Poly[hexaaquatris(μ_3-3-carboxypyrazole-5-carboxylato)(3-carboxypyrazole-5-carboxylato-κO)(μ_2-pyrazole-3,5-dicarboxylato)dicerium(III)]

Xin-Hua Li

School of Chemistry and Materials Science, Wenzhou Normal College, Zhejiang, Wenzhou 325027, People's Republic of China

Correspondence e-mail: lixinhua01@126.com

In the title compound, $[\text{Ce}_2(\text{C}_5\text{H}_2\text{N}_2\text{O}_4)(\text{C}_5\text{H}_3\text{N}_2\text{O}_4)_4(\text{H}_2\text{O})_6]_n$, each Ce atom is nine-coordinated by three water molecules, four 3-carboxypyrazole-5-carboxylate monoanions (two pairs of symmetry-related anions), and a pyrazole-3,5-dicarboxylate dianion. Two symmetry-related Ce atoms are bridged by a pyrazole-3,5-dicarboxylate dianion, which lies across a twofold rotation axis. There are two independent 3-carboxypyrazole-5-carboxylate monoanions which differ in their coordination modes; one is monodentate and the other is tetradentate. The Ce atoms are bridged by both pyrazole-3,5-dicarboxylate dianions and 3-carboxypyrazole-5-carboxylate monoanions, generating a three-dimensional network structure.

Comment

3,5-Pyrazoledicarboxylic acid (H₃pdc), is a multifunctional ligand; it has multiple coordination sites that allow structures of higher dimensions and it also has abstractable protons that allow various acidity-dependent coordination modes (Pan *et al.*, 2000). A variety of H₃pdc coordination compounds have been synthesized and reported in the literature (Pan, Ching *et al.*, 2001; Pan, Frydel *et al.*, 2001). Much of the work has been focused on coordination polymers containing transition metal and post-transition metal elements. Rare-earth metal compounds have seldom been investigated. Owing to their high coordination number and special magnetic (Retailleau *et al.*, 2004) and fluorescence properties, the lanthanide series is likely to provide new materials (Yu *et al.*, 2000) that possess specific properties and desired features. In this paper, we
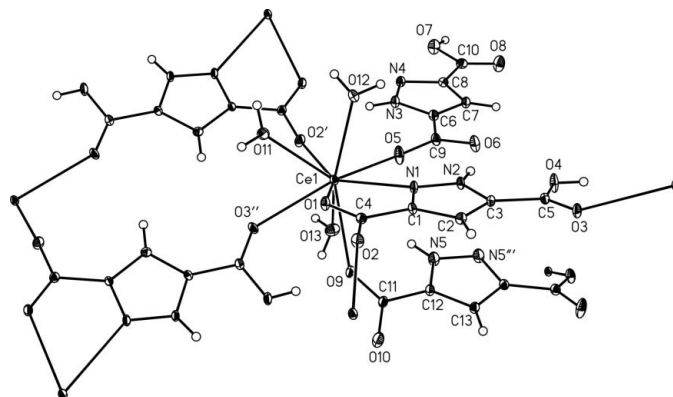

Figure 1
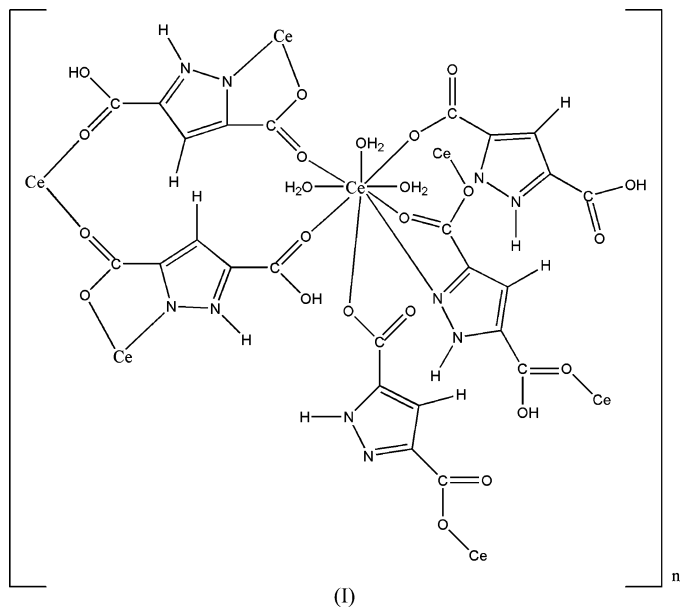A segment of the polymeric structure of (I), showing 50% probability displacement ellipsoids. [Symmetry codes: (') $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; ('') $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; (''') $-x, y, \frac{1}{2} - z$.]

report the synthesis and structure of a new cerium coordination polymer, $[Ce_2(C_5H_2N_2O_4)(C_5H_3N_2O_4)_4(H_2O)_6]_n$, (I).

(I)

In (I), each Ce ion is nine-coordinated, with bonds to four H_2pdc^- anions, an $Hpdc^{2-}$ dianion and three water molecules. The $Hpdc^{2-}$ dianion is coordinated in bidentate fashion, with one O atom of each carboxylate group bound to a Ce and thereby bridging two symmetry-related Ce ions. There are two independent pyrazole-3,5-dicarboxylate anions which differ in their coordination modes; one binds in monodentate mode and the other in tetradentate mode. Therefore, mono- and tetradentate coordination modes of H_2pdc^- anions and the bidentate mode of the $Hpdc^{2-}$ dianion are included in the title compound, with multi-bridging modes of the carboxylate group (Fig. 1).

From Table 1 we can see that the Ce—O5—C9 angle is nearly linear (ca 165°), which is unusual. It should be noted that atom H5N of the $Hpdc^{2-}$ dianion is necessarily disordered over two half-occupied positions, as this ligand lies across a twofold axis. In addition, the displacement parameter for N5 is the largest of any N atom, consistent with slightly different positions when it is C—NH versus C═N. There are also two potential (weak) hydrogen-bonding contacts for N5, one at a distance of 3.180 (2) Å to O5 and the other at a distance of 3.258 (2) Å to O13. The latter is a nearly linear interaction.

There are many weak interactions in this compound, such as O—H···O and N—H···O hydrogen bonds (Table 2). Ce ions, water molecules and H_3pdc ligands interact through coordination bonds and weak interactions, generating a three-dimensional framework.

Experimental

The title compound was synthesized by adding an aqueous (10 ml) solution of ammonium ceric nitrate, $(NH_4)_2Ce(NO_3)_6$ (1.0 g, 2 mmol),

to a methanol and ethanol mixed solution (10 ml) of pyrazole-3,5-dicarboxylic acid (0.4 g, 2 mmol) and 2,2′-dithiosalicylic acid (0.6 g, 2 mmol) at room temperature. The reaction mixture was filtered; colorless prism-shaped crystals separated from the solution after about three months. The transparent prismatic crystals were collected, washed with distilled water and dried in air.

Crystal data

$[Ce_2(C_5H_2N_2O_4)$- $(C_5H_3N_2O_4)_4(H_2O)_6]$	$D_x = 2.178$ Mg m^{-3}
$M_r = 1162.80$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 3147 reflections
$a = 19.2347$ (16) Å	$\theta = 2.0–25.1°$
$b = 13.2563$ (11) Å	$\mu = 2.66$ mm^{-1}
$c = 16.7559$ (15) Å	$T = 298$ (2) K
$\beta = 123.909$ (1)°	Prism, colorless
$V = 3545.8$ (5) Å^3	$0.15 \times 0.07 \times 0.07$ mm
$Z = 4$	

Data collection

Bruker APEX area-detector diffractometer	3147 independent reflections
φ and ω scans	2864 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)	$R_{int} = 0.028$
	$\theta_{max} = 25.1°$
$T_{min} = 0.80$, $T_{max} = 0.82$	$h = -22 \rightarrow 21$
9143 measured reflections	$k = -15 \rightarrow 14$
	$l = -19 \rightarrow 19$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0194P)^2 + 12.7824P]$
$R[F^2 > 2\sigma(F^2)] = 0.029$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.060$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.05$	$\Delta\rho_{max} = 0.74$ e Å^{-3}
3147 reflections	$\Delta\rho_{min} = -0.39$ e Å^{-3}
304 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Selected geometric parameters (Å, °).

Ce1—O2^i	2.391 (2)	Ce1—O13	2.560 (3)
Ce1—O5	2.438 (3)	Ce1—O9	2.641 (3)
Ce1—O12	2.519 (3)	Ce1—N1	2.642 (3)
Ce1—O11	2.550 (3)	Ce1—O3^{ii}	2.661 (3)
Ce1—O1	2.554 (2)		
O2^i—Ce1—O5	75.96 (9)	O13—Ce1—O9	64.50 (9)
O2^i—Ce1—O12	82.05 (12)	O2^i—Ce1—N1	144.09 (10)
O5—Ce1—O12	73.43 (12)	O5—Ce1—N1	71.64 (9)
O2^i—Ce1—O11	74.28 (10)	O12—Ce1—N1	74.32 (11)
O5—Ce1—O11	131.65 (11)	O11—Ce1—N1	117.54 (10)
O12—Ce1—O11	65.45 (11)	O1—Ce1—N1	61.59 (8)
O2^i—Ce1—O1	145.08 (9)	O13—Ce1—N1	115.30 (10)
O5—Ce1—O1	132.87 (9)	O9—Ce1—N1	72.68 (9)
O12—Ce1—O1	88.24 (11)	O2^i—Ce1—O3^{ii}	85.69 (9)
O11—Ce1—O1	71.18 (9)	O5—Ce1—O3^{ii}	148.06 (10)
O2^i—Ce1—O13	69.02 (10)	O12—Ce1—O3^{ii}	130.13 (10)
O5—Ce1—O13	74.54 (11)	O11—Ce1—O3^{ii}	64.69 (10)
O12—Ce1—O13	141.00 (12)	O1—Ce1—O3^{ii}	75.20 (8)
O11—Ce1—O13	126.26 (10)	O13—Ce1—O3^{ii}	74.55 (9)
O1—Ce1—O13	130.29 (9)	O9—Ce1—O3^{ii}	69.05 (8)
O2^i—Ce1—O9	131.31 (9)	N1—Ce1—O3^{ii}	130.22 (9)
O5—Ce1—O9	104.10 (9)	C4—O1—Ce1	124.0 (2)
O12—Ce1—O9	145.77 (11)	C4—O2—Ce1^{iii}	158.9 (3)
O11—Ce1—O9	124.17 (9)	C5—O3—Ce1^{iv}	133.5 (2)
O1—Ce1—O9	68.22 (9)	C9—O5—Ce1	164.4 (3)

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

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O4—H4$\cdots$O9^{iv}	0.82	1.70	2.515 (4)	172
O4—H4$\cdots$O10^{iv}	0.82	2.66	3.253 (4)	131
O7—H7$\cdots$O10^{v}	0.82	1.96	2.760 (4)	165
O11—H11$B\cdots$O10^{i}	0.77 (3)	2.34 (3)	3.061 (5)	157 (6)
O11—H11$A\cdots$N4^{iii}	0.80 (3)	2.05 (3)	2.816 (4)	163 (5)
O12—H12$B\cdots$O10^{i}	0.80 (3)	2.21 (3)	2.994 (5)	169 (6)
O12—H12$A\cdots$O6^{vi}	0.80 (3)	1.97 (3)	2.751 (4)	164 (5)
O13—H13$A\cdots$O10^{vii}	0.82	2.43	3.174 (5)	152
O13—H13$B\cdots$O8^{viii}	0.82	2.12	2.884 (4)	156
N2—H2$N\cdots$O6	0.86	1.85	2.695 (4)	165
N3—H3$N\cdots$O1^{i}	0.86	2.16	2.904 (4)	145
N5—H5$N\cdots$O13	0.86	2.46	3.266 (4)	156
N5—H5$N\cdots$O5	0.86	2.61	3.190 (5)	126

Symmetry codes: (i) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (iii) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (iv) $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$; (v) $-x, y + 1, -z + \frac{1}{2}$; (vi) $-x, -y + 1, -z$; (vii) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; (viii) $x + \frac{1}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$.

Water H atoms were refined subject to the restraint O—H = 0.82 (3) Å. The other H atoms were positioned geometrically and allowed to ride on their parent atoms at distances of 0.82 (O—H), 0.86 (N—H) and 0.93 Å (C—H), with U_{iso}(H) = 1.2U_{eq}(parent atom).

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

References

Bruker (2002). *SMART, SAINT and SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.

Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Pan, L., Ching, N., Huang, X. & Li, J. (2001). *Chem. Eur. J.* **7**, 4431–4437.

Pan, L., Frydel, T., Sander, M. B., Huang, X. Y. & Li, J. (2001). *Inorg. Chem.* **40**, 1271–1276.

Pan, L., Huang, X. Y., Li, J., Wu, Y. G. & Zheng, N. W. (2000). *Angew. Chem. Int. Ed. Engl.* **39**, 527–530.

Retailleau, L., Vonarb, R., Perrichon, V., Jean, E. & Bianchi, D. (2004). *Energy Fuels*, **18**, 872–878.

Sheldrick, G. M. (1997). *SHELXS97 and SHELX97*. University of Göttingen, Germany.

Yu, R., Wang, D., Kumada, N. & Kinomura, N. (2000). *Chem. Mater.* **12**, 12–16.