metal-organic compounds

Poly[[tetraaquadi-μ_3-oxalato-μ_2-oxalato-diprasedymium(III)] dihydrate]

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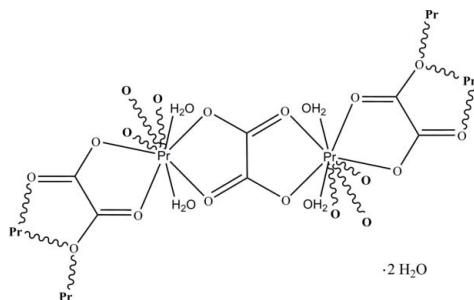Correspondence e-mail: ypcai8@yahoo.com

In the title compound, $\{[Pr_2(C_2O_4)_3(H_2O)_4] \cdot 2H_2O\}_n$, the three-dimensional network structure has the Pr^{III} ion coordinated by nine O atoms in a distorted tricapped trigonal-prismatic geometry. The coordinated and uncoordinated water molecules interact with the carboxylate O atoms to consolidate the network via O—H···O hydrogen bonds.

Related literature

For general background, see: Benson $et\ al.$ (2000).

Experimental

Crystal data

$[Pr_2(C_2O_4)_3(H_2O)_4] \cdot 2H_2O$
$M_r = 653.98$
Monoclinic, $P2_1/c$
$a = 9.8834\ (5)$ Å
$b = 8.2811\ (4)$ Å
$c = 10.1818\ (5)$ Å
$\beta = 99.053\ (1)°$
$V = 822.95\ (7)$ Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 5.95$ mm^{-1}
$T = 298$ K
$0.26 \times 0.22 \times 0.16$ mm

Data collection

Bruker SMART diffractometer
Absorption correction: multi-scan ($SADABS$; Sheldrick, 1996)
$T_{min} = 0.307$, $T_{max} = 0.450$
4111 measured reflections
1487 independent reflections
1397 reflections with $I > 2\sigma(I)$
$R_{int} = 0.023$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.016$
$wR(F^2) = 0.035$
$S = 1.07$
1487 reflections
139 parameters
9 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.44$ e Å^{-3}
$\Delta\rho_{min} = -0.54$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O7—H7A···O9^i	0.85 (1)	1.89 (1)	2.732 (3)	171 (3)
O7—H7B···O1^{ii}	0.85 (1)	1.94 (2)	2.732 (3)	155 (4)
O8—H8A···O2^{iii}	0.84 (1)	2.06 (1)	2.900 (3)	175 (4)
O8—H8A···O3^{iv}	0.84 (1)	2.59 (4)	3.026 (3)	114 (3)
O8—H8B···O9^v	0.84 (1)	2.12 (2)	2.949 (4)	167 (6)
O9—H9B···O6^{vi}	0.83 (1)	1.99 (1)	2.820 (3)	178 (4)
O9—H9A···O8	0.84 (1)	2.05 (1)	2.881 (4)	173 (4)

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

Data collection: $SMART$ (Bruker, 1998); cell refinement: $SAINT$ (Bruker, 1999); data reduction: $SAINT$; program(s) used to solve structure: $SHELXS97$ (Sheldrick, 2008); program(s) used to refine structure: $SHELXL97$ (Sheldrick, 2008); molecular graphics: $SHELXTL$ (Sheldrick, 2008); software used to prepare material for publication: $SHELXTL$.

References

Benson, D. A., Karsch-Mizrachi, I., Lipman, D. J., Ostell, J., Rapp, B. A. & Wheeler, D. L. (2000). $Genbank.\ Nucl.\ Acids\ Res.$ **28**, 15–18.
Bruker (1998). $SMART$. Bruker AXS Inc., Madison, Wisconsin, USA.
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supporting information

Poly[[tetraaquadi-*μ*₃-oxalato-*μ*₂-oxalato-diprasedymium(III)] dihydrate]

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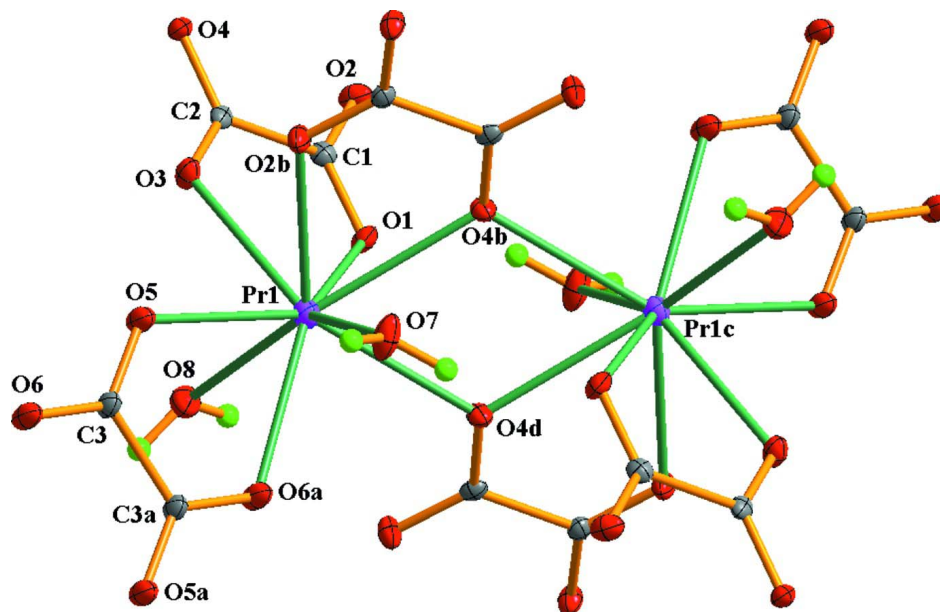
S1. Comment

Though complexes including oxalato and praseodymium(III) have been extensively investigated, the crystal structure of praseodymium oxalate with one-dimensional, two-dimensional and three-dimensional topologies and different solvent molecules have constantly being reported recently. In this paper, we would like to report the synthesis and crystal structure of a three-dimensional network complex including oxalato and praseodymium(III) with one lattice water molecule per unsymmetrical unit. The hydrothermal reaction of Pr_6O_{11} and oxalic acid in H_2O afforded the Pr^{III} title polymeric complex, $[(Pr(C_2O_4)_{1.5}(H_2O)_2).H_2O]_n$. The Pr^{III} ion is coordinated by nine O atoms from two water molecules and four carboxylate groups of oxalate ligands in an irregular coordination geometry (Figure 1). Two oxalate groups of the oxalate anions bridge two symmetry-related Pr^{III} atoms, giving rise to a layer-like structure extending along [100] (Figure 2). These parallel layers are further connected *via* chelating coordination of oxalate anions into a three-dimensional network (Figure 3) along [010] plane. Moreover, the coordinated/non-coordinated water molecules interact with the carboxylate oxygen atoms from the layers *via* O—H···O hydrogen bonds (Table 1), which contributes to the additional stability of the structure.

S2. Experimental

A suspension of praseodymium oxide (205 mg, 0.20 mmol) in in water (20 ml) was slowly added to a solution of oxalic acid (0.10 mmol) in water (10 ml). The resultant mixture was sealed in a 50 cm³ stainless steel reactor with Teflon liner and kept under autogenous pressure at 100 ° for 78 h, and then cooled to room temperature at a rate of 0.5 °. min⁻¹. Colorless block crystals of the compound suited for single-crystal X-ray diffraction analyses formed with a yield of approximate 65%. The assigned structure was substantiated by elemental analysis; calculated for $C_3H_6O_9Pr$: C 11.01, H 1.83%; found: C 10.96, H 1.95%.

S3. Refinement

The structure was solved using direct methods followed by Fourier synthesis. Non-H atoms were refined anisotropically. The water H atoms were located in a difference Fourier map, and were refined with distance restraints of O—H = 0.84(0.01) and H···H 1.428 (0.002) |%A, but their U_{iso} values were set equal to 1.5 U_{eq}(parent atom O).

Figure 1

The structure of the title compound (I) with 30% probability ellipsoids. Symmetry code a: $1 - x, -y, 1 - z$; b: $-x, -1/2 + y, 0.5 - z$; c: $-x, -y, 1 - z$; d: $x, 0.5 - y, 1/2 + z$.
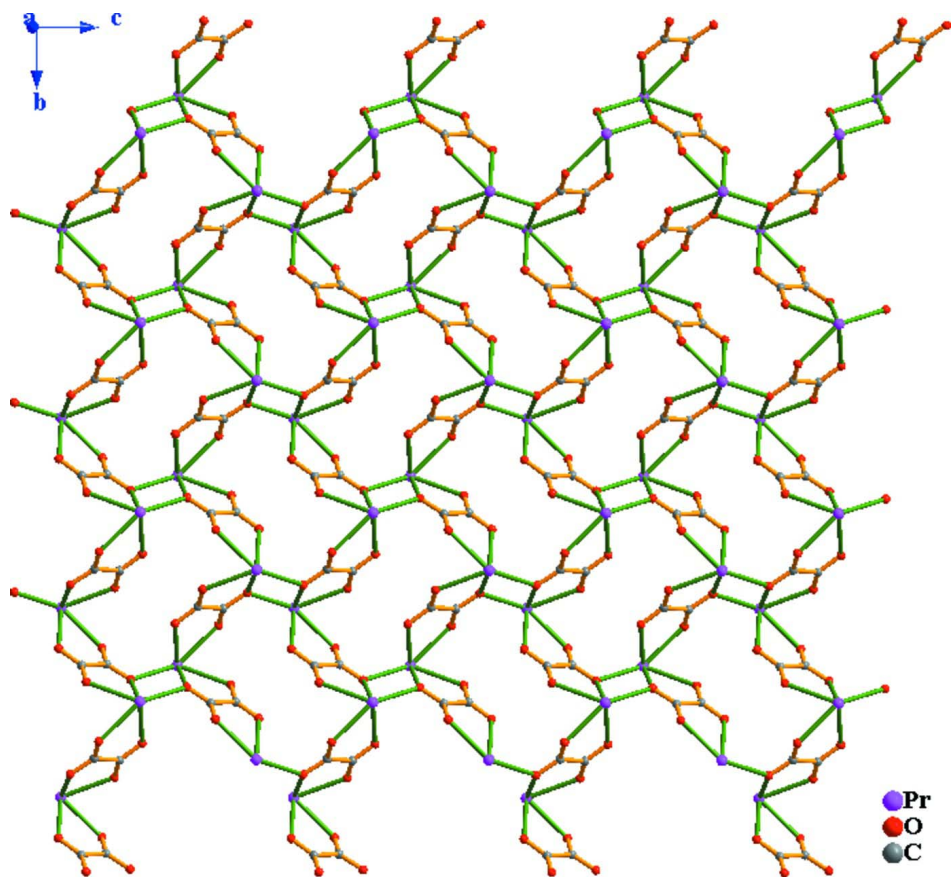
Figure 2

A view of one-dimensional chain constructed by hydrogen bonding interactions. Symmetry code a: *x* - 1,*y*,*z*.

Poly[[tetraaquadi-*μ*₃-oxalato-*μ*₂-oxalato-diprasedymium(III)] dihydrate]

Crystal data

[Pr$_2$(C$_2$O$_4$)$_3$(H$_2$O)$_4$]·2H$_2$O	$F(000) = 620$
$M_r = 653.98$	$D_x = 2.639$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 9.8834$ (5) Å	Cell parameters from 3328 reflections
$b = 8.2811$ (4) Å	$\theta = 3.2$–28.6°
$c = 10.1818$ (5) Å	$\mu = 5.95$ mm^{-1}
$\beta = 99.053$ (1)°	$T = 298$ K
$V = 822.95$ (7) Å^3	Block, yellow
$Z = 2$	$0.26 \times 0.22 \times 0.16$ mm

Data collection

Bruker SMART diffractometer	4111 measured reflections
Radiation source: fine-focus sealed tube	1487 independent reflections
Graphite monochromator	1397 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.023$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	$\theta_{max} = 25.3°$, $\theta_{min} = 2.1°$
	$h = -11\rightarrow11$
	$k = -9\rightarrow9$
$T_{min} = 0.307$, $T_{max} = 0.450$	$l = -12\rightarrow7$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.016$
$wR(F^2) = 0.035$
$S = 1.07$
1487 reflections
139 parameters
9 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0087P)^2 + 0.7364P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.007$
$\Delta\rho_{max} = 0.44$ e Å^{-3}
$\Delta\rho_{min} = -0.54$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), Fc*=kFc[1+0.001xFc$^2\lambda^3$/sin(2θ)]$^{-1/4}$
Extinction coefficient: 0.0127 (4)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*-factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Pr1	0.185002 (15)	0.098389 (18)	0.437068 (15)	0.01483 (9)
O1	0.0042 (2)	0.3167 (2)	0.4302 (2)	0.0210 (5)
O2	−0.1229 (2)	0.4945 (3)	0.2991 (2)	0.0249 (5)
O3	0.1838 (2)	0.3092 (3)	0.2610 (2)	0.0229 (5)
O4	0.0564 (2)	0.4802 (3)	0.12614 (19)	0.0196 (5)
O5	0.4011 (2)	0.0665 (3)	0.3529 (2)	0.0275 (5)
O6	0.6199 (2)	−0.0090 (3)	0.3924 (2)	0.0287 (5)
O7	0.1928 (2)	−0.2047 (3)	0.4324 (3)	0.0357 (6)
H7A	0.255 (3)	−0.260 (3)	0.406 (4)	0.054*
H7B	0.153 (3)	−0.250 (4)	0.490 (3)	0.054*
O8	0.3072 (3)	0.3550 (3)	0.5421 (2)	0.0296 (5)
H8A	0.252 (3)	0.393 (4)	0.589 (3)	0.044*
O9	0.3963 (3)	0.5983 (3)	0.3724 (3)	0.0353 (6)
H9B	0.393 (4)	0.566 (5)	0.2945 (16)	0.053*
C1	−0.0222 (3)	0.4050 (3)	0.3291 (3)	0.0172 (6)
C2	0.0829 (3)	0.3968 (3)	0.2319 (3)	0.0162 (6)
C3	0.5054 (3)	0.0165 (4)	0.4261 (3)	0.0200 (7)
H8B	0.3907 (13)	0.358 (8)	0.576 (4)	0.13 (3)*
H9A	0.370 (7)	0.534 (5)	0.427 (3)	0.13 (3)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pr1	0.01116 (11)	0.01772 (12)	0.01591 (11)	0.00145 (6)	0.00305 (7)	0.00222 (6)
O1	0.0236 (11)	0.0229 (11)	0.0185 (11)	0.0044 (9)	0.0094 (9)	0.0063 (9)
O2	0.0248 (12)	0.0312 (12)	0.0191 (11)	0.0126 (10)	0.0051 (10)	0.0018 (9)
O3	0.0186 (11)	0.0244 (11)	0.0274 (12)	0.0049 (9)	0.0090 (10)	0.0067 (10)
O4	0.0179 (11)	0.0261 (11)	0.0149 (11)	0.0013 (9)	0.0033 (9)	0.0049 (9)
O5	0.0183 (12)	0.0451 (14)	0.0198 (12)	0.0077 (10)	0.0052 (10)	0.0090 (10)
O6	0.0195 (12)	0.0478 (14)	0.0204 (12)	0.0121 (10)	0.0078 (10)	0.0095 (11)
O7	0.0351 (14)	0.0252 (13)	0.0533 (17)	0.0080 (11)	0.0273 (13)	0.0110 (11)
O8	0.0303 (14)	0.0317 (13)	0.0272 (13)	−0.0058 (11)	0.0057 (11)	−0.0034 (10)
O9	0.0397 (15)	0.0410 (15)	0.0274 (14)	0.0031 (12)	0.0118 (13)	−0.0034 (12)
C1	0.0182 (16)	0.0162 (14)	0.0170 (15)	−0.0001 (12)	0.0023 (13)	−0.0043 (12)
C2	0.0188 (16)	0.0156 (14)	0.0141 (15)	−0.0066 (12)	0.0022 (12)	−0.0034 (12)
C3	0.0170 (16)	0.0257 (16)	0.0183 (16)	0.0030 (13)	0.0064 (13)	0.0042 (13)

Geometric parameters (Å, º)

Pr1—O5	2.438 (2)	O4—Pr1ᵛ	2.552 (2)
Pr1—O6ⁱ	2.495 (2)	O4—Pr1ⁱᵛ	2.566 (2)
Pr1—O3	2.501 (2)	O5—C3	1.244 (4)
Pr1—O7	2.512 (2)	O6—C3	1.251 (4)
Pr1—O1	2.535 (2)	O6—Pr1ⁱ	2.495 (2)
Pr1—O2ⁱⁱ	2.537 (2)	O7—H7A	0.847 (10)
Pr1—O4ⁱⁱⁱ	2.552 (2)	O7—H7B	0.845 (10)
Pr1—O4ⁱⁱ	2.566 (2)	O8—H8A	0.842 (10)
Pr1—O8	2.590 (2)	O8—H8B	0.844 (10)
O1—C1	1.257 (4)	O9—H9B	0.832 (10)
O2—C1	1.240 (4)	O9—H9A	0.839 (10)
O2—Pr1ⁱᵛ	2.537 (2)	C1—C2	1.545 (4)
O3—C2	1.231 (4)	C3—C3ⁱ	1.549 (6)
O4—C2	1.271 (4)		
O5—Pr1—O6ⁱ	65.72 (7)	O3—Pr1—O8	70.89 (8)
O5—Pr1—O3	74.28 (7)	O7—Pr1—O8	144.46 (8)
O6ⁱ—Pr1—O3	128.45 (7)	O1—Pr1—O8	72.97 (8)
O5—Pr1—O7	81.61 (7)	O2ⁱⁱ—Pr1—O8	134.18 (7)
O6ⁱ—Pr1—O7	72.19 (8)	O4ⁱⁱⁱ—Pr1—O8	98.79 (7)
O3—Pr1—O7	132.90 (8)	O4ⁱⁱ—Pr1—O8	140.47 (7)
O5—Pr1—O1	136.09 (7)	C1—O1—Pr1	119.53 (18)
O6ⁱ—Pr1—O1	134.01 (7)	C1—O2—Pr1ⁱᵛ	120.07 (19)
O3—Pr1—O1	63.82 (6)	C2—O3—Pr1	119.75 (18)
O7—Pr1—O1	137.35 (7)	C2—O4—Pr1ᵛ	116.09 (18)
O5—Pr1—O2ⁱⁱ	74.00 (7)	C2—O4—Pr1ⁱᵛ	118.63 (18)
O6ⁱ—Pr1—O2ⁱⁱ	127.17 (7)	Pr1ᵛ—O4—Pr1ⁱᵛ	117.51 (8)
O3—Pr1—O2ⁱⁱ	65.42 (7)	C3—O5—Pr1	120.94 (18)
O7—Pr1—O2ⁱⁱ	69.33 (8)	C3—O6—Pr1ⁱ	119.5 (2)

O1—Pr1—O2ⁱⁱ	98.71 (7)	Pr1—O7—H7A	125 (2)
O5—Pr1—O4ⁱⁱⁱ	143.64 (7)	Pr1—O7—H7B	114 (2)
O6ⁱ—Pr1—O4ⁱⁱⁱ	79.71 (7)	H7A—O7—H7B	115.0 (15)
O3—Pr1—O4ⁱⁱⁱ	140.53 (7)	Pr1—O8—H8A	104 (2)
O7—Pr1—O4ⁱⁱⁱ	77.27 (7)	Pr1—O8—H8B	124 (4)
O1—Pr1—O4ⁱⁱⁱ	76.71 (6)	H8A—O8—H8B	115.7 (15)
O2ⁱⁱ—Pr1—O4ⁱⁱⁱ	123.63 (6)	H9B—O9—H9A	117.4 (16)
O5—Pr1—O4ⁱⁱ	134.60 (7)	O2—C1—O1	127.3 (3)
O6ⁱ—Pr1—O4ⁱⁱ	130.37 (7)	O2—C1—C2	117.6 (3)
O3—Pr1—O4ⁱⁱ	100.79 (7)	O1—C1—C2	115.1 (3)
O7—Pr1—O4ⁱⁱ	69.15 (7)	O3—C2—O4	125.1 (3)
O1—Pr1—O4ⁱⁱ	68.99 (7)	O3—C2—C1	118.2 (3)
O2ⁱⁱ—Pr1—O4ⁱⁱ	63.66 (6)	O4—C2—C1	116.7 (3)
O4ⁱⁱⁱ—Pr1—O4ⁱⁱ	62.49 (8)	O5—C3—O6	126.3 (3)
O5—Pr1—O8	81.77 (8)	O5—C3—C3ⁱ	117.6 (3)
O6ⁱ—Pr1—O8	72.37 (8)	O6—C3—C3ⁱ	116.1 (3)

Symmetry codes: (i) −x+1, −y, −z+1; (ii) −x, y−1/2, −z+1/2; (iii) x, −y+1/2, z+1/2; (iv) −x, y+1/2, −z+1/2; (v) x, −y+1/2, z−1/2.

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
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O9—H9A···O8	0.84 (1)	2.05 (1)	2.881 (4)	173 (4)

Symmetry codes: (iii) x, −y+1/2, z+1/2; (vi) x, y−1, z; (vii) −x, −y, −z+1; (viii) −x, −y+1, −z+1; (ix) −x+1, −y+1, −z+1; (x) −x+1, y+1/2, −z+1/2.