A novel three-dimensional heterometallic coordination polymer: poly[[hexaaquabis[μ_3-3,5-dicarboxylatopyrazolato-κ^5O^3,N^2:N^1,O^5:$O^{5'}$]-(μ_2-oxalato-κ^4O^1,O^2:$O^{1'},O^{2'}$)-copper(II)dierbium(III)] trihydrate]

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The title novel heterometallic 3d–4f coordination polymer, $\{[CuEr_2(C_5HN_2O_4)_2(C_2O_4)(H_2O)_6]\cdot 3H_2O\}_n$, has a three-dimensional metal–organic framework composed of two types of metal atoms (one Cu^{II} and two Er^{III}) and two types of bridging anionic ligands [3,5-dicarboxylatopyrazolate(3−) (ptc^{3-}) and oxalate]. The Cu^{II} atom is four-coordinated in a square geometry. The Er^{III} atoms are both eight-coordinated, but the geometries at the two atoms appear different, *viz.* triangular dodecahedral and bicapped trigonal prismatic. One of the oxalate anions is located on a twofold axis and the other lies about an inversion centre. Both oxalate anions act as bis-bidentate ligands bridging the latter type of Er atoms in parallel zigzag chains. The pdc^{3-} anions act as quinquedentate ligands not only chelating the Cu^{II} and the triangular dodecahedral Er^{III} centres in a bis-bidentate bridging mode, but also connecting to Er^{III} centres of both types in a monodentate bridging mode. Thus, a three-dimensional metal–organic framework is generated, and hydrogen bonds link the metal–organic framework with the uncoordinated water molecules. This study describes the first example of a three-dimensional 3d–4f coordination polymer based on pyrazole-3,5-dicarboxylate and oxalate, and therefore demonstrates further the usefulness of pyrazoledicarboxylate as a versatile multidentate ligand for constructing heterometallic 3d–4f coordination polymers with interesting architectures.

Comment

Much attention has been focused on the construction of heterometallic 3d–4f complexes since 1985 (Bencini *et al.*, 1985), not only because of their potential applications in magnetism (Mereacre *et al.*, 2007), luminescence (Sun *et al.*, 2006) and gas storage (Wang *et al.*, 2007) but also owing to their fascinating structures (Andruh, 2007; Yabe *et al.*, 2007; Ren *et al.*, 2008). With the purpose of the design and synthesis of 3d–4f coordination polymers with interesting architectures and topologies, a variety of multifunctional bridging ligands have been extensively employed, such as 2,2':6',2''-terpyridine (Figuerola *et al.*, 2006), pyridine-2,4,6-tricarboxylic acid (Gao *et al.*, 2006), iminodiacetate (Manna *et al.*, 2007) and amino acids (Zhang *et al.*, 2004). In view of the potential coordination sites afforded by the carboxylate O and pyrazole N atoms of pyrazole-3,5-dicarboxylic acid (H_3pdc), the fully deprotonated pdc^{3-} ligand can act as a mono-, bi- or multidentate ligand to link metal centres, generating coordination polymers, as is reported in the literature (Xia *et al.*, 2007; King *et al.*, 2004). However, no three-dimensional heterometallic 3d–4f coordination polymers based on pyrazole-3,5-dicarboxylate have been reported before. In this paper, we describe the synthesis of a novel 3d–4f coordination polymer, namely, $\{[CuEr_2(pdc)_2(C_2O_4)(H_2O)_6]\cdot 3H_2O\}_n$, (I), by the reaction of H_3pdc with Er_2O_3 and CuO *via* a hydrothermal method; the compound has been characterized by IR, elemental analysis and X-ray single-crystal analysis.


(I)
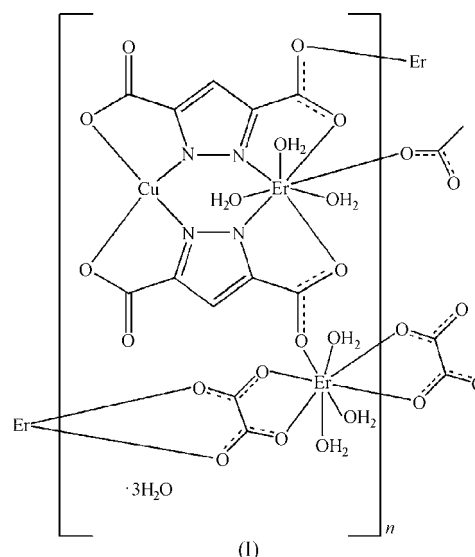
Since no oxalate was directly introduced into the starting reaction mixture, we suppose that the oxalate ligand was synthesized *in situ* through an oxidation–hydrolysis reaction from pyrazole-3,5-dicarboxylic acid (see scheme below); similar situations have occurred in other systems (Cheng *et al.*, 2007; Li *et al.*, 2006).
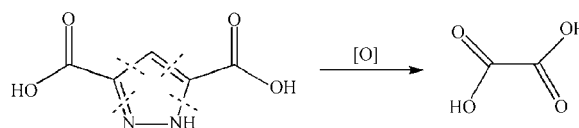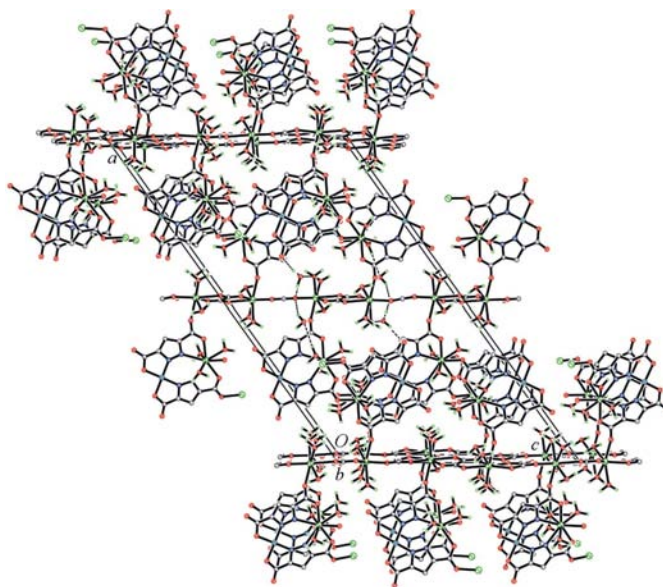

X-ray crystal structure analysis reveals that the title complex crystallizes in the centrosymmetric space group $C2/c$ with two crystallographically independent oxalate ligands on twofold axes; one of the oxalate anions is located on a twofold axis and the other lies about an inversion centre. A perspective view of the molecular structure of the title complex is

metal-organic compounds

depicted in Fig. 1, and selected bond lengths and angles are listed in Table 1.

As illustrated in Fig. 1, the title complex consists of two types of metal atoms (one Cu^{II} and two Er^{III} atoms) and two types of bridged ligands (ptc^{3-} and oxalate anions). The Cu^{II} atom assumes a square geometry, coordinated to two ptc^{3-} anions through carboxylate O and pyrazole N atoms in a bis-chelating fashion (O1/N1 and O5/N3). The Cu—O(N) bond lengths [1.887 (8)–1.964 (6) Å] and the angles around the Cu^{II} atom [82.6 (3)–97.3 (4)°] are in good agreement with those in related Cu^{II} (King *et al.*, 2004) and Cu–Ln complexes (Liang *et al.*, 2001; Costes *et al.*, 2004; Wu *et al.*, 2005). It is interesting to find two crystallographically independent eight-coordinated Er^{III} atoms (Er1 and Er2) in the title complex, and the geometries at Er1 and Er2 appear different when analysed using the usual considerations of Haigh (1995). Atom Er1 assumes a triangular dodecahedral geometry, coordinated to three aqua ligands and three pdc^{3-} anions, that is, to one carboxylate O atom from a ptc^{3-} anion in a monodentate fashion (O4^i) and two pairs of carboxylate O and pyrazole N atoms from two different ptc^{3-} ligands in a bis-chelating fashion (O3/N2 and O7/N4). The Er1—O(N) bond lengths range from 2.295 (7) to 2.492 (8) Å, comparable to those observed in other Er^{III} complexes (Xia *et al.*, 2007; Lu *et al.*, 2002). In contrast, atom Er2 assumes a bicapped trigonal prismatic geometry, coordinated to three aqua ligands, one carboxylate O atom from a pdc^{3-} ligand and four O atoms from two different oxalate ligands in a bis-chelating fashion.
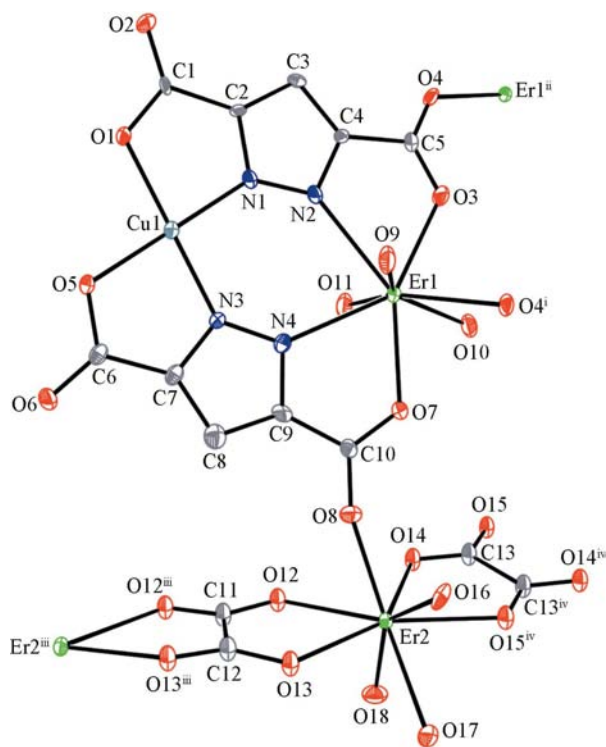
Figure 2
The packing of the title complex, viewed along the *b* axis, showing a three-dimensional metal–organic framework. Dashed lines indicate hydrogen bonds.

The oxalate anions are both located on twofold axes, acting as bis-bidentate ligands to bridge Er2 atoms in a zigzag chain, as is observed in other Er^{III} complexes (Li *et al.*, 2006; Lu *et al.*, 2002). It is noted that the oxalate–Er2 chains lie parallel to one another. The bond lengths around atom Er2 [2.222 (7)– 2.438 (7) Å] are in the normal range for Er^{III} atoms (Feng & Mao, 2007; Song & Mao, 2005; Subhan *et al.*, 2002). As quinquedentate ligands, the pdc^{3-} anions link three different metal atoms, on the one hand chelating the Cu^{II} and Er^{III} centres in a bis-bidentate bridging mode to form a nearly coplanar building block, $[CuEr1(pdc)_2]^-$, and on the other hand connecting to a different Er^{III} centre (Er1 or Er2) in a monodentate bridging mode. In this way, the parallel oxalate– Er2 chains are connected by pairs of $[CuEr1(pdc)_2]^-$ blocks. Thus, a three-dimensional metal–organic framework is generated through the bridging ligands (Fig. 2).

Furthermore, the solvent water molecules are located in cavities of the metal–organic framework, allowing them to participate in various O—H···O hydrogen bonds with the coordinated water molecules and carboxylate O atoms. These hydrogen bonds are all in the normal range; details are available in the archived CIF. It is noted that the potential free volume accessible for water molecules determined by *PLATON* calculations (Spek, 2003) is about 2.1%. According to Kitagawa *et al.* (2004), the pore size in the polymer is about 4.7 Å (< 5 Å), falling into the ultramicropore range. Therefore, the polymeric structure is considered to be poor for gas storage.

Figure 1
The Cu^{II} and Er^{III} coordination environments in (I). Displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted for clarity. [Symmetry codes: (i) $-x + \frac{3}{2}$, $y - \frac{1}{2}$, $-z + \frac{1}{2}$; (ii) $-x + \frac{3}{2}$, $y + \frac{1}{2}$, $-z + \frac{1}{2}$; (iii) $-x + 2$, y, $-z + \frac{1}{2}$; (iv) $-x + 2$, $-y + 2$, $-z + 1$.]

Experimental

All chemicals were of analytical grade and were used without further purification. The hydrothermal reaction was performed in a 25 ml

Teflon-lined stainless steel autoclave under autogenous pressure. A mixed solution of H_3pdc (0.070 g, 0.4 mmol), Er_2O_3 (0.038 g, 0.1 mmol), CuO (0.016 g, 0.2 mmol) and water (3 ml) was placed in the autoclave and heated at 413 K for 5 d. After the sample had been cooled slowly at a rate of 10 K h^{-1} to room temperature, purple–red crystals of the title complex were obtained and air-dried by filtration (*ca* 15% yield based on Er). Analysis calculated for $C_{12}H_{20}CuEr_2N_4O_{21}$: C 15.10, H 2.11, N 5.87%; found: C 15.14, H 2.02, N 5.85%. IR (KBr discs, ν_{max}, cm^{-1}): 3449 (*vs*), 1629 (*vs*), 1571 (*s*), 1525 (*m*), 1511 (*m*), 1403 (*m*), 1339 (*vs*), 1283 (*s*), 1064 (*m*), 1018 (*m*), 858 (*w*), 806 (*m*), 776 (*w*), 613 (*w*), 493 (*w*), 436 (*w*).

Crystal data

$[CuEr_2(C_5HN_2O_4)_2(C_2O_4)(H_2O)_6]\cdot 3H_2O$	$\beta = 125.607\ (4)°$
$M_r = 954.38$	$V = 4864.6\ (19)$ Å^3
Monoclinic, $C2/c$	$Z = 8$
$a = 37.829\ (9)$ Å	Mo $K\alpha$ radiation
$b = 6.9457\ (16)$ Å	$\mu = 7.81$ mm^{-1}
$c = 22.772\ (5)$ Å	$T = 295\ (2)$ K
	$0.4 \times 0.3 \times 0.2$ mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer	11670 measured reflections
	4281 independent reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)	3070 reflections with $I > 2\sigma(I)$
$T_{min} = 0.07$, $T_{max} = 0.21$	$R_{int} = 0.074$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.046$	310 parameters
$wR(F^2) = 0.080$	H-atom parameters constrained
$S = 0.86$	$\Delta\rho_{max} = 1.54$ e Å^{-3}
4281 reflections	$\Delta\rho_{min} = -0.89$ e Å^{-3}

Table 1
Selected bond lengths (Å).

Cu1—N1	1.887 (8)	Er1—N4	2.459 (8)
Cu1—N3	1.907 (8)	Er1—N2	2.492 (8)
Cu1—O5	1.945 (7)	Er1—Er2	6.3657 (16)
Cu1—O1	1.964 (6)	Er2—O8	2.222 (7)
Cu1—Er1	4.5260 (18)	Er2—O18	2.308 (7)
Cu1—Er2	8.558 (2)	Er2—O13	2.325 (7)
Er1—O9	2.295 (7)	Er2—O14	2.336 (7)
Er1—O7	2.295 (7)	Er2—O17	2.356 (7)
Er1—O3	2.310 (7)	Er2—O16	2.360 (7)
Er1—O11	2.323 (7)	Er2—O15^{iv}	2.368 (6)
Er1—O4^i	2.338 (7)	Er2—O12	2.438 (7)
Er1—O10	2.366 (7)		

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

All H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms [C—H = 0.93 Å, O—H = 0.92–0.95 Å and U_{iso}(H) = 1.2U_{eq}(C,O)].

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); 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*.

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