COOH})(\text{CH}_2\text{COOH})_2]$ is important for the understanding of their behaviour in the environment. In particular, structural data for citrate complexes of lanthanides can be useful for the prediction of the behaviour of radioactive fission products. Recently, several structures of lanthanide citrate complexes have appeared (Baggio & Perec, 2004; Dickins *et al.*, 2002; Liu *et al.*, 2005; Vanhoyland *et al.*, 2005; Yuan *et al.*, 2005). We present here the structure of the title Nd^{III} complex, (I), with two different organic ligands, *viz.* citrate and oxalate.The Nd atom in (I) is ten-coordinate (Fig. 1). Its coordination environment consists of seven O atoms of three different citrate anions, two O atoms of the oxalate anion and one coordinated water molecule. The coordination of the Nd atom (Fig. 2) can be described as 'irregular decahexahedral' (Voliotis & Rimsky, 1975), in which atom O1_w of the water molecule occupies a unique position (the only one sharing six edges). The Nd—O distances are given in Table 1.Each citrate anion is linked to three Nd atoms, *viz.* to one atom in a tridentate fashion by the OH group and two O atoms of different carboxylate groups, to two atoms in a bidentate manner with the formation of four-membered metallacycles

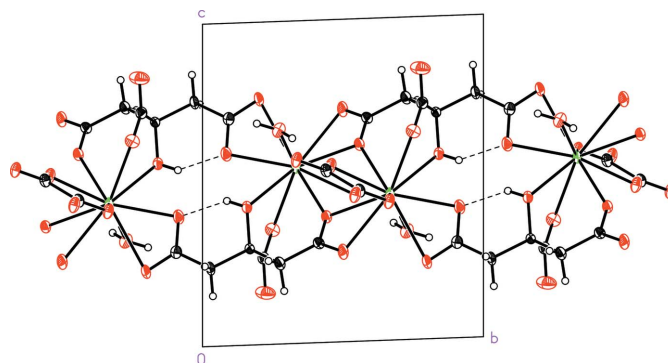

Figure 1

A view of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are represented by circles of arbitrary size. Dashed lines indicate the hydrogen-bonding interactions. [Symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $1 - x, -y, 1 - z$; (iii) $-x, 1 - y, 1 - z$.]

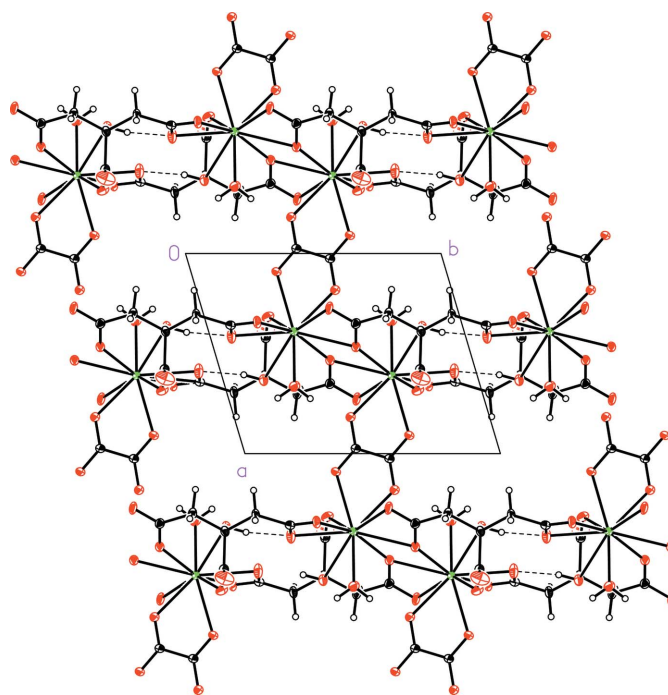

Figure 2

Coordination polyhedron of the Nd atom in the structure of (I).

(Fig. 3). One O atom of a four-membered metallacycle is bridging between two Nd atoms. Thus, the coordination polyhedra of Nd atoms form pairs sharing one edge. The corresponding Nd...Nd distance is 4.3158 (5) Å. The bridging function of the citrate anions results in the formation of anionic chains in the [010] direction. The coordination mode of the HCit^{3-} anion in this structure differs from those known


Figure 3

Anionic chain in the structure of (I). Dashed lines indicate the hydrogen-bonding interactions.


Figure 4

Anionic layer $[\text{Nd}_2(\text{HCit})_2\text{C}_2\text{O}_4(\text{H}_2\text{O})_2]_n^{2n-}$ in the structure of (I). Dashed lines indicate the hydrogen-bonding interactions.

for other Ln compounds (Baggio & Pereg, 2004; Dickens *et al.*, 2002; Liu *et al.*, 2005; Vanhoyland *et al.*, 2005; Yuan *et al.*, 2005) but is the same as that found in a Bi complex (Asato *et al.*, 1991).

The oxalate anions occupy special positions on inversion centres and are linked in a bidentate fashion, with the formation of five-membered metallacycles, to two Nd atoms from different chains. As a result, anionic layers in the (001) plane are formed (Fig. 4). Guanidinium cations and water molecules of crystallization are situated between these anionic layers. A number of hydrogen bonds can be found in the structure (only the hydrogen bonds with located H atoms are listed in Table 2), the proton donors in these bonds being coordinated and uncoordinated water molecules, guanidinium cations and the OH groups of citrate anions. In the last case, the hydrogen bonds are intramolecular.

Experimental

For the preparation of (I), 0.5 M H₄Cit (1 ml) was added to a 0.1 M aqueous solution (4.5 ml) of Nd(NO₃)₃; the pH of the resulting solution was brought to 6.5 with [(CH₃)₄N]OH, and then 0.1 M [(NH₂)₃C]NO₃ (7.5 ml) was added. After six months, long thin plates had appeared. The composition of the crystals was determined by X-ray structural analysis. A possible origin of oxalate is decomposition of citrate in the presence of guanidinium.

Crystal data

(CH ₆ N ₃) ₂ [Nd ₂ (C ₆ H ₅ O ₇) ₂ (C ₂ O ₄)(H ₂ O) ₂ ·7H ₂ O	$\gamma = 73.464 (3)^\circ$
$M_r = 1037.02$	$V = 869.90 (6) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 1$
$a = 8.2017 (4) \text{ \AA}$	$D_x = 1.980 \text{ Mg m}^{-3}$
$b = 10.0447 (3) \text{ \AA}$	Mo $K\alpha$ radiation
$c = 11.0222 (5) \text{ \AA}$	$\mu = 3.06 \text{ mm}^{-1}$
$\alpha = 87.892 (3)^\circ$	$T = 298 (2) \text{ K}$
$\beta = 89.505 (2)^\circ$	Plate, light pink
	$0.16 \times 0.06 \times 0.02 \text{ mm}$

Data collection

Nonius KappaCCD area-detector diffractometer	8213 measured reflections
φ and ω scans	3033 independent reflections
Absorption correction: multi-scan (MULABS in PLATON; Spek, 2003)	2588 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.790$, $T_{\max} = 0.922$	$R_{\text{int}} = 0.055$
	$\theta_{\text{max}} = 25.0^\circ$

Refinement

Refinement on F^2	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.033$	$w = 1/[\sigma^2(F_o^2) + (0.0305P)^2]$
$wR(F^2) = 0.074$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{\text{max}} = 0.001$
3033 reflections	$\Delta\rho_{\text{max}} = 1.15 \text{ e \AA}^{-3}$
248 parameters	$\Delta\rho_{\text{min}} = -1.01 \text{ e \AA}^{-3}$

Table 1

Selected bond lengths (Å).

Nd—O1	2.626 (3)	Nd—O5 ⁱ	2.590 (4)
Nd—O2	2.451 (4)	Nd—O6 ⁱⁱ	2.490 (3)
Nd—O4	2.470 (3)	Nd—O7 ⁱⁱ	2.751 (4)
Nd—O8	2.469 (3)	Nd—O9 ⁱⁱⁱ	2.499 (3)
Nd—O4 ⁱ	2.630 (3)	Nd—O1w	2.503 (4)

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

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1 \cdots O6	0.82 (2)	1.85 (3)	2.596 (5)	151 (5)
O1W—H1A \cdots O9 ^{iv}	0.84 (2)	1.99 (2)	2.796 (5)	162 (4)
N1—H1C \cdots O5 ^v	0.86	2.05	2.893 (7)	166
N1—H1D \cdots O3	0.86	2.21	2.993 (7)	151
N2—H2B \cdots O2W ^{vi}	0.86	2.16	2.995 (8)	164
N3—H3C \cdots O7 ^{vii}	0.86	2.14	2.964 (7)	161

Symmetry codes: (iv) $x+1, y, z$; (v) $x-1, y, z$; (vi) $-x+1, -y+1, -z$; (vii) $x-1, y+1, z$.

H atoms of CH₂ and NH₂ groups were refined as riding in idealized positions (C—H = 0.97 Å and N—H = 0.86 Å) with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$. H atoms of the OH group and the coordinated water molecule were located in a difference Fourier map and refined with restraints on O—H bond lengths and the H—O—H angle. The H atoms of the water molecules of crystallization were not located. These are partially disordered. The O4w atom is split between two positions with occupancies 0.5. The O5W atom was also given an occupancy of 0.5 to avoid short O \cdots O contacts. The largest electron-density peak in the final difference Fourier synthesis is 1.24 Å from H5B; the deepest hole is 0.98 Å from Nd.

Data collection: COLLECT (Nonius, 1998); cell refinement: HKL (Otwinowski & Minor, 1997); data reduction: HKL; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997a); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997a); molecular graphics: SHELXTL (Sheldrick, 1997b); software used to prepare material for publication: SHELXTL.

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