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Key indicators

Single-crystal X-ray study
 $T = 293\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.005\text{ \AA}$
 R factor = 0.032
 wR factor = 0.065
Data-to-parameter ratio = 14.0For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Diaquabis(nicotinato- κO)bis(1,10-phenanthroline- $\kappa^2\text{N},\text{N}'$)praseodymium(III) trihydrate

The structure of the title compound, $[\text{Pr}(\text{C}_6\text{H}_4\text{NO}_2)_3(\text{C}_{12}\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$, is composed of a discrete neutral Pr complex and solvent water molecules. The Pr^{III} center is nine-coordinate and exhibits a monocapped square-antiprismatic coordination geometry formed by three O atoms of distinct nicotinate groups, four N atoms of two 1,10-phenanthroline molecules and two aqua ligands.

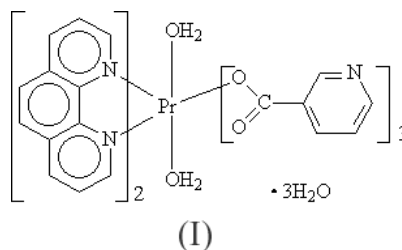
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Comment

The structures and properties of many lanthanide compounds containing 1,10-phenanthroline (phen) and acid groups have been reported, for example, tetrabenzoato- $O:O'$ -bis-[(benzoato- O,O')(1,10-phenanthroline- N,N')lanthanum(III)] (Shi *et al.*, 2001), aquatris(1,10-phenanthroline)(*trans*-2,3-dimethylacrylato)ytterbium(III) (Lu *et al.*, 2000), di- μ -methacrylato- $O:O'$ -bis[(1,10-phenanthroline- N,N')bis(methacrylato- O,O')ytterbium(III)] (Lu *et al.*, 1999) and bis(pivalato)-bis(1,10-phenanthroline)nitratoprasedymium(III) (Pisarevskii *et al.*, 1995). Furthermore, the nicotinate group has been widely investigated in metal coordination complexes and has shown diverse coordination modes (Clegg *et al.*, 1995; Chapman *et al.*, 2001). A europium(III) complex, diaquabis(nicotinato- O,O')(nicotinato- O)(1,10-phenanthroline)-europium(III) dimethylsulfoxide solvate (Palkina *et al.*, 1995), containing both nicotinate and phen ligands, has been reported; this complex contains one phen group in each molecule. We report here the structure of the title Pr^{III} compound, (I), which contains two phen and three nicotinate groups in each molecule. The structural differences may be attributed to the different solvents used in the preparation of the compounds.



Compound (I) is composed of a discrete neutral Pr complex and solvent water molecules (Fig. 1 and Table 1). The Pr^{III} ion is nine-coordinated by four O atoms of three distinct nicotinate groups, four N atoms of two phen molecules and two aqua ligands. The coordination geometry can best be described as monocapped square antiprismatic, where N7/O8/O5/O3 and O7/O2/N4/N5 form the two square planes and atom N6 is in the monocapping position. The mean Pr—

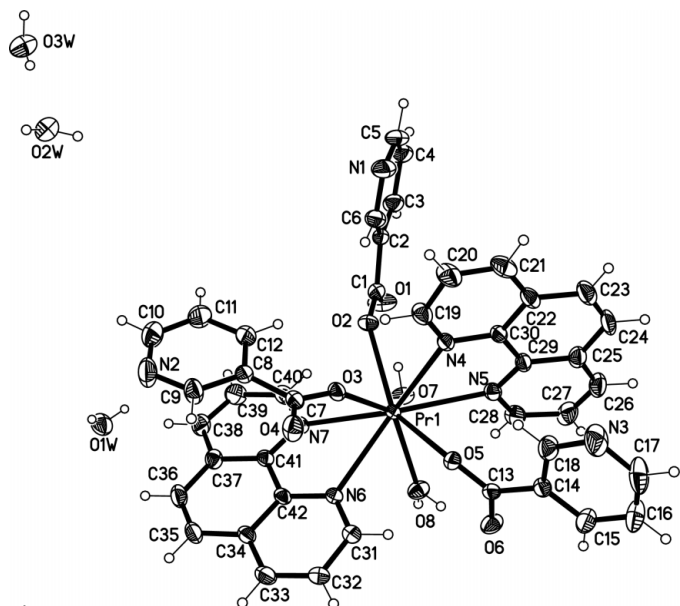


Figure 1
The asymmetric unit of the title compound, showing the atom-numbering scheme and 30% probability displacement ellipsoids.

O(nicotinate) bond length is 2.440 (2) Å, which is slightly shorter than that of the Pr–O(aqua) bonds [mean 2.482 (2) Å], and the Pr–N bond distances lie in a narrow range from 2.695 (2) to 2.730 (2) Å, with a mean value of 2.710 (2) Å.

The dihedral angle between the two phen planes is 82.4 (4)°. Non-coordinated carboxyl atom O1 participates in a hydrogen-bonding interaction (Table 2) with aqua atom O7, with an O···O distance of 2.626 (3) Å. The C8/C9/N2/C10–C12 pyridyl ring of one of the nicotinate groups forms an intramolecular π – π interaction with the benzene ring (C34–C37/C41/C42) of one of the phen ligands. The center-to-center and perpendicular distances are 3.684 (2) and 3.638 (2) Å, respectively, with a dihedral angle of 12.6 (2)° between the two rings. The Pr complex and solvent water molecules are held together by intermolecular hydrogen bonds (Table 2) to form a two-dimensional double layer parallel to the *ab* plane.

Experimental

To a solution of nicotinic acid (0.6 mmol) dissolved in water–EtOH (2:1, 30 ml) was added a solution of Pr(NO₃)₃ (0.2 mmol) and phen (0.4 mmol) in EtOH (25 ml). The resulting solution was then filtered and left to stand at room temperature. Crystals of (I) suitable for X-ray analysis were obtained after several days (yield *ca* 45%).

Crystal data

[Pr(C₆H₄NO₂)₃(C₁₂H₈N₂)₂·
(H₂O)₂]₃·3H₂O
M_r = 957.70
Triclinic, *P* $\bar{1}$
a = 9.058 (3) Å
b = 12.922 (5) Å
c = 17.826 (6) Å
 α = 84.966 (5)°
 β = 80.597 (5)°
 γ = 84.398 (5)°
V = 2043.1 (12) Å³

Z = 2
D_x = 1.557 Mg m^{−3}
Mo *K* α radiation
Cell parameters from 885
reflections
 θ = 2.9–26.3°
 μ = 1.26 mm^{−1}
T = 293 (2) K
Prism, colorless
0.24 × 0.24 × 0.22 mm

Data collection

Bruker SMART CCD area-detector
diffractometer
 φ and ω scans
Absorption correction: multi-scan
(SADABS; Sheldrick, 1996;
Blessing, 1995)
*T*_{min} = 0.751, *T*_{max} = 0.769
11 836 measured reflections

8275 independent reflections
7083 reflections with *I* > 2 σ (*I*)
*R*_{int} = 0.023
 θ _{max} = 26.4°
h = −11 → 11
k = −16 → 12
l = −17 → 22

Refinement

Refinement on *F*²
R [*F*² > 2 σ (*F*²)] = 0.032
wR(*F*²) = 0.065
S = 1.03
8275 reflections
590 parameters

H atoms treated by a mixture of
independent and constrained
refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0268P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
(Δ/σ)_{max} = 0.003
 $\Delta\rho$ _{max} = 0.32 e Å^{−3}
 $\Delta\rho$ _{min} = −0.42 e Å^{−3}

Table 1

Selected geometric parameters (Å, °).

Pr1–O2	2.474 (2)	Pr1–N4	2.718 (2)
Pr1–O3	2.364 (2)	Pr1–N5	2.696 (2)
Pr1–O5	2.482 (2)	Pr1–N6	2.730 (2)
Pr1–O7	2.487 (2)	Pr1–N7	2.695 (2)
Pr1–O8	2.476 (2)		
O3–Pr1–N6	67.33 (7)	O7–Pr1–N6	118.65 (8)
O2–Pr1–N6	130.77 (7)	N7–Pr1–N6	60.48 (7)
O8–Pr1–N6	68.63 (8)	N5–Pr1–N6	137.34 (7)
O5–Pr1–N6	75.96 (7)	N4–Pr1–N6	126.93 (7)

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
O2W–H2WA···O4 ⁱ	0.83 (2)	1.91 (2)	2.729 (3)	171 (4)
O2W–H2WB···O5 ⁱ	0.82 (3)	2.09 (2)	2.894 (3)	169 (4)
O3W–H3WA···O2W	0.81 (4)	1.99 (2)	2.784 (4)	164 (4)
O3W–H3WB···O1W ⁱⁱ	0.81 (3)	1.96 (2)	2.771 (4)	179 (4)
O7–H7A···O1	0.83 (2)	1.82 (2)	2.626 (3)	164 (3)

Symmetry codes: (i) 2 − *x*, 1 − *y*, 1 − *z*; (ii) 1 + *x*, *y* − 1, *z*.

H atoms attached to C atoms were included at calculated positions and treated as riding atoms [*C*–H = 0.93 Å and *U*_{iso}(H) = 1.2*U*_{eq}(parent atom)]. H atoms of water molecules were located in difference density maps and refined isotropically, with the restraint O–H = 0.82 (2).

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINTE* (Bruker, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXTL*.

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