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Hydrothermal Synthesis and Crystal Structure of a New 3*d*–4*f* Complex Generated from the IDA Ligand[1]

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Abstract—An interesting 3*d*–4*f* complex $[CeCo(HIDA)(IDA)_2]_n$ (I) (IDA = iminodiacetic acid) was synthesized under hydrothermal conditions and characterized by IR, TG, and single-crystal X-ray diffraction analysis. Complex I crystallizes in the monoclinic system, space group *C*2/*c* with *a* = 9.7033(19), *b* = 24.141(5), *c* = 8.5810(17) Å, β = 115.01(3)°, *V* = 1821.6(6) Å^3, *Z* = 4, ρ_c = 2.152 g/cm^3, *F*(000) = 1148. Crystallographic data for I were collected at 293 K with a Rigaku R-axis Rapid IP diffractometer using graphite monochromatic MoK_α radiation (λ = 0.71073 Å) and IP technique, GOOF = 0.994, the final *R* = 0.0245 and *wR* = 0.0763 ($I > 2\sigma(I)$). Complex I is a two-dimensional layer structure, in which the Ce(III) center is surrounded by ten oxygen atoms from different IDA ligands. The Co(II) center is six-coordinated by four oxygen atoms and two nitrogen atoms from two different IDA ligands. The carboxylic oxygen atom connected such units along the *z* axis to form a one-dimensional chain-like structure. The IDA ligand connects neighboring chains to form a two-dimensional layer structure.

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INTRODUCTION

The design and synthesis of heterometallic organic complexes, such as 3*d*–4*f* or 3*d*–5*f* metal systems, have attracted increasing attention. The intense interest in this field is not only because of their intriguing structures but also for their outstanding applications in areas of magnetism, electrical conductivity, nonlinear optics, gas storage, and molecular recognition [1–3]. Although a number of 3*d*–4*f* complexes with discrete structures were obtained by self-assemble reaction in solution, the synthesis of this kind of complexes, especially high-dimensional 3*d*–4*f* networks, is still less successful [5–8]. As it has been well established, the lanthanide ions behave as hard acids and they usually connect with oxygen atoms, while *d*-block metal ions are borderline acids, which have strong tendency to link both oxygen and nitrogen atoms. So, a general approach to construct the 3*d*–4*f* complex is self-assembly of mixed metal ions and proper ligands containing mixed-donor atoms [4–9]. Based on this point, a lot of rigid aromatic multicarboxylate ligands have been widely employed in the preparation of the 3*d*–4*f* complexes [10, 11]. This kind of ligand has a rigid conformation and would facilitate the construction of the final networks with regular shape that can reasonably be designed [12]. In contrast, 3*d*–4*f* complexes with flexible carboxylate ligands as functional building units are less explored [13]. Despite a challenge in the predictability of the topology in the resulting networks, the unique structural and coordination versatility of flexible ligands provide the great possibility for the construction of novel frameworks.

To synthesize new 3*d*–4*f* complexes, as well as to enrich the coordination chemistry of flexible ligands, we choose IDA (IDA—iminodiacetic acid) as functional building block based on the following consideration. Firstly, different from the rigid dicarboxylate ligands, IDA exhibits conformational and coordination versatility due to single-bonded carbon chains. Secondly, they contain two bridging moieties, which lead to a variety of connection modes with transitional metal centers and provide abundant structural motifs. Thirdly, it cannot only act as bridging ligand to connect different building blocks, but also can chelate to metal centers. Furthermore, recent studies reveal that the IDA and its derivatives can serve as bioinorganic model compounds to illustrate conformation changes at the protein conformation for metal-protein centers in the absence or presence of appropriate substrates [14]. However, up to now, only a lot of low-dimensional coordination polymers with simple coordination modes are synthesized from IDA and 3*d* metal ions [15–18]. Here, we induce Ce(III) to the Co(II)–IDA system and synthesized an interesting 3*d*–4*f* complex $[CeCo(HIDA)(IDA)_2]_n$ (**I**).

EXPERIMENTAL

All chemicals were purchased of reagent grade and used without further purification. Elemental analyses (C, H, N) were performed on a Perkin Elemer 2400 CHN elemental analyzer. FT-IR spectra were recorded

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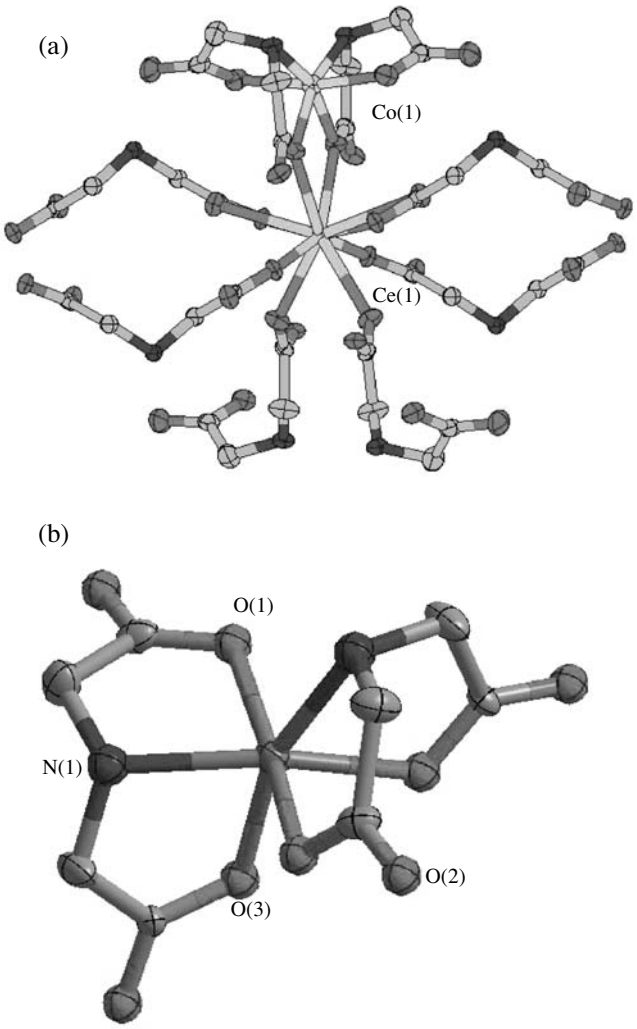

Fig. 1. The coordination environment of Ce^{3+} ion (a) and Co^{2+} ion (b) in complex **I**.

in the range 4000–400 cm^{-1} on an Alpha Centaut FTIR spectrophotometer using a KBr pellet. TG analyses were performed on a Perkin Elmer TGA7 instrument in flowing N_2 with a heating rate of 10°C min^{-1}. All measurements were performed at room temperature.

Hydrothermal syntheses. The best crystals were prepared from the reaction of $Ce(NO_3)_3 \cdot 3H_2O$ (0.11 g, 0.30 mmol), $Co(OAc)_2 \cdot 4H_2O$ (0.10 g, 0.40 mmol), and IDA (0.13 g, 1.00 mmol) in 8 ml of water. The resulting mixture was stirred for 30 min. The final solution was transferred into a 23-ml Teflon-lined autoclave and crystallized at 140°C for 5 days. After slowly cooling to room temperature, the purple crystals were collected in about 62% yield by filtration and air-drying.

For $C_{12}H_{13}N_3O_{12}CeCo$ (**I**)

anal. calcd, %:	C, 24.47;	H, 2.23;	N, 7.14.
Found, %:	C, 24.69;	H, 2.57;	N, 7.29.

IR spectrum (ν, cm^{-1}): 3354 s (H_2O), 1559 s $\nu_{as}(COO^-)$, 1463 v.s $\nu_s(COO^-)$, 1407 s $\nu_s(COO^-)$.

X-ray structure determination. Single crystal of complex **I** with dimension 0.331 × 0.296 × 0.287 mm was glued on a glass fiber. Data were collected on a Rigaku R-axis Rapid IP diffractometer at 293 K using graphite monochromate MoK_α radiation (λ = 0.71073 Å) and IP technique. Empirical absorption correction was applied. The structure was solved by the direct method and refined by the full-matrix least-squares method on F^2 using the SHELXTL–97 crystallographic software package [19, 20]. Anisotropic thermal parameters were used to refine all non-hydrogen atoms. Hydrogen atoms were located from difference Fourier maps. Further details of the X-ray structural analysis are given in Table 1. Selected bond lengths and angles are listed in Table 2. The atomic coordinates and other parameters of structure **I** have been deposited with the Cambridge

Table 1. Crystallographic data and details of the experiment and refinement of structures **I**

Parameter	Value
Formula weight	590.30
Crystal system	Monoclinic
Space group	*C*2/*c*
Unit cell dimensions:	
a, Å	9.7033(19)
b, Å	24.141(5)
c, Å	8.5810(17)
β, deg	115.01(3)
V, Å^3	1821.6(6)
Z	4
ρ_{calcd}, g/cm^3	2.152
μ, mm^{-1}	1.361
F(000)	1148
Crystal size, mm	0.331 × 0.296 × 0.287
θ range, deg	3.38–24.99
Reflections collected	6998
Independent reflections (R_{int})	3657 (0.0189)
Max and min transmission	0.7404 and 0.6336
Goodness-of-fit on F^2	1.009
Parameters	133
Final *R* indices ($I > 2\sigma(I)$)*	$R_1 = 0.0245$ $wR_2 = 0.0763$
R indices (all data)	$R_1 = 0.0250$ $wR_2 = 0.0770$
Largest diff. peak and hole, *e* Å^{-3}	2.122 and –0.885

* $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$.

Table 2. Selected bond distances (Å) and angles (deg) for complex **I***

Bond	*d*, Å	Bond	*d*, Å
Ce(1)–O(5)$^{\#1}$	2.442(2)	Ce(1)–O(6)	2.756(2)
Ce(1)–O(3)$^{\#1}$	2.595(2)	Co(1)–O(1)$^{\#1}$	2.057(3)
Ce(1)–O(5)$^{\#2}$	2.705(2)	Co(1)–N(1)$^{\#1}$	2.154(3)
Ce(1)–O(6)$^{\#1}$	2.756(2)	Ce(1)–O(5)	2.442(2)
Co(1)–O(1)	2.057(3)	Ce(1)–O(3)	2.595(2)
Co(1)–N(1)	2.154(3)	Ce(1)–O(5)$^{\#3}$	2.705(2)
Ce(1)–O(4)	2.564(2)	Co(1)–O(3)$^{\#1}$	2.100(2)
Ce(1)–O(4)$^{\#1}$	2.564(2)	Co(1)–O(3)	2.100(2)
Angle	ω, deg	Angle	ω, deg
O(5)$^{\#1}$Ce(1)O(5)	145.72(12)	O(5)$^{\#1}$Ce(1)O(6)$^{\#1}$	113.83(7)
O(3)$^{\#1}$Ce(1)O(5)$^{\#3}$	64.88(8)	O(3)$^{\#1}$Ce(1)O(3)	65.05(9)
O(5)$^{\#1}$Ce(1)O(4)	78.55(7)	O(4)Ce(1)O(6)$^{\#1}$	137.93(7)
O(5)$^{\#1}$Ce(1)O(6)	77.50(7)	O(4)$^{\#1}$Ce(1)O(5)$^{\#2}$	128.37(8)
O(5)$^{\#1}$Ce(1)O(3)$^{\#1}$	74.93(7)	O(5)$^{\#2}$Ce(1)O(6)$^{\#1}$	126.26(7)
O(4)Ce(1)O(6)	77.67(8)	O(3)Ce(1)O(5)$^{\#2}$	64.88(7)
O(4)Ce(1)O(3)$^{\#1}$	140.27(7)	O(4)$^{\#1}$Ce(1)O(5)$^{\#3}$	66.56(8)
O(5)$^{\#2}$Ce(1)O(6)	47.40(7)	O(5)$^{\#1}$Ce(1)O(4)$^{\#1}$	73.07(8)
O(4)$^{\#1}$Ce(1)O(3)	140.27(7)	O(3)Ce(1)O(5)$^{\#3}$	101.43(7)
O(5)Ce(1)O(6)$^{\#1}$	77.50(7)	O(5)Ce(1)O(4)	73.07(8)
O(5)$^{\#1}$Ce(1)O(5)$^{\#2}$	118.49(9)	O(5)Ce(1)O(6)	113.83(7)
O(3)$^{\#1}$Ce(1)O(6)$^{\#1}$	80.55(7)	O(5)Ce(1)O(3)$^{\#1}$	139.20(8)
O(4)Ce(1)O(5)$^{\#2}$	66.56(8)	O(3)$^{\#1}$Ce(1)O(6)	68.14(7)
O(5)$^{\#3}$Ce(1)O(6)$^{\#1}$	47.40(7)	O(5)$^{\#1}$Ce(1)O(3)	139.20(8)
O(5)$^{\#1}$Ce(1)O(5)$^{\#3}$	66.55(8)	O(5)$^{\#3}$Ce(1)O(6)	126.26(7)
O(4)Ce(1)O(5)$^{\#3}$	128.37(8)	O(4)Ce(1)O(3)	129.21(7)
O(5)Ce(1)O(4)$^{\#1}$	78.55(7)	O(4)$^{\#1}$Ce(1)O(6)$^{\#1}$	77.67(8)
O(5)$^{\#2}$Ce(1)O(5)$^{\#3}$	164.58(11)	O(5)Ce(1)O(5)$^{\#2}$	66.55(8)
O(4)$^{\#1}$Ce(1)O(4)	67.61(12)	O(3)Ce(1O(6)$^{\#1}$	68.14(7)
O(4)$^{\#1}$Ce(1)O(6)	137.93(7)	O(3)$^{\#1}$Ce(1)O(5)$^{\#2}$	101.43(7)
O(4)$^{\#1}$Ce(1)O(3)$^{\#1}$	129.21(7)	O(6)Ce(1)O(6)$^{\#1}$	142.90(10)
O(3)Ce(1)O(6)	80.55(7)	O(5)Ce(1)O(5)$^{\#3}$	118.49(9)
O(5)Ce(1)O(3)	74.93(7)		

* Symmetry transformations used to generate equivalent atoms: $^{\#1}$ $-x + 1, y, -z + 1/2$; $^{\#2}$ $-x + 1, -y + 1, -z$; $^{\#3}$ $x, -y + 1, z + 1/2$.

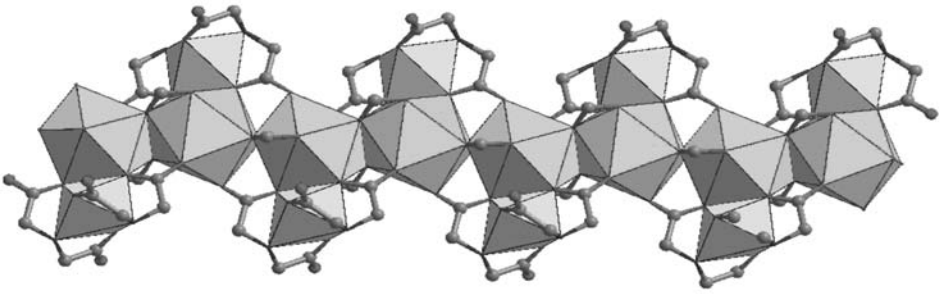

Fig. 2. The one-dimensional chain-like structure of complex **I**.

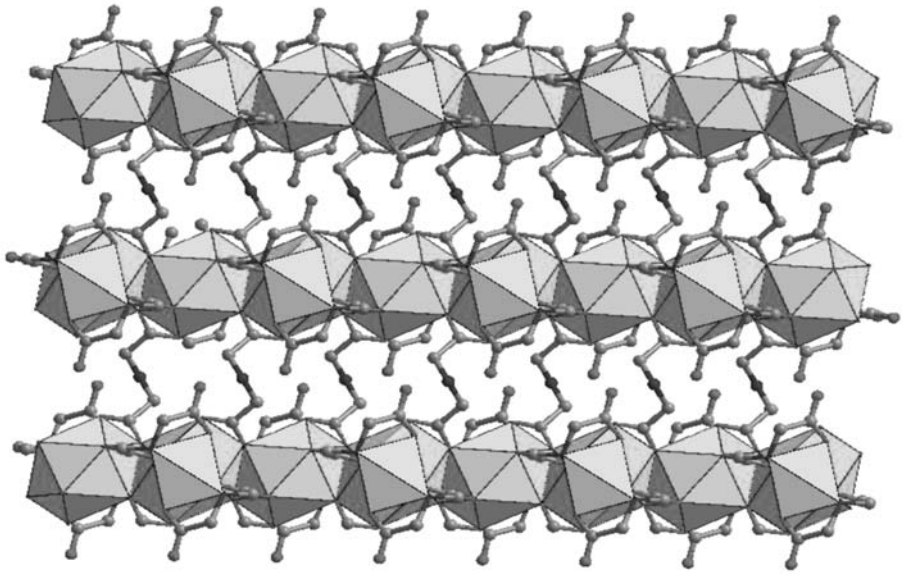

Fig. 3. The two-dimensional layer structure of complex **I**.

Crystallographic Data Center (no. 716853; deposit@ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The single-crystall X-ray analysis reveals complex **I** is an interesting two-dimensional network. There exist two kinds of metal ions, one is Ce(III) and the other is Co(II) (Fig. 1). The Ce(III) ion connects with ten oxygen atoms from different IDA ligands, the Ce–O distance ranges from 2.442 to 2.756 Å, and the OCeO bond angles is in a range of 47.40° to 145.72°. Unlike Ce(III), Co(II) links with four oxygen atoms and two nitrogen atoms from two different IDA ligands. The average Co(II)–O distance is 2.057 Å and the Co(II)–N distance is 2.100 Å. The Ce^{3+} ion links with Co^{2+} ion and forms a CeCo unit. A carboxylic oxygen atom connected such units along the *z* axis to form a one-dimensional chain-like structure (Fig. 2). The IDA ligand connects neighboring chains to form two-dimensional layer structure (Fig. 3). To our knowledge, a lot of coordination polymers constructed from IDA ligands have been synthesized. However, complexes constructed from 4*f* metal ions and IDA, especially 3*d*–4*f* complexes have rarely been studied.

For complex **I**, the absorption peaks at 1559, 1407, and 1348 cm^{-1} display the asymmetric and symmetric vibrations, respectively; Δ (represents the separation between γ_{as}(COO) and γ_s(COO)) is 152 and 211 cm^{-1}. This value is consistent with the coordination modes of IDA ligands in this complex.

The thermal stability properties were studied on the single crystal samples in the range from 25 to 800°C. The first weight loss (66.18%) began at 420°C and the decomposition of organic ligands began at 576°C. This value is consistent with the calculated value (66.39%).

In summary, under hydrothermal conditions, we successfully combined the merits of Ce, Co, and IDA

and synthesized one 3*d*–4*f* complex with the two-dimensional layer structure.

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