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Mono- and heterometallic europium (III) and terbium (III) complexes: Synthesis, crystal structures and luminescent properties

Yan-Ju Xiong, Pei-Ling Huang, Xiao-Wei Zhang, Wei-Yan Huang, Qiu-Hong Huang, Qian Cheng, Jie-Fang Fang, Yun Li, Fei-Fei Zhu, Shan-Tang Yue *

School of Chemistry and Environment, South China Normal University, Guangzhou 510006, PR China

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Four new rare earth organometallic coordination polymers $[Eu^{III}(Hbidc)(pdc)\cdot 2(H_2O)]_2\cdot 4H_2O$ (**1**), $[Tb^{III}(Hbidc)(pdc)\cdot 2(H_2O)]_2$ (**2**), and $\{[Ln^{III}Ag^{I}(bidc)(pdc)\cdot 2(H_2O)]\}_n\cdot H_2O$ (Ln = Eu (**3**), Tb (**4**)) (H_2bidc = 1H-benzimidazole-5,6-dicarboxylic acid, H_2pdc = 2,6-pyridine dicarboxylic acid) have been synthesized through self-assembly reactions. The X-ray single crystal diffraction indicates that these complexes are isomorphous, namely triclinic P − 1. Interlayer O–H···O and C–H···O hydrogen bonding has been observed in the structure of four complexes, generating 1D zigzag infinite chain, 2D plane layer, and even 3D ladder-like supramolecular framework. Addition of silver nitrate to chemicals leads to massive restructuring and emission intensity enhancement of complexes **3** and **4**. Furthermore, thermal stabilities and luminescent of **1**–**4** have also been discussed in detail.

The rigorous study and rational design of unique functional metal–organic frameworks (MOFs) have been of interest during recent years [1]. Much work has focused on the construction of 3d–4f mono- and heterometallic MOFs [2]. This is mainly due to their captivating topological structures and intriguing photoluminescence [3]. Trivalent lanthanide ion Ln (III), such as Tb (III) and Eu (III), may thus become outstanding candidates for the intense narrow emission bands from f–f transitions that have long excited state lifetimes and large Stokes shifts [4].

Based on the hard–soft acid-base theory, multidentate ligands with N- and O- donor atoms are good candidates for creating lanthanide organometallic compounds. Therefore, here, we chose two N-heterocyclic carboxylic acids, 1H-benzimidazole-5,6-dicarboxylicacid ($\mathbf{L_1}$) [5] and 2,6-pyridine dicarboxylic acid ($\mathbf{L_2}$) [6] as the target ligands, both of which have multiple coordination sites. In the present study, we synthesized two new monometallic Tb (III) and Eu (III) complexes ($[Eu^{III}(Hbidc)(pdc)\cdot 2(H_2O)]_2\cdot 4H_2O$ (**1**), $[Tb^{III}(Hbidc)(pdc)\cdot 2(H_2O)]_2$ (**2**)) and two heterometallic Tb (III)/Eu (III) and Ag (I) coordination polymers ($\{[Ln^{III}Ag^{I}(Hbidc)(pdc)\cdot 2(H_2O)]\}_n\cdot H_2O$ (Ln = Eu (**3**), Tb (**4**))).

1–**4** were obtained with colorless block crystals [7], and the crystal data and structure refinements are put in order in Table 1. All chemicals purchased were of reagent-grade quality and used without further purification. A mixture of L_1, L_2 and $Eu(NO_3)_3\cdot 6H_2O$ in a 1:1:1 molar ratio, and 10 mL water was dissolved in a 25 mL Teflon reactor and mixed with stirring. The NaOH solution ($0.2\ mol\cdot L^{-1}$) was added to adjust the pH to 6.8–7.0. The reaction vessel was heated to 160 °C for 3 days under autogenous pressure, then cooled to room temperature at a rate of 10 °C/h. Compound **2** was prepared using a similar method as **1** with $Tb(NO_3)_3\cdot 6H_2O$ instead of $Eu(NO_3)_3\cdot 6H_2O$. While, with the addition of silver nitrate, compounds **3** and **4** were obtained by the mixture of L_1, L_2, $AgNO_3$ and $Ln(NO_3)_3\cdot 6H_2O$ in molar ratio of 5:5:3:5, and the NaOH solution ($0.2\ mol\cdot L^{-1}$) was added to adjust the pH to 7.0–7.2.

Compounds **1** and **2** are structurally similar except for the coordination number of water molecules based on similar crystal parameters from single-crystal X-ray analysis. In complex **2**, the ligand L_1 presents μ_2-(η^2:η^2)-bridging mode (Scheme 1(1a)). In Fig. 1a, the Tb (III) center is nine-coordinated by four oxygen atoms from two L_1 ligands, two oxygen atoms from a coordinated water molecule, and two oxygen atoms and one nitrogen atom from one L_2 ligand, respectively, developing a distorted tricapped trigonal prismatic coordination geometry. The Tb–O bond distances range from 2.373(6) to 2.502(6) Å and the Tb–N bond length is 2.469(7) Å.

Intermolecular and intramolecular hydrogen bonding interaction is broadly utilized to produce novel supramolecular topological structures. In our work, hydrogen bonds have been observed in the structure of four complexes. The packing diagram for complex **2** reveals the presence of a 1D linear array (along the *a* axis) that is illustrated by the intermolecular hydrogen bonds (green thick line) between O1 from L_2 and O2W from coordinated water molecule through H2W with a H···O distance of 2.0370 Å and a O–H···O angle of 167.802° (Fig. 2b). Besides, the adjacent molecules are also connected by intramolecular hydrogen bonds between O6 (O7) from L_1 and O1W from coordinated water

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* Corresponding author.

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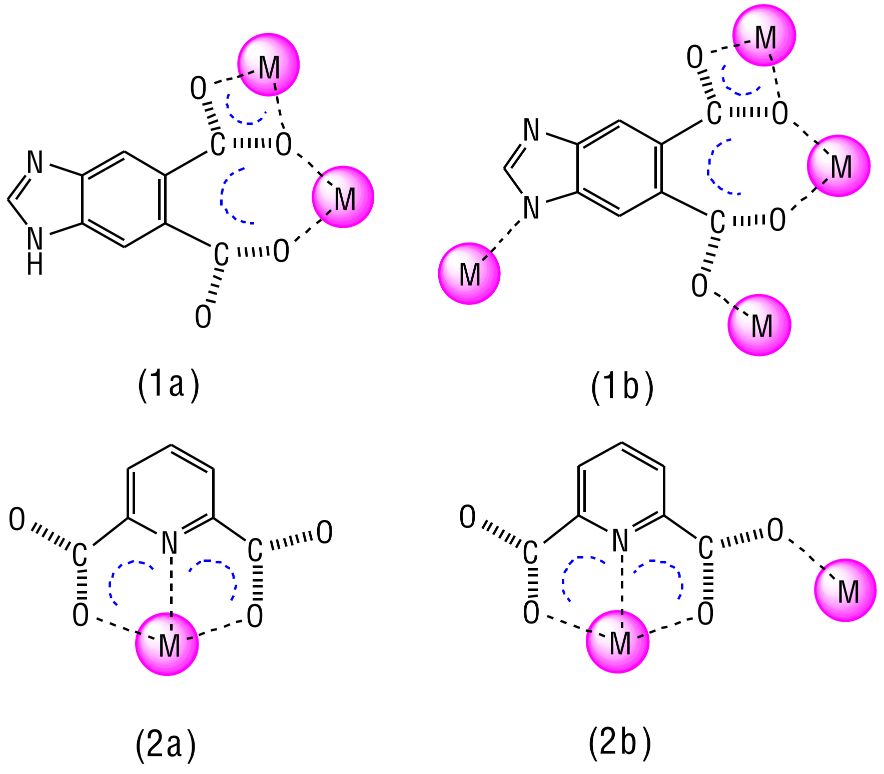
Table 1
Crystal data and structure refinements for the compounds **1**–**4**.

Complex	1	2	3	4
Empirical formula	$C_{32}H_{32}Eu_2N_6O_{24}$	$C_{32}H_{24}Tb_2N_6O_{20}$	$C_{16}H_{13}AgEuN_3O_{11}$	$C_{16}H_{13}AgTbN_3O_{11}$
Formula weight	1188.58	1130.43	683.13	690.09
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
Space group	P −1	P −1	P −1	P −1
a (Å)	9.0345(14)	8.997(4)	9.1332(8)	9.1026(16)
b (Å)	10.6006(14)	10.570(5)	10.5300(9)	10.530(2)
c (Å)	10.7896(14)	10.731(5)	10.6352(9)	10.6113(19)
α (deg)	77.7900(10)	77.823(4)	93.2530(10)	93.186(3)
β (deg)	71.4670(10)	71.205(4)	108.8870(10)	109.070(3)
γ (deg)	84.0920(10)	84.064(4)	108.0490(10)	107.945(3)
Volume ($Å^3$)	956.9(2)	943.7(8)	906.00(13)	900.6(3)
Z	1	1	2	2
D_{calcd} ($g\ cm^{-3}$)	2.063	1.989	2.504	2.545
M (Mo Kα) (mm^{-1})	3.353	3.810	4.585	5.056
F (000)	584	548	656	660
Data/restraints/parameters	3387/0/255	4320/0/268	3204/0/289	3211/0/264
Goodness-of-fit on F^2	3.144	1.107	0.713	1.006
Final R indices, [I >2σ(I)]	R1 = 0.0686 wR2 = 0.1717	R1 = 0.0567 wR2 = 0.1620	R1 = 0.0221 wR2 = 0.0774	R1 = 0.0643 wR2 = 0.1673
R indices (all data)	R1 = 0.0717 wR2 = 0.1736	R1 = 0.0612 wR2 = 0.1677	R1 = 0.0228 wR2 = 0.0787	R1 = 0.0694 wR2 = 0.1740

molecule (Fig. 2c). The 1D linear structure is connected along the *c* axis by the intermolecular hydrogen bonding interaction between O3 and O2W through H2W with a H···O distance of 1.9598 Å and a O–H···O angle of 169.688°, generating a 2D network extending along the *ac* plane (Fig. 2a). Fig. 2d shapes like a ladder which is the three-dimensional topology framework of **2**.

Compounds **3** and **4** crystallize in space group P −1 and are isostructural, herein, only the structure of complex **3** is described in detail here. With the accretion of silver nitrate and adjusting of pH, the coordination modes of L_1 and L_2 have made significant change, which are very different from Scheme 1(1a and 2a). The nitrogen atom and one of the 6-carboxylate oxygen atoms coordinate to the silver center, while one of the 6-carboxylate oxygen atoms and the 5-carboxylate coordinate to two europium centers with the μ_4-(η^1:η^1:η^2:η^2)-bridging mode (Scheme 1(1b–2b)). The view of coordination environment of Eu (III), Ag (I) and ligand ions in **3** is shown in Fig. 1b. The coordination situation of Eu (III) center is the same as the Tb (III) center in **2**, while, the two-coordinated Ag (I) ions express linear coordination geometry [the angle of N–Ag(4)–N is close to180°]. The Eu–O bond distances range from 2.364(2) to 2.525(2) Å. The bond angles of O–Eu–O are in the range of 51.88(8)–145.95(9)°. O7 and O10 from L_1 both link Eu_1 and Eu_2, forming a μ_2-OH bridged



Scheme 1. Coordination modes of H_2bidc and H_2pdc.