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A novel 2-D interlinking zigzag-chain d–f mixed-metal coordination polymer generated from an organometallic ligand

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A flexible organometallic ligand, 1,1′-ferrocenedicarboxylic acid, was incorporated in the self-assembly of a d–f mixed-metal coordination polymer featuring a 2-D interlinking zigzag-chain network and bearing two kinds of bridging conformations.

There has been considerable interest in inorganic–organic hybrid coordination polymers,[1] which are not only of interesting from a structural chemistry point of view, but also have potential applications in the design of new materials with a range of properties, such as catalysis,[2] sorption,[3] photochemistry,[4] or magnetism.[5] During the past few decades, flexible monodentate ditopic N-donor ligand linkers, such as 4,4′-bipyridine, 4,4′-trimethyllenedipyridine, 1,2-bis(4-pyridyl)ethane and pyrazine, have been used to construct coordination polymers.[6–8] Later, another approach to obtain analogical coordination polymeric structures was made by the reaction of metal ions with similar O-donor ligands, such as bipyridine *N*,*N*'-dioxide,[9] or rigid multifunctional linkers, such as polycarboxylates: terephthalic acid,[3a,10] trimesic acid, [4c,11] and benzenetetracaboxylic acid.[12] Most coordination polymers consist of transition metal centres linked by one or two kinds of polydentate ligands, while lanthanide coordination polymers are less documented.[12,13] The coordination chemistry of d–f heterometal polymers has received much less attention,[14] even though their inherent charge-transfer and redox active properties are interesting. Derivatives of ferrocene offer potential for developing new optical, electrical, magnetic or catalytic materials.[15,16] Unlike other aromatic multicarboxylic acids, 1,1′-ferrocenedicarboxylic acid is a more flexible linker which may lead to various metal geometries under different coordination modes, so that it can be used as a flexible organometallic bridging ligand to construct heterometallic complexes. We herein report a novel d–f mixed-metal coordination polymer generated by 1,1′-ferrocenedicarboxylic acid (H_2Fcdc), $[Eu_2(Fcdc)_3(H_2O)_4]_n{\cdot}nH_2O$ (**1**), featuring a two-dimensional interlinking zigzag-chain d–f mixed-metal network, and bearing two different bridging conformations in the solid state.

Complex **1** was prepared by layering an isopropanol solution of H_2Fcdc on an aqueous solution of $EuCl_3$ at a molar ratio of 1 : 1 in the presence of triethylamine. The X-ray diffraction analysis revealed that **1** crystallizes in the monoclinic system, space group $P2/n$; elemental analysis and the IR data of **1** are consistent with the formula and the functional groups present.†‡

Complex **1** is an extended Eu–Fcdc two-dimensional network consisting of a crystallographically distinct Eu atom, bridging Fcdc linkers and aqua ligands.(Fig. 1, Fig. 2) In addition, a water molecule of crystallisation lies on a 2-fold axis is also observed in the asymmetry unit. It should be pointed out that the bridging Fcdc linkers exhibit two types of conformation modes (Scheme 1, Fig. 2): the *anti*-form mode, which is six-coordinate and μ_4-bridging and the *syn*-form mode, which is four-coordinate and μ_2-bridging. In the *anti*-form Fcdc, as the Fe atom lies at the inversion centre, the torsion angle of the two carboxylate groups is 180°, but that in the *syn*-form is twisted at *ca.* 60°. Due to its high flexibility, the aromatic ligand Fcdc may link metal nodes in different planes by variable conformations. It is noteworthy that these two kinds of bridging coordination modes have not previously been documented. Until very recently, only one Fcdc bridging polymer have been reported, in which the Fcdc bridge is in *anti*-form with four-coordination and μ_2-bridging.[17] The 2-D network in **1** is constructed from a dinuclear $Eu_2C_6O_{12}$ cluster subunit that is linked by six

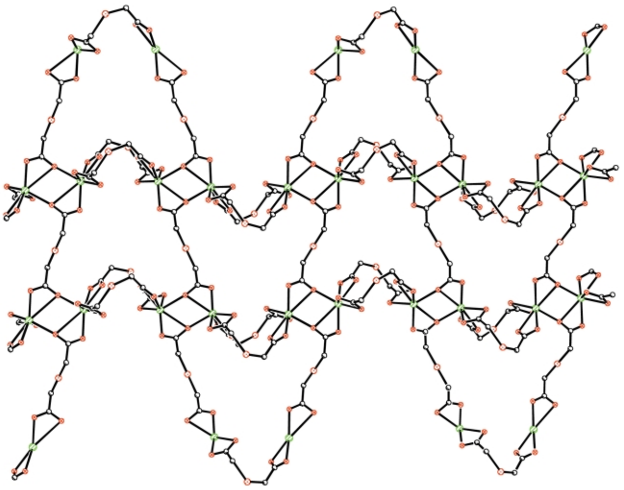


Fig. 1 Two-dimensional network of **1**; the water molecules are omitted and Cp ring is substituted by C for clarity.

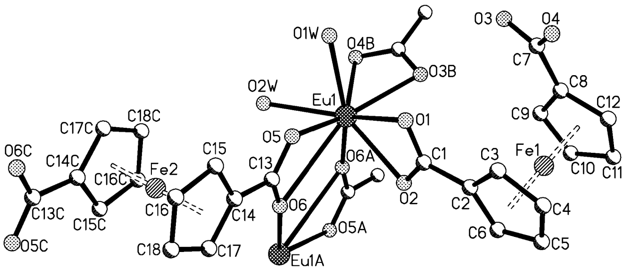
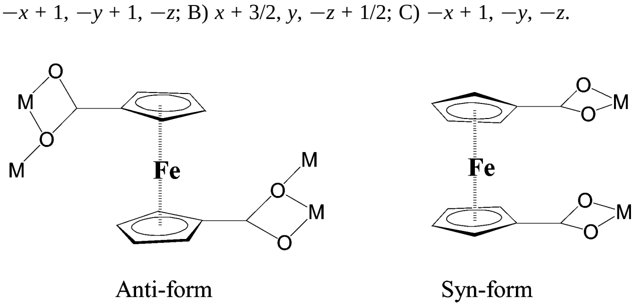


Fig. 2 The coordination environment of Eu atom in **1**. Symmetry codes: A) $-x + 1, -y + 1, -z$; B) $x + 3/2, y, -z + 1/2$; C) $-x + 1, -y, -z$.



Scheme 1 Two bridging conformation modes of Fcdc.

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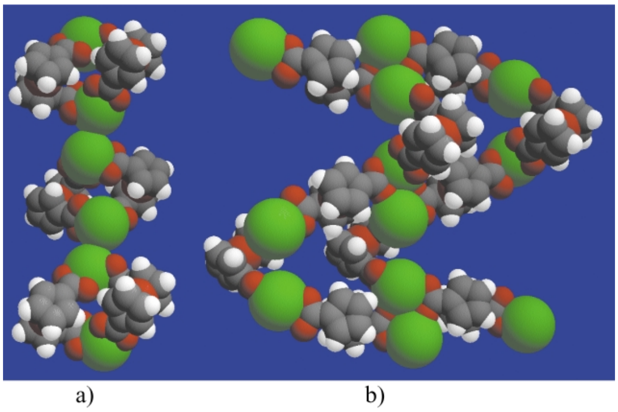

Fig. 3 (a) The double zigzag chains along the Eu_2 metal line. (b) Two large zigzag chains connected by one Eu_2 line.

ferrocenes in two directions; the two Eu centres in the subunit are separated by 4.42 Å (Fig. 2). Each Eu atom is nine coordinated by two carboxylate groups in *anti*-form, two carboxylate groups in *syn*-form and two aqua ligands and the coordination polyhedron about the Eu atom can be described as a distorted monocapped square antiprism. Both coordinating water molecules and the solvates participate in H-bonding interaction with carboxylate groups or other water molecules; this plays a significant role in furnishing the 2-D network structure. It should be mentioned that the 2-D network consists of two types of interlinking zigzag chains (Fig. 1, Fig. 3). Along the *c* axis, two Fcdc linkers of *syn*-form connect a pair of dinuclear Eu_2 subunits at the end of each Eu atom, forming an Eu_2 metal line (the two neighbouring Eu_2 subunits are separated by 6.16 Å). As the two carboxylate groups from two Cp rings in a *syn*-form Fcdc have a torsion angle of *ca.* 60°, it seems that two strands of ferrocene wrap around the Eu_2 line to form double small zigzag chains: –*syn*-Fc–Eu–Eu–*syn*-Fc– (Fig. 3(a)). From another direction, each Eu atom is chelated by an *anti*-form Fcdc linker, which connects a pair of Eu_2 clusters in two neighbouring metal lines, it may be assumed that the *anti*-form Fcdc linkers connect two neighbouring Eu_2 lines to form a large zigzag chain: –*syn*-Fc–Eu–*anti*-Fc–Eu–*syn*-Fc– (Fig. 3(b)), so that every large zigzag chain connects two neighbouring small zigzag chains, whilst every small chain links two neighbouring large chains. From these zigzag chain interconnections, a 2-D interlinking zigzag-chain network is constructed (Fig. 1). To our knowledge, this is the first d–f mixed-metal coordination polymer exhibiting an interlinking zigzag-chain layer; it is also the only example of a lanthanide coordination polymer connected by ferrocene.

Compared to most derivatives of ferrocene, complex **1** is very stable under light at room temperature, and does not dissolve in water, or common solvents such as ethanol, acetone, chloroform and acetonitrile. In summary, a novel Fe–Eu mixed-metal coordination polymer **1** has been synthesized, which features a two-dimensional interlinking zigzag-chain network and two new types of bridging conformation modes. Its physicochemical properties are currently under investigation.

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Notes and references

† *Synthesis* of complex **1**: an isopropanol (8 ml) mixture of H_2Fcdc (0.2 mmol) and triethylamine (1.5 mmol) was layered on an aqueous solution (12 ml) of $EuCl_3·6H_2O$ (0.2 mmol) in a long tube, which was sealed and stored in the dark at room temperature for four weeks. Orange plate crystals which stuck to the tube wall were collected, and washed with 2 × 8 ml water and 2 × 8 ml ethanol, then dried at 50 °C, to give 16 mg (20% yield based on H_2Fcdc) of product. Elemental analysis for $C_{36}H_{34}Eu_2Fe_3O_{17}$. Calc.: C, 35.73; H, 2.83. Found: C, 35.82; H, 2.98%. IR (KBr, cm^{-1}): 3615.5w, 3325.1m(br), 1523.1s, 1482.7vs, 1395.0s, 1355.0s, 1213.5w, 1191.0m, 1109.5w, 1024.4w, 924.1w, 793.6m, 675.2w, 607.7w, 548.0m, 503.1m.

‡ *Crystal data* for **1**: $C_{36}H_{34}Eu_2Fe_3O_{17}$, M_r = 1210.10, monoclinic, space group $P2/n$ (no.13), a = 11.277 (2), b = 10.339(2), c = 17.503(3) Å, β = 91.238(3)°, V = 2040.3(6) $Å^3$, D_c = 1.970 g cm^{-3}. Data collection (1.97 ≤ 2θ ≤ 27.51°) were performed at 293(2) K on a Bruker AXS SMART CCD diffractometer (Mo-Kα, λ = 0.71073 Å). The structure was solved with direct methods and refined with full-matrix least squares (SHELX-97),[18] giving a final $R1$ value of 0.0505 for 264 parameters and 4599 unique reflections with $I > 2\sigma(I)$, and $wR2$ of 0.1315 for all reflections for **1**. CCDC reference number 190096. See http://www.rsc.org/suppdata/cc/b2/b206823k/ for crystallographic data in CIF or other electronic format.

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