

Polymeric aqua(nitrato- κ^2O,O')(1,10-phenanthroline- κ^2N,N')(2,3-pyrazinedicarboxylato- κ^2N,O)europium(III) monohydrate

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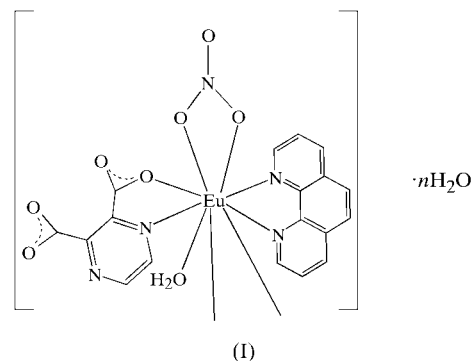
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In polymeric $\{[\text{Eu}(\text{pzdc})(\text{NO}_3)(\text{phen})(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$ [pzdc is 2,3-pyrazinedicarboxylate ($\text{C}_6\text{H}_2\text{O}_4$) and phen is 1,10-phenanthroline ($\text{C}_{12}\text{H}_8\text{N}_2$)], each europium(III) ion is coordinated by seven O atoms (from three pzdc anions, a nitrate anion and a water molecule) and the two N atoms of the phen ligand, resulting in a nine-coordinated europium(III) center with a distorted monocapped square-antiprismatic coordination polyhedron. Four pzdc anions bridge four europium(III) ions, forming a parallelogram unit, the four vertices of which are occupied by the four pzdc anions. Moreover, each parallelogram unit links six other adjacent parallelogram units, forming a two-dimensional network with disordered lattice water molecules.

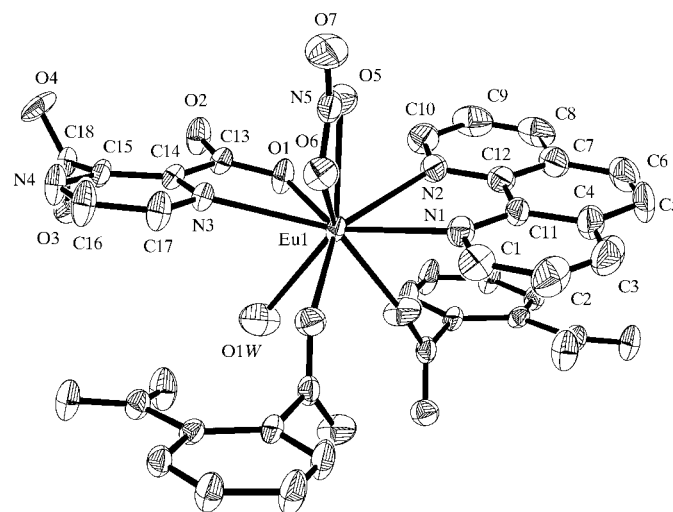
Comment

In recent years, more and more attention has been focused on coordination polymers with multifunctional ligands, as the presence of different functional groups allows incorporation of interesting properties into the resulting coordination networks (Ayyappan *et al.*, 2001). Among the various organic ligands, 2,3-pyrazinedicarboxylic acid is a commonly used multifunctional ligand. Its complexes with *d*-block transition metals have been well studied; compounds that have been structurally documented include polymeric $[\text{Cu}(\text{pzdc})\cdot\text{HCl}]_x$, $[\text{Cu}(\text{pzdc})(\text{H}_2\text{O})_2]_x\cdot 2x\text{H}_2\text{O}$, $[\text{Fe}(\text{pzdc})(\text{H}_2\text{O})_2]_x\cdot 2x\text{H}_2\text{O}$ and $[\text{Mn}(\text{pzdc})(\text{H}_2\text{O})_2]_x\cdot 2x\text{H}_2\text{O}$ (pzdc is 2,3-pyrazinedicarboxylate; O'Connor *et al.*, 1982; Mao *et al.*, 1996*a,b*; Gao *et al.*, 1999). However, the lanthanide complexes of this ligand are almost structurally unexplored. Because lanthanide and *d*-block transition metal ions differ in their coordination number, pzdc may coordinate with them in a different manner, so we selected the europium–pzdc–phen system (phen is 1,10-phenanthroline) in order to extend this research. In the title compound, $[\text{Eu}(\text{pzdc})(\text{NO}_3)(\text{phen})(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$, (I), the europium(III) ion is linked to four different ligands.

In (I), each europium(III) ion coordinates to three O atoms from three carboxylate groups of three pzdc anions with a typical (Li *et al.*, 2002) Eu–O(carboxylate) distance range [2.331 (3)–2.398 (3) Å; Table 1], one water molecule with a longer Eu–O distance [2.530 (4) Å], one heterocyclic N atom with an Eu–N distance of 2.597 (4) Å, and the two N atoms of



the phen molecule in a chelating fashion with Eu–N distances of 2.570 (4) and 2.582 (4) Å, resulting in a distorted monocapped square-antiprismatic coordination polyhedron (Fig. 1). The square plane formed by atoms O5, O6, N1 and N2, with a mean deviation of 0.228 Å, is significantly distorted, but the mean deviation of the other square plane, containing atoms O1, N3, O3ⁱⁱ and O4ⁱ [symmetry codes: (i) $x, \frac{3}{2} - y, z - \frac{1}{2}$; (ii) $1 - x, y - \frac{1}{2}, \frac{3}{2} - z$], is only 0.085 Å, comparable with the deviations found in the Eu–phen analogue $[\text{Eu}_2(p\text{-BDC})_3(\text{phen})_2(\text{H}_2\text{O})_2]_n$ (*p*-BDC is 1,4-benzenedicarboxylate; Wang *et al.*, 2003). To complete the coordination environment of the europium(III) center, atom O1W is located at the cap. The pzdc anion acts as a tetradentate ligand, bridging three europium(III) ions, and adopts only one bridging mode. Four pzdc anions bridge four europium(III) ions, forming a parallelogram unit with approximate dimensions of 10.293 × 13.176 Å, the four vertices of which are occupied by the four


Figure 1

The coordination environment of the independent cation in (I), with the atom-numbering scheme (displacement ellipsoids are shown at the 50% probability level).

pzdc anions. Moreover, each parallelogram unit links six other adjacent parallelogram units, forming a two-dimensional network (Fig. 2). The pzdc anion displays three types of

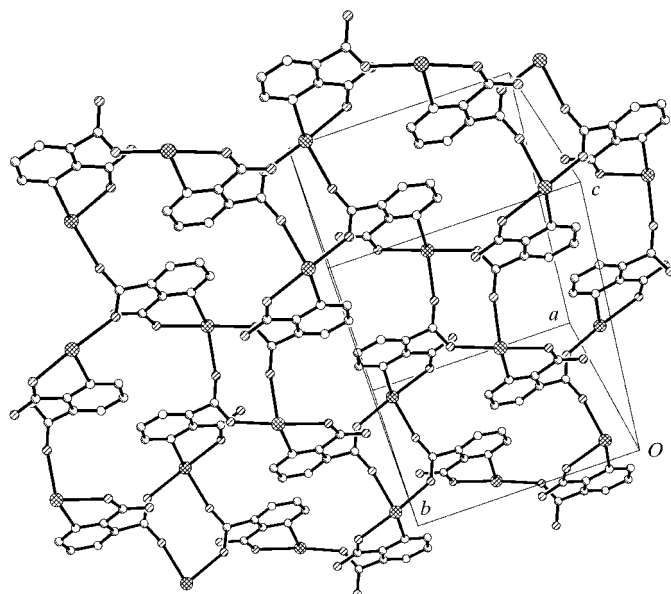


Figure 2

The two-dimensional network of (I). H atoms, nitrate anions, water molecules and 1,10-phenanthroline molecules have been omitted for clarity.

bridging; bridging by the anion is also found in $[\text{Eu}_2(\text{pzdc})_3(\text{H}_2\text{O})]_x \cdot 2x\text{H}_2\text{O}$, which exhibits a microporous three-dimensional network structure (Zheng, *et al.*, 2002). Limited studies of this anion suggest that the different binding modes arise from the manner in which the carboxy group is oriented with respect to the aromatic ring. However, functioning as a chelate, the phen ligand prevents the oligomeric compounds from adopting high dimensionality (Plater *et al.*, 1999). This behavior is evidenced in the title compound, which has a two-dimensional structure.

Experimental

The title compound was synthesized, using a hydrothermal method, from a mixture of 2,3-pyrazinedicarboxylic acid (1 mmol, 0.17 g), $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (1 mmol, 0.45 g), 1,10-phenanthroline (3 mmol, 0.54 g) and water (20 ml) in a 30 ml Teflon-lined stainless steel reactor. The solution was heated at 432 K for 5 d. After the reaction system had been cooled slowly to room temperature, colorless prismatic crystals were collected and washed with distilled water.

Crystal data

$[\text{Eu}(\text{C}_6\text{H}_2\text{O}_4)(\text{NO}_3)(\text{C}_{12}\text{H}_8\text{N}_2)(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$
 $M_r = 596.30$
 Monoclinic, $P2_1/c$
 $a = 12.3427$ (3) Å
 $b = 10.4806$ (3) Å
 $c = 15.7966$ (4) Å
 $\beta = 101.947$ (1)°
 $V = 1999.17$ (9) Å³
 $Z = 4$

$D_x = 1.981$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 4140 reflections
 $\theta = 2.4\text{--}27.1$ °
 $\mu = 3.20$ mm⁻¹
 $T = 298$ (2) K
 Prism, colorless
 $0.28 \times 0.18 \times 0.17$ mm

Data collection

Bruker SMART APEX area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 2002)
 $T_{\min} = 0.468$, $T_{\max} = 0.612$
 11 996 measured reflections
 4497 independent reflections

3676 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.035$
 $\theta_{\max} = 27.5$ °
 $h = -14 \rightarrow 15$
 $k = -13 \rightarrow 11$
 $l = -14 \rightarrow 20$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.038$
 $wR(F^2) = 0.095$
 $S = 1.04$
 4497 reflections
 301 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0545P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 1.65$ e Å⁻³
 $\Delta\rho_{\min} = -0.82$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Eu1—O1	2.331 (3)	Eu1—O6	2.555 (3)
Eu1—O4 ⁱ	2.344 (3)	Eu1—N2	2.570 (4)
Eu1—O3 ⁱⁱ	2.398 (3)	Eu1—N1	2.582 (4)
Eu1—O5	2.513 (4)	Eu1—N3	2.597 (4)
Eu1—O1W	2.530 (4)		
O1—Eu1—O4 ⁱ	101.81 (13)	O5—Eu1—N2	71.21 (12)
O1—Eu1—O3 ⁱⁱ	139.30 (11)	O1W—Eu1—N2	124.56 (14)
O4 ⁱ —Eu1—O3 ⁱⁱ	86.81 (12)	O6—Eu1—N2	109.83 (12)
O1—Eu1—O5	79.64 (12)	O1—Eu1—N1	139.69 (12)
O4 ⁱ —Eu1—O5	141.25 (13)	O4 ⁱ —Eu1—N1	73.01 (14)
O3 ⁱⁱ —Eu1—O5	117.52 (11)	O3 ⁱⁱ —Eu1—N1	80.96 (12)
O1—Eu1—O1W	74.50 (12)	O5—Eu1—N1	81.23 (13)
O4 ⁱ —Eu1—O1W	69.71 (14)	O1W—Eu1—N1	134.25 (13)
O3 ⁱⁱ —Eu1—O1W	71.50 (12)	O6—Eu1—N1	71.42 (12)
O5—Eu1—O1W	143.97 (13)	N2—Eu1—N1	63.99 (13)
O1—Eu1—O6	119.06 (11)	O1—Eu1—N3	64.48 (11)
O4 ⁱ —Eu1—O6	138.55 (13)	O4 ⁱ —Eu1—N3	139.47 (14)
O3 ⁱⁱ —Eu1—O6	67.28 (11)	O3 ⁱⁱ —Eu1—N3	83.08 (11)
O5—Eu1—O6	50.27 (11)	O5—Eu1—N3	76.57 (12)
O1W—Eu1—O6	125.49 (13)	O1W—Eu1—N3	69.85 (13)
O1—Eu1—N2	76.32 (12)	O6—Eu1—N3	71.20 (11)
O4 ⁱ —Eu1—N2	71.62 (12)	N2—Eu1—N3	132.77 (12)
O3 ⁱⁱ —Eu1—N2	142.69 (12)	N1—Eu1—N3	142.57 (12)

Symmetry codes: (i) $x, \frac{3}{2} - y, z - \frac{1}{2}$; (ii) $1 - x, y - \frac{1}{2}, \frac{3}{2} - z$.

H atoms of water molecules were placed at idealized positions but were not refined; their $U_{\text{iso}}(\text{H})$ values were set at $1.2U_{\text{eq}}(\text{O})$. Atom O2W is disordered over two sites, the occupancies of which were fixed at 0.5. All other H atoms were positioned geometrically and allowed to ride on their parent atoms at distances of 0.93 Å, with $U_{\text{iso}}(\text{H})$ values of $1.2U_{\text{eq}}(\text{C})$. The final difference Fourier map had a large peak near atom Eu1.

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: XP (Bruker, 2002); software used to prepare material for publication: SHELXL97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1173). Services for accessing these data are described at the back of the journal.

References

- Ayyappan, P., Evans, O. R. & Lin, W. B. (2001). *Inorg. Chem.* **40**, 4627–4632.
- Bruker (2002). *SADABS*, *SAINT*, *SMART* and *XP*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Gao, S., Ma, B. Q., Yi, T., Wang, Z. M., Liao, C. S., Yan, C. H. & Xu, G. X. (1999). *Chem. Lett.* pp. 773–774.
- Li, X., Jin, L. P., Zheng, X. J., Lu, S. Z. & Zhang, J. H. (2002). *J. Mol. Struct.* **607**, 59–67.
- Mao, L., Retting, S. J., Thompson, R. C., Trotter, J. & Xia, S. H. (1996a). *Can. J. Chem.* **74**, 433–444.
- Mao, L., Retting, S. J., Thompson, R. C., Trotter, J. & Xia, S. H. (1996b). *Can. J. Chem.* **74**, 2413–2423.
- O'Connor, C. J., Klein, C. L., Majeste, R. J. & Trefonas, L. M. (1982). *Inorg. Chem.* **21**, 64–67.
- Plater, M. J., Foreman, M. R. St J., Coronado, E., Comez-Garcia, C. J. & Slawin, A. M. Z. (1999). *J. Chem. Soc. Dalton Trans.* pp. 4209–4216.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Wang, M., Xia, J., Jin, L., Cai, G. & Lu, S. (2003). *J. Mol. Struct.* **655**, 443–449.
- Zheng, X. J., Jin, L. P. & Lu, S. Z. (2002). *Eur. J. Inorg. Chem.* pp. 3356–3363.