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**Poly[[tetraaquapraesodymium(III)- μ -
(iminodiacetato- $O,O':O':O'',O''':O''')$]
dichloride hydrate]**

JUN-RAN LI, ZHE-MING WANG, CHUN-HUA YAN, LI-PING ZHOU AND TIAN-ZHU JIN

State Key Laboratory of Rare Earth Materials Chemistry and Applications, PKU-HKU Joint Laboratory in Rare Earth Materials and Bioinorganic Chemistry, Department of Chemistry, Peking University, Beijing 100871, People's Republic of China. E-mail: chyan@chemms.chem.pku.edu.cn

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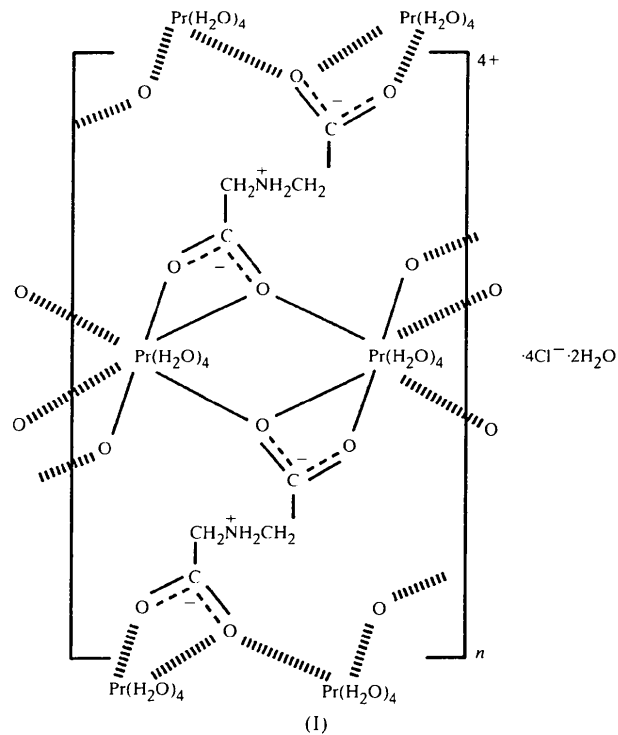
Abstract

The title compound, $[\text{Pr}(\text{C}_4\text{H}_6\text{NO}_4)(\text{H}_2\text{O})_4]\text{Cl}_2 \cdot \text{H}_2\text{O}$, consists of $[\text{Pr}(\text{OOCCH}_2\text{NH}_2\text{CH}_2\text{COO})(\text{H}_2\text{O})_4]$ sheets, Cl^- ions and solvent water molecules. Within the sheets, each Pr ion is linked by four bridging iminodiacetate ligands and is further coordinated by four water molecules giving a distorted bicapped square antiprism coordination environment with an average Pr—O distance of 2.573(2) Å. The Cl^- ions and the solvent water molecules lie between these sheets and form numerous hydrogen bonds with the coordinated water and the $-\text{NH}_2^-$ group of the ligand.

Comment

Amino acids and polyamino acids are widely used to form rare earth complexes (Huang, 1997). Among them

those with iminodiacetic acid were studied extensively about 30 years ago, but the available crystal structures are quite limited (Albertsson & Oskarsson, 1968, 1974; Li *et al.*, 1997; Oskarsson, 1971). This might be due to the fact that crystal structures in this series are often isostructural, as well as the often poor quality of crystals obtained (Albertsson & Oskarsson, 1974; Oskarsson, 1971). Recently, we synthesized the title compound, (I), and obtained crystals of high quality. Its structure belongs to a new type, which is reported here.



Each praeosodymium(III) ion in (I) is coordinated by four carboxylate groups from four iminodiacetate ligands and each ligand links four different praeosodymium ions (Fig. 1). All the carboxylate groups have a bidentate and a bridging-type mode (Dong *et al.*, 1990; Imai *et al.*, 1987). For each carboxylate group, the two O atoms coordinate to one Pr^{3+} ion and one of them, the μ -O, coordinates to another Pr^{3+} ion. Along the *c* direction, Pr^{3+} ions are connected by the μ -O atoms (O2 and O3) to form chains, which are connected by the ligands to build up a two-dimensional network parallel to the *ac* plane. This connection mode is quite different from the structures of all other known complexes of rare earth ions with iminodiacetic acid (Albertsson & Oskarsson, 1968, 1974; Li *et al.*, 1997; Oskarsson, 1971).

The coordination environment around the Pr^{3+} ion is a distorted bicapped square antiprism made up of six O atoms from four carboxylate groups and four coordinated water molecules, *i.e.* the Pr^{3+} ion is decacoordinated [coordination number (CN) = 10]. The μ -O atoms give one long and one short Pr—

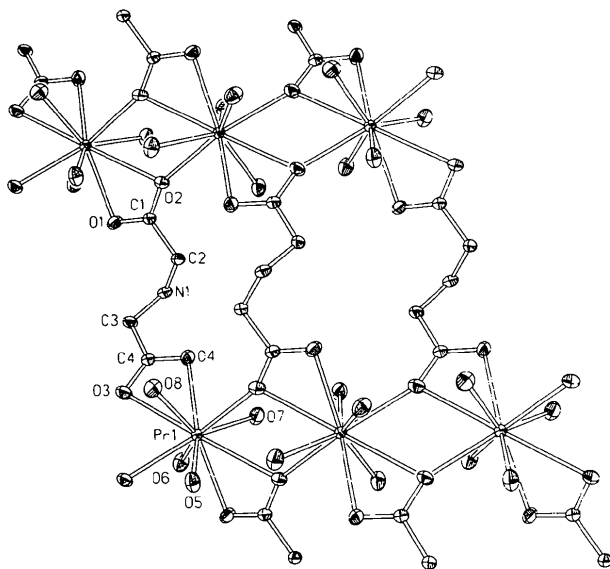


Fig. 1. The molecular view of (I) showing the sheet structure. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

O distance, as was observed for those compounds containing bidentate and bridging carboxylate groups (Deiters & Meyer, 1996; Imai *et al.*, 1987; Wang *et al.*, 1996). Among the ten Pr—O distances, the two distances of 2.760 (2) and 2.761 (2) Å, between the Pr³⁺ ion and the capped O atoms, are obviously longer than the other eight Pr—O distances, which are in the range 2.488 (2)–2.635 (2) Å. The average Pr—O distance of 2.573 (2) Å is compatible with those for other Pr³⁺ ions with CN = 10, for example, in [Pr(CH₃-CH₂COO)₃(H₂O)₃] (Deiters & Meyer, 1996) and [Pr₃-(ClCH₂COO)₉{(CH₃)₂SO}₄] (Sugita & Ouchi, 1988), and longer than those for Pr³⁺ ions with lower CN (Albertsson & Oskarsson, 1974; Deiters & Meyer, 1996; Sugita & Ouchi, 1988; Wang *et al.*, 1994, 1996). The Pr···Pr distance between two adjacent Pr³⁺ ions linked by μ-O atoms is 4.5224 (1) Å.

The iminodiacetate ligand, containing the -NH₂⁺ group, has a conformation similar to that of ligand 1 in [Pr₂(H₂O)₄(C₄H₆NO₄)₂(C₄H₅NO₄)]Cl₂·3H₂O (Albertsson & Oskarsson, 1974), and the bond distances and angles are comparable with those reported for compounds containing iminodiacetate (Albertsson & Oskarsson, 1974; Li *et al.*, 1997; Oskarsson, 1971).

The positively charged sheets are stacked along the *b* direction with the Cl⁻ ions and solvent water molecules located between these sheets. The Cl⁻ ions balance the positive charges of the sheets as well as forming many hydrogen bonds with the -NH₂⁺ groups and the water molecules. Of the two unique Cl⁻ ions, one forms two N—H···Cl-type and four O—H···Cl-type hydrogen bonds, while the other accepts four O—H···Cl hydrogen bonds. The solvent water forms three hydrogen

bonds connecting two Cl⁻ ions and one coordinated water. All the hydrogen bond lengths are in agreement with those found in [Nd(OCOCH₂NHCH₂OCO)]Cl₂·3H₂O (Oskarsson, 1971) and [Pr₂(H₂O)₄(C₄H₆NO₄)₂-(C₄H₅NO₄)]Cl₂·3H₂O (Albertsson & Oskarsson, 1974), and they play an important role in holding the sheets together in the crystal structure.

Experimental

The title complex was obtained in an attempt to prepare a heteronuclear praeosmium and nickel complex with iminodiacetic acid. PrCl₃, NiCl₂ and iminodiacetic acid were mixed in a molar ratio of 4:1:2 in water at pH 2. Green crystals were obtained by slow evaporation of the solution at room temperature. Elemental analysis, found: Pr 32.50, C 11.05, N 3.15, H 3.65%; calculated for C₄H₁₆Cl₂NO₉Pr: Pr 32.47, C 11.07, N 3.23, H 3.72%.

Crystal data

[Pr(C₄H₆NO₄)(H₂O)₄]Cl₂·
H₂O
M_r = 433.99
Monoclinic
*P*2₁/*c*
a = 9.5728 (3) Å
b = 16.3086 (6) Å
c = 9.0007 (3) Å
β = 112.114 (3)°
V = 1301.81 (8) Å³
Z = 4
D_x = 2.214 Mg m⁻³
D_m not measured

Data collection

Enraf–Nonius CAD-4
MACH3 diffractometer
θ/*2θ* scans
Absorption correction:
ψ scan (North *et al.*,
1968)
T_{min} = 0.302, *T_{max}* = 0.351
4020 measured reflections
3821 independent reflections
3596 reflections with
I > 2σ(*I*)

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.019
wR(*F*²) = 0.047
S = 1.163
3821 reflections
219 parameters
All H-atom parameters
refined
w = 1/[σ²(*F_o*²) + (0.0184*P*)²
+ 1.5215*P*]
where *P* = (*F_o*² + 2*F_c*²)/3

Mo *Kα* radiation
λ = 0.71073 Å
Cell parameters from 25
reflections
θ = 9.80–14.00°
μ = 4.186 mm⁻¹
T = 293 (2) K
Block
0.40 × 0.33 × 0.25 mm
Green

R_{int} = 0.012
θ_{max} = 30.04°
h = 0 → 13
k = 0 → 22
l = -12 → 11
3 standard reflections
frequency: 60 min
intensity decay: -3.8%

(Δ/σ)_{max} = 0.001
Δρ_{max} = 0.803 e Å⁻³
Δρ_{min} = -0.957 e Å⁻³
Extinction correction:
SHELX97 (Sheldrick,
1997)
Extinction coefficient:
0.0114 (2)
Scattering factors from
International Tables for
Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Pr1—O2 ⁱ	2.4881 (16)	O1—Pr1 ⁱⁱ	2.5313 (15)
Pr1—O5	2.4883 (18)	O2—C1	1.263 (2)
Pr1—O7	2.5006 (18)	O2—Pr1 ^v	2.4881 (16)
Pr1—O4	2.5070 (15)	O2—Pr1 ^{ix}	2.7607 (16)
Pr1—O8	2.5298 (18)	O3—C4	1.259 (2)
Pr1—O1 ⁱⁱⁱ	2.5313 (15)	O3—Pr1 ^{xi}	2.5313 (16)
Pr1—O3 ⁱⁱⁱ	2.5313 (16)	O4—C4	1.248 (3)
Pr1—O6	2.6352 (19)	N1—C3	1.485 (3)
Pr1—O3	2.7603 (17)	N1—C2	1.487 (3)
Pr1—O2 ⁱⁱ	2.7607 (16)	C1—C2	1.510 (3)
O1—C1	1.245 (2)	C3—C4	1.507 (3)
O2 ⁱ —Pr1—O5	73.43 (6)	O4—Pr1—O6	84.77 (6)
O2 ⁱ —Pr1—O7	136.02 (6)	O8—Pr1—O6	135.42 (6)
O5—Pr1—O7	135.51 (6)	O1 ⁱⁱⁱ —Pr1—O6	65.98 (6)
O2 ⁱ —Pr1—O4	111.10 (5)	O3 ⁱⁱⁱ —Pr1—O6	140.11 (6)
O5—Pr1—O4	142.20 (6)	O2 ⁱ —Pr1—O3	62.11 (5)
O7—Pr1—O4	68.17 (6)	O5—Pr1—O3	121.29 (6)
O2 ⁱ —Pr1—O8	81.54 (6)	O7—Pr1—O3	103.18 (6)
O5—Pr1—O8	69.08 (7)	O4—Pr1—O3	48.99 (5)
O7—Pr1—O8	134.31 (6)	O8—Pr1—O3	68.26 (6)
O4—Pr1—O8	74.47 (6)	O1 ⁱⁱⁱ —Pr1—O3	128.23 (5)
O2 ⁱ —Pr1—O1 ⁱⁱⁱ	80.07 (5)	O3 ⁱⁱⁱ —Pr1—O3	120.12 (6)
O5—Pr1—O1 ⁱⁱⁱ	74.00 (6)	O6—Pr1—O3	68.33 (6)
O7—Pr1—O1 ⁱⁱⁱ	79.66 (6)	O2 ⁱ —Pr1—O2 ⁱⁱ	121.08 (6)
O4—Pr1—O1 ⁱⁱⁱ	143.33 (6)	O5—Pr1—O2 ⁱⁱ	66.60 (6)
O8—Pr1—O1 ⁱⁱⁱ	142.09 (6)	O7—Pr1—O2 ⁱⁱ	69.03 (6)
O2 ⁱ —Pr1—O3 ⁱⁱⁱ	150.17 (6)	O4—Pr1—O2 ⁱⁱ	127.16 (5)
O5—Pr1—O3 ⁱⁱⁱ	82.57 (6)	O8—Pr1—O2 ⁱⁱ	119.17 (5)
O7—Pr1—O3 ⁱⁱⁱ	73.80 (6)	O1 ⁱⁱⁱ —Pr1—O2 ⁱⁱ	48.83 (5)
O4—Pr1—O3 ⁱⁱⁱ	77.75 (5)	O3 ⁱⁱⁱ —Pr1—O2 ⁱⁱ	61.61 (5)
O8—Pr1—O3 ⁱⁱⁱ	73.38 (6)	O6—Pr1—O2 ⁱⁱ	104.90 (5)
O1 ⁱⁱⁱ —Pr1—O3 ⁱⁱⁱ	110.38 (5)	O3—Pr1—O2 ⁱⁱ	171.64 (5)
O2 ⁱ —Pr1—O6	69.70 (6)	Pr1 ^v —O2—Pr1 ^{ix}	118.90 (6)
O5—Pr1—O6	128.96 (6)	Pr1 ^{ix} —O3—Pr1	117.37 (6)
O7—Pr1—O6	66.43 (6)		

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

Table 2. Hydrogen-bonding geometry (Å, °)

D—H...A	D—H	H...A	D...A	D—H...A
N1—H5...Cl1 ⁱ	0.91 (3)	2.40 (3)	3.248 (2)	155 (3)
N1—H6...Cl1	0.81 (3)	2.47 (3)	3.259 (2)	165 (3)
O5—H7...Cl2 ⁱⁱ	0.76 (4)	2.37 (4)	3.118 (2)	173 (3)
O5—H8...O6 ⁱⁱⁱ	0.80 (4)	1.96 (4)	2.744 (3)	165 (4)
O6—H9...Cl1 ^{iv}	0.84 (5)	2.60 (4)	3.354 (2)	149 (4)
O6—H10...Cl2 ^v	0.77 (4)	2.39 (5)	3.128 (2)	161 (4)
O7—H11...O8 ⁱⁱⁱ	0.72 (5)	2.42 (5)	2.870 (3)	123 (5)
O7—H11...Cl2 ^{vi}	0.72 (5)	2.71 (5)	3.312 (2)	143 (5)
O7—H12...Cl1	0.81 (4)	2.40 (4)	3.202 (2)	169 (4)
O8—H13...Cl2 ^{vi}	0.75 (4)	2.39 (4)	3.140 (2)	172 (4)
O8—H14...O9	0.79 (4)	1.99 (4)	2.778 (3)	175 (3)
O9—H15...Cl1 ^{vii}	0.93 (5)	2.38 (5)	3.219 (2)	151 (4)
O9—H16...Cl1 ^{vii}	0.96 (5)	2.30 (5)	3.249 (3)	168 (4)

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

All H atoms were located by difference Fourier synthesis and refined isotropically. The refinement gives $X-H$ ($X = C, N, O$) distances in the range 0.72 (5)–0.92 (4) Å and all bond angles involving H atoms are reasonable. U_{iso} values for H atoms are in the range 0.025 (7)–0.078 (15) Å².

Data collection: CAD-4 ARGUS (Enraf-Nonius, 1996). Cell refinement: CAD-4 ARGUS. Data reduction: MolEN (Fair, 1990). Program(s) used to solve structure: SHELX97 (Sheldrick, 1997). Program(s) used to refine structure: SHELX97. Molecular graphics: SHELXTL/PC (Sheldrick, 1990). Software used to prepare material for publication: SHELX97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1068). Services for accessing these data are described at the back of the journal.

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Diaqua{hydrogen bis[1-(2-pyridyl)ethanone oximato-*N,N'*]}nickel(II) perchlorate hydrate

AARNE PAJUNEN, MARJATTA ORAMA AND HEIKKI SAARINEN

Department of Chemistry, University of Helsinki, Box 55, FIN-00014 University of Helsinki, Finland. E-mail: aarne.pajunen@helsinki.fi

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Abstract

In the title compound, [Ni(C₇H₈N₂O)(C₇H₉N₂O)(H₂O)₂]ClO₄·H₂O, the Ni atom lies on a twofold axis