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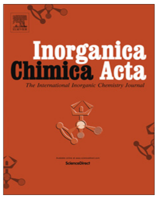

Research paper

Two heterometallic Dy^{III}-Co^{II} complexes: Structural change from discrete ionic-pair to coordination polymer

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ABSTRACT

Two novel heterometallic complexes with formula of $\{[Co_2(HTRI)_3(H_2O)_6][Dy_2Co(HCAM)_6(H_2O)_4]\cdot 22H_2O\}$ (**1**, H_3CAM = 4-hydroxyl-2,6-pyridicarboxylic acid; HTRI = 1,2,4-triazole) and $\{[Dy_2Co_3(HTRI)_2(HCAM)_6(H_2O)_{10}]\cdot 2CH_3OH\cdot 13H_2O\}_n$ (**2**) have been obtained. Single-crystal X-ray diffraction analyses reveal that complexes **1** and **2** show similar molecular elements, but display different structural features: a discrete ionic-pair for complex **1** and an infinite 1D chain for complex **2**, which is probably due to the different coordination modes of HTRI. Luminescent properties have been studied for complexes **1** and **2**, and show the characteristic fluorescence of Dy(III) ions.

1. Introduction

In the past two decades, crystal engineering has attracted great interest in coordination chemistry and supramolecular chemistry. The rational design and synthesis of transition metal-lanthanide (3d-4f) coordination polymers (CPs) is one of the hottest topics in the field of crystal engineering due to their intriguing architectures and special functionalities such as luminescence, catalysis, magnetism and molecular adsorption [1–3]. Since the first 3d-4f complex was produced in 1972 [4], a number of 3d-4f heteropolymetallic complexes have been successfully obtained by conventional self-assembly reaction [5]. However, the rational strategy leading to extended structures of 3d-4f heteronuclear CPs or discrete multinuclear aggregation is still a challenge owing to the variable and versatile coordination behavior of 4f metals as well as the competitive reactions between 3d and 4f metals chelated by the same ligands.

To obtain the desired heterometallic CPs, the strategy would be to utilize the organic ligands with proper coordination sites preferring to two different metal ions [6]. The organic ligands can also mediate the intermolecular interactions between 3d and 4f ions, and further improve the magnetic and optical properties. Polydentate ligands, such as Schiff-base [7], pyridinol [8], alcamines [9], pyridine-carboxylic acid [10,11], are proved to be good candidates to construct heterometallic 3d-4f complexes. Because these ligands contain both O and N donors and match the point that the 4f ions prefer to O donors and 3d ions to N donors.

Hydrothermal and solvothermal methods are the most extended synthetic routes used to design 3d-4f complexes with mixed ligands. In this respect, we produced two novel heterometallic complexes with formula of $\{[Co_2(HTRI)_3(H_2O)_6][Dy_2Co(HCAM)_6(H_2O)_4]\cdot 22H_2O\}$ (**1**, H_3CAM = 4-hydroxyl-2,6-pyridicarboxylic acid; H_3TRI = 1,2,4-triazole) and $\{[Dy_2Co_3(HTRI)_2(HCAM)_6(H_2O)_{10}]\cdot 2CH_3OH\cdot 13H_2O\}_n$ (**2**) by hydrothermal and solvothermal methods, respectively. Single-crystal X-ray diffraction analyses reveal that complex **1** comprises a discrete ionic-pair and complex **2** features a 1D chain. The structures are extended to 3D frameworks through rich hydrogen bonding interactions. Luminescent properties indicate the characteristic fluorescence of Dy(III) ions.

2. Experimental section

2.1. General material and method

All reagents and solvents were purchased commercially and used without further purification. Elemental analyses for C, H and N were carried out on a Perkin-Elmer analyzer at the Institute of Elemento-Organic Chemistry in Nankai University. Fluorescent spectra were recorded at room temperature on an F-7000 FL Spectrophotometer.

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2.2. Synthesis of {$[Co_2(HTRI)_3(H_2O)_6][Dy_2Co(HCAM)_6(H_2O)_4]\cdot 22H_2O$} (**1**)

A mixture of H_3CAM (0.0572 g, 0.3 mmol), HTRI (0.0065 g, 0.1 mmol), $Dy(NO)_3\cdot 6H_2O$ (0.0445 g, 0.1 mmol), $CoAc_2\cdot 6H_2O$ (0.0508 g, 0.2 mmol) and water (4 mL) were sealed in a Teflon-lined stainless vessel (25 mL) and heated at 100 °C for 96 h. The vessel was then cooled down to room temperature. Block-shaped red crystals were obtained. Yield: 62.7 mg (53.8% based on Dy). Anal. Calc. for $Dy_2Co_3C_{48}H_{93}N_{15}O_{63}$ (**1**): C 24.12, H 3.92, N 8.80%; found: C 24.23, H 3.89, N 8.83%.

2.3. Synthesis of {$[Dy_2Co_3(HTRI)_2(HCAM)_6(H_2O)_{10}]\cdot 2CH_3OH\cdot 13H_2O$}$_n$ (**2**)

A mixture of H_3CAM (0.0529 g, 0.3 mmol), HTRI (0.0224 g, 0.3 mmol), $Dy(OH)_3$ (0.0230 g, 0.1 mmol), $CoCl_2\cdot 6H_2O$ (0.0739 g, 0.3 mmol), water (3 mL) and anhydrous methanol (3 mL) were sealed in a Teflon-lined stainless vessel (25 mL) and heated at 80 °C for 96 h. The vessel was then cooled down to room temperature. Rod-like red crystals were obtained. Yield: 53.3 mg (44.9% based on Dy). Anal. Calc. for $Dy_2Co_3C_{48}H_{78}N_{12}O_{55}$ (**2**): C 26.15, H 3.57, N 7.62%; found: C 26.18, H 3.52, N 7.69%.

2.4. Crystallographic data collection and refinement

Suitable single crystal for **1** and **2** were selected for single-crystal X-ray diffraction analysis. Data were collected on an Xcalibur, Eos diffractometer with a Mo-Kα radiation ($\lambda = 0.71073$ Å). All non-hydrogen atoms were solved using direct methods. All the calculations were solved by SHELXS-97 (direct methods) and refined by SHELXL-97 (full-matrix least-squares on F^2) program [12]. The lattice water molecules in complexes **1** and **2** are highly disordered, and the hydrogen atoms of water molecules cannot be confirmed. The crystal data and structure refinements are summarized in Table 1.

Table 1
Data collections and processing parameters for **1** and **2**.

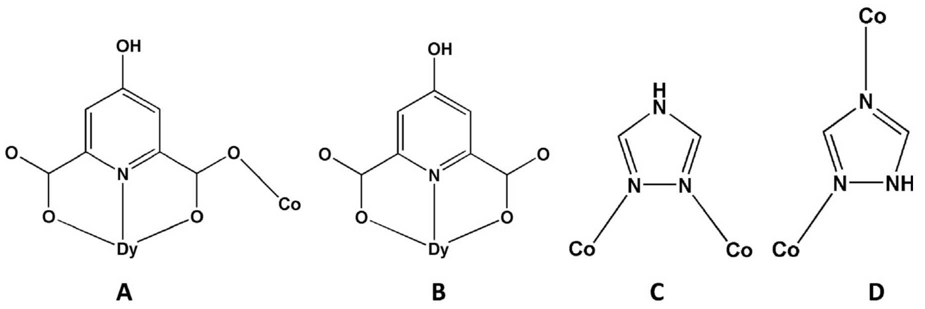
Complexes	1	2
Empirical formula	$Dy_2Co_3C_{48}H_{93}N_{15}O_{63}$	$Dy_2Co_3C_{48}H_{78}N_{12}O_{55}$
Formula weight	2390.11	2204.98
T /K	120.05(10)	153(2)
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	P-1
a (Å)	11.9555(4)	12.2792(11)
b (Å)	33.0166(16)	12.7577(12)
c (Å)	24.4468(11)	14.8152(12)
α (deg)	90.00	66.961(8)
β (deg)	116.656(3)	86.400(7)
γ (deg)	90.00	66.043(9)
V (Å^3)	8624.3(6)	1939.0(3)
Z	4	1
ρ_{calc} (g.cm^{-3})	1.841	1.888
μ (mm^{-1})	2.402	2.654
Refections collected/uniques	32186/15141	12202/6800
R_{int}	0.0759	0.0512
S on F^2	1.063	1.035
R_1/wR_2 ($I > 2\sigma(I)$)	0.0824/0.1542	0.0535/0.1093
R_1/wR_2 (all data)	0.1404/0.1863	0.0690/0.1200
Largest different peak/hole (e.Å^{-3})	2.483/−2.098	1.722/−1.150

3. Results and discussion

We use two different methods to produce two DyCo complexes (**1** and **2**). Firstly, the mixture of H_3CAM (0.3 mmol), HTRI (0.1 mmol), $Dy(NO)_3\cdot 6H_2O$ (0.1 mmol), $CoAc_2\cdot 6H_2O$ (0.2 mmol) and water (4 mL) under hydrothermal condition results an ionic-pair complex (**1**). In order to produce coordination polymer, we tried many times by adopting different reagents with different ratio and/or different solvent. As a result, we use H_3CAM (0.3 mmol), HTRI (0.3 mmol), $Dy(OH)_3$ (0.1 mmol), $CoCl_2\cdot 6H_2O$ (0.3 mmol), water (3 mL) and anhydrous methanol (3 mL) under solvothermal condition to synthesize a 1D coordination polymer (**2**). As shown in Scheme 1, the coordination modes of $HCAM^{2-}$ ligands are uniform in complexes **1** and **2** (Scheme 1A and B), and the difference is the coordination modes of HTRI (Scheme 1C for complex **1** and Scheme 1D for complex **2**).

3.1. Crystal structure of {$[Co_2(HTRI)_3(H_2O)_6][Dy_2Co(HCAM)_6(H_2O)_4]\cdot 22H_2O$} (**1**)

Single-crystal X-ray diffraction result reveals that complex **1** crystallizes in the monoclinic system, space group $P2_1/c$. As shown in Fig. 1, the asymmetric unit of **1** consists of two crystallographically independent Dy^{III} ions, three Co^{II} ions, three HTRI molecules, six $HCAM^{2-}$ anions, and ten coordinated and twenty-two lattice water molecules. The Dy1 center is located in a nine-coordinate tri-capped trigonal prismal geometry with three chelated $HCAM^{2-}$ ligands via ONO mode. The coordination environment of Dy2 is the same as Dy1. The distances of Dy–O bonds range from 2.372(10) to 2.444(7) Å, while the Dy-N bond lengths are from 2.458(9) to 2.485 (10) Å, which are in the normal range [13]. The O–Dy–O bond angles range from 74.31(27) to 148.12(26)° and the O–Dy–N bond angles range from 63.57(32) to 141.54(29)°. The coordination geometry of Co1 center is a distorted octahedron with six O atoms from two $HCAM^{2-}$ ligands and four terminal water molecules. The Co2 and Co3 ions exhibit the similar coordination environment, which consist of three O atoms from three terminal water molecules and three N atoms from three HTRI ligands. The bond lengths of Co-O range from 2.054(11) to 2.162(9) Å and those of Co–N are in the range of 2.092(12)–2.137(10) Å, which are similar to those reported Co^{II} complexes [14,15].



Scheme 1. The coordination modes of $HCAM^{2-}$ and HTRI in complexes **1** and **2**.