

Poly[[aqua(μ_4 -1,4-cyclohexanedicarboxylato)-praseodymium(III)] hemihydrate]

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In the title compound, $\{[\text{Pr}(\text{C}_{12}\text{H}_{15}\text{O}_6)(\text{H}_2\text{O})]\cdot 0.5\text{H}_2\text{O}\}_n$, the central praseodymium(III) cation is nine-coordinated by O atoms from six different chdc^{2-} ligands (chdc^{2-} is the 1,4-cyclohexanedicarboxylate dianion) and one terminal water molecule. An interesting feature of the compound is the presence of two strands of *cis*- chdc^{2-} ligands wrapped around each other, held together by praseodymium(III) cations to form a double-stranded chain. *trans*- Chdc^{2-} ligands further bridge adjacent double-stranded chains to yield a three-dimensional framework.

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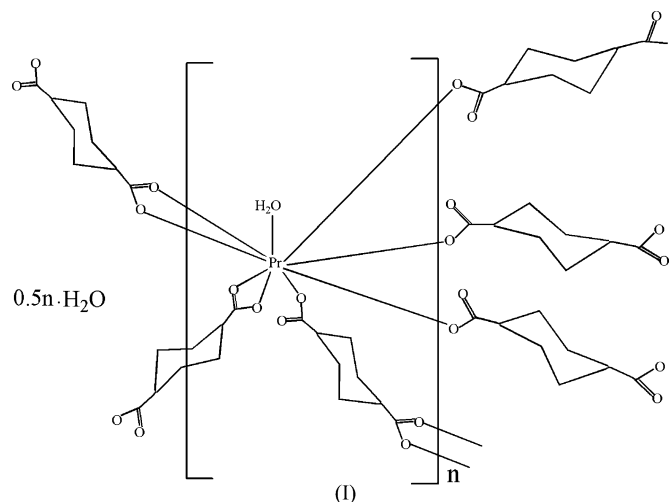
Key indicators

Single-crystal X-ray study
 $T = 292 \text{ K}$
 Mean $\sigma(\text{C}-\text{C}) = 0.008 \text{ \AA}$
 H-atom completeness 84%
 Disorder in solvent or counterion
 R factor = 0.036
 wR factor = 0.085
 Data-to-parameter ratio = 17.1

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Comment

The rational synthesis and design of inorganic–organic hybrid materials *via* multidentate ligands have received considerable attention, owing to their novel structures and special functional properties (Eddaoudi *et al.*, 2001). Rigid spacer ligands such as benzene di- and tri-carboxylates successfully generate various extended structures with metal ions (Yang *et al.*, 2005). However, the control of the conformation of flexible ligands in the synthetic reactions is still an exciting challenge to chemists (Ma *et al.*, 2003). A guiding principle of our work is the attempt to construct high-dimensional structures by control of the conformations of flexible spacer ligands (Kim & Jung, 2002). In this paper, we have 1,4-cyclohexanedicarboxylic acid (chdcH_2) as a spacer ligand, which possesses two possible configurations of two carboxylate groups (*trans* and *cis* configurations). We present here a new compound, $[\text{Pr}(\text{trans}\text{-chdc}^{2-})_{0.5}(\text{cis}\text{-chdc}^{2-})_{0.5}(\text{H}_2\text{O})]_n \cdot 0.5n\text{H}_2\text{O}$, (I), obtained under hydrothermal conditions using aqueous NaOH solution at 413 K.



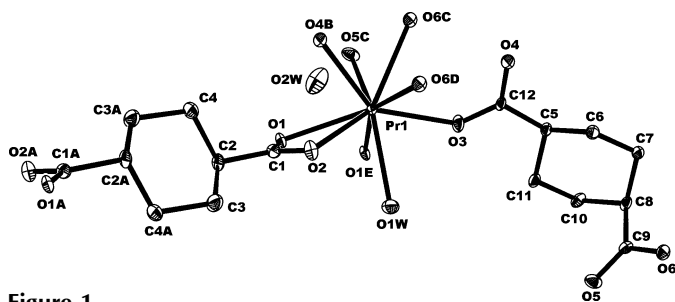


Figure 1

View of the local coordination of praseodymium(III) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity. [Symmetry codes: (A) $-x, -y, -z$; (B) $1-x, -y, 1-z$; (C) $x, -1+y, z$; (D) $1-x, 1-y, 1-z$; (E) $-x, -y, 1-z$.]

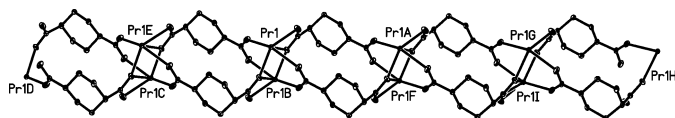


Figure 2

The double-stranded chain structure of (I), along the b axis. H atoms have been omitted for clarity. [Symmetry codes: (A) $x, -1+y, z$; (B) $1-x, -y, 1-z$; (C) $1-x, 1-y, 1-z$; (D) $1-x, 2-y, 1-z$; (E) $x, 1+y, z$; (F) $1-x, -1-y, 1-z$; (G) $x, -2+y, z$; (H) $1-x, -3-y, 1-z$; (I) $1-x, -2-y, 1-z$.]

Selected bond lengths and angles for (I) are given in Table 1. The single-crystal analysis of the structure reveals that compound (I) is a three-dimensional network built up by *trans*-chdc²⁻ and *cis*-chdc²⁻ ligands with Pr^{III} cations. The *trans*-chdc²⁻ ligand lies about an inversion centre. In (I), the Pr^{III} cation is nine-coordinated by O atoms from six different chdc²⁻ ligands and one terminal water molecule (Fig. 1). One *trans*-chdc²⁻ and one *cis*-chdc²⁻ carboxylate ligand coordinate four Pr^{III} cations in bidentate mode. The Pr–O(carboxylate) bond lengths range from 2.393 (4) to 2.699 (4) Å, and the Pr–O1W distance is 2.616 (4) Å. The O–Pr–O bond angles range from 51.11 (12) to 152.55 (12)° (Bi *et al.*, 2004). The interesting feature of (I) is the presence of two strands of *cis*-chdc²⁻ ligands wrapped around each other, held together by Pr^{III} cations to form a double-strand chain along the b axis (Fig. 2). As depicted in Fig. 3, the *trans*-chdc²⁻ ligands further bridge adjacent double-stranded chains to yield a three-dimensional framework.

Although the H atoms of the water molecules could not be located, the separations between the O atoms of water molecules and carboxylate ligands indicate the presence of strong O–H...O hydrogen interactions [O2W...O2 = 2.921 (10) Å, O1W...O5ⁱ = 2.813 (7) Å; symmetry code: (i) $-x, 1-y, 1-z$].

Experimental

PrCl₃·7H₂O (0.39 g, 1.0 mmol) and 1,4-cyclohexanedicarboxylic acid (0.17 g, 1.0 mmol) were dissolved in distilled water (20 ml) and the pH value was adjusted to 5.0 with dilute aqueous NaOH solution. The solution was heated in a 25 ml Teflon-lined reaction vessel at 413 K for 72 h and then cooled to room temperature over a period of 6 h. Green crystals of (I) were collected in a yield of 42%.

Crystal data

[Pr(C₁₂H₁₅O₆)(H₂O)]·0.5H₂O
 $M_r = 423.18$
 Triclinic, $P\bar{1}$
 $a = 7.9451$ (16) Å
 $b = 9.0421$ (18) Å
 $c = 10.538$ (2) Å
 $\alpha = 72.22$ (3)°
 $\beta = 84.09$ (3)°
 $\gamma = 84.01$ (3)°
 $V = 714.9$ (3) Å³

$Z = 2$
 $D_x = 1.966$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 7113 reflections
 $\theta = 3.2$ – 27.5 °
 $\mu = 3.44$ mm⁻¹
 $T = 292$ (2) K
 Block, green
 $0.37 \times 0.33 \times 0.24$ mm

Data collection

Rigaku R-Axis RAPID diffractometer
 ω scans
 Absorption correction: multi-scan (ABSCOR; Higashi, 1995)
 $T_{\min} = 0.313$, $T_{\max} = 0.438$
 7113 measured reflections

3257 independent reflections
 2757 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.046$
 $\theta_{\max} = 27.5$ °
 $h = -9 \rightarrow 10$
 $k = -11 \rightarrow 11$
 $l = -13 \rightarrow 13$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.036$
 $wR(F^2) = 0.085$
 $S = 1.11$
 3257 reflections
 191 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.041P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.78$ e Å⁻³
 $\Delta\rho_{\min} = -0.78$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

O1–Pr ⁱ	2.500 (4)	O5–Pr ⁱⁱⁱ	2.511 (4)
O1–Pr ⁱ	2.580 (3)	O6–Pr ^{iv}	2.408 (4)
O2–Pr ⁱ	2.516 (4)	O6–Pr ⁱⁱⁱ	2.699 (4)
O3–Pr ⁱ	2.393 (4)	O1W–Pr ⁱ	2.616 (4)
O4–Pr ⁱⁱ	2.408 (4)		
O3–Pr ⁱ –O4 ⁱⁱ	137.42 (13)	O1 ⁱ –Pr ⁱ –O1	70.49 (13)
O3–Pr ⁱ –O6 ^{iv}	75.37 (14)	O5 ^v –Pr ⁱ –O1	83.31 (13)
O4 ⁱⁱ –Pr ⁱ –O6 ^{iv}	76.49 (14)	O2–Pr ⁱ –O1	51.11 (12)
O3–Pr ⁱ –O1 ⁱ	78.93 (12)	O3–Pr ⁱ –O1W	71.29 (14)
O4 ⁱⁱ –Pr ⁱ –O1 ⁱ	130.31 (13)	O4 ⁱⁱ –Pr ⁱ –O1W	143.14 (15)
O6 ^{iv} –Pr ⁱ –O1 ⁱ	152.55 (12)	O6 ^{iv} –Pr ⁱ –O1W	95.81 (14)
O3–Pr ⁱ –O5 ^v	98.96 (15)	O1 ⁱ –Pr ⁱ –O1W	66.56 (14)
O4 ⁱⁱ –Pr ⁱ –O5 ^v	73.44 (16)	O5 ^v –Pr ⁱ –O1W	133.60 (14)
O6 ^{iv} –Pr ⁱ –O5 ^v	126.36 (13)	O2–Pr ⁱ –O1W	69.98 (14)
O1 ⁱ –Pr ⁱ –O5 ^v	67.05 (14)	O1–Pr ⁱ –O1W	82.42 (12)
O3–Pr ⁱ –O2	131.96 (15)	O3–Pr ⁱ –O6 ^v	73.70 (13)
O4 ⁱⁱ –Pr ⁱ –O2	73.22 (14)	O4 ⁱⁱ –Pr ⁱ –O6 ^v	69.92 (13)
O6 ^{iv} –Pr ⁱ –O2	81.39 (13)	O6 ^{iv} –Pr ⁱ –O6 ^v	78.72 (14)
O1 ⁱ –Pr ⁱ –O2	109.65 (12)	O1 ⁱ –Pr ⁱ –O6 ^v	103.21 (12)
O5 ^v –Pr ⁱ –O2	128.40 (14)	O5 ^v –Pr ⁱ –O6 ^v	49.57 (12)
O3–Pr ⁱ –O1	145.73 (13)	O2–Pr ⁱ –O6 ^v	141.20 (13)
O4 ⁱⁱ –Pr ⁱ –O1	76.23 (12)	O1–Pr ⁱ –O6 ^v	127.57 (12)
O6 ^{iv} –Pr ⁱ –O1	130.23 (12)	O1W–Pr ⁱ –O6 ^v	144.80 (13)

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

All H atoms attached to C atoms were positioned geometrically and refined as riding atoms, with C–H = 0.97–0.98 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. During the refinement of (I), atom O2W exhibited very large atomic displacement parameters. The occupancy of this atom was refined using a fixed isotropic displacement parameter and converged to 50%. The occupancy was then fixed and anisotropic displacement parameters used for the O atom. The H atoms of the water molecules could not be located in difference Fourier maps and were not included in the model.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *PROCESS-AUTO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus* (Sheldrick, 1990); software used to prepare material for publication: *SHELXL97*.

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References

- Bi, W., Cao, R., Sun, D., Yuan, D., Li, X., Wang, Y., Li, X. & Hong, M. (2004). *Chem. Commun.* pp. 2104–2105.
- Eddaoudi, M., Moler, D. B., Li, H., Chen, B., Reineke, T. M., O’Keeffe, M. & Yaghi, O. M. (2001). *Acc. Chem. Res.* **34**, 319–330.
- Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.
- Kim, Y. J. & Jung, D.-Y. (2002). *Chem. Commun.* pp. 908–909.
- Ma, J.-F., Yang, J., Zheng, G.-L., Li, L. & Liu, J.-F. (2003). *Inorg. Chem.* **42**, 7531–7534.
- Rigaku (1998). *PROCESS-AUTO*. Rigaku Corporation, Tokyo, Japan.

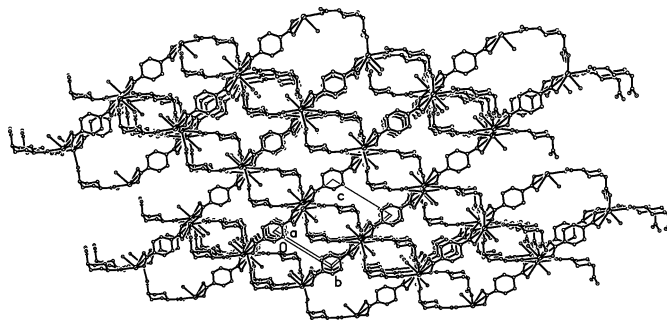


Figure 3

Packing diagram for (I) viewed along the *a* axis. H atoms have been omitted for clarity.

- Sheldrick, G. M. (1990). *SHELXTL-Plus*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Yang, J., Ma, J.-F., Liu, Y.-Y., Li, S.-L. & Zheng, G.-L. (2005). *Eur. J. Inorg. Chem.* 2174–2180