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Synthesis, structures and luminescent properties of 4d–4f heterometallic coordination frameworks based on lanthanide oxalate substructures with nicotinate bridging ligands

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ABSTRACT

Four transition–lanthanide metal–organic coordination polymers, namely $[Ag_2Ln(nic)_4(H_2O)_4 \cdot (ClO_4) \cdot H_2O]$ [Ln = Eu (**1**), Gd (**2**)] and $[AgLn(nic)_2(ox)_{0.5}(H_2O)_2 \cdot (ClO_4) \cdot H_2O]$ [Ln = Tb (**3**), Yb (**4**)] (nic = nicotinate; ox = oxalate) have been synthesized by the hydrothermal reactions of 4d and 4f metal salts with N-/O-donor ligands. The isostructural complexes **1** and **2** exhibit novel 2D wave-like heterometallic layers constructed by the assembly of 1D chains of lanthanide–carboxylate with $Ag(nic)_2$ subunits. Complexes **3** and **4** show another unusual 3D heterometallic coordination framework constructed from 2D lanthanide–oxalate layers and pillar-like $Ag(nic)_2$ subunits. Furthermore, the luminescent properties of complexes **1** and **3** were studied.

1. Introduction

The study of lanthanide–transition metal (Ln–M) complexes has gained great recognition over the last decade because of their fascinating structural diversity and the intriguing topological networks they form. With these materials being at the interface between synthetic chemistry and materials science they are also studied to investigate potential uses due to their magnetic behavior, their conductive, luminescent and non-linear optical properties [1–4], and their use in bimetallic catalysis [5]. In a recent review by Shore and others, existing Ln–M coordination polymers were summarized and a rational classification was proposed according to the different types of interactions between Ln–M: (a) Ln–M direct bonds; (b) ionic associations; and (c) Ln–linker–M type assemblies. In particular, a large number of examples of Ln–linker–M systems have been successfully obtained by the spontaneous assembly of metal ions with different chemical characteristics with diverse N-/O-donor ligands [6]. Important for the targeted synthesis of these linked Ln/M complexes is that the lanthanide and transition metal ions have different affinities for the N- and O-donors, which provides an approach for the construction of novel multi-dimensional heterometallic coordination frameworks with intriguing structural motifs and luminescent properties [7].

So far, most of the work has been done in the field of constructing 3d–4f coordination complexes. 4d–4f coordination frameworks, however, have been much less investigated [8,7b,13b]. Herein, we chose nicotinic acid (nic) with both N- and O-donor atoms as a potential linker between lanthanide and transition metals, and the oxalate anion as an excellent bridging ligand for linking the lanthanide metal centers. In the process of further investigating the aforementioned strategic method and the factors that affect the formation of new coordination polymers with high-dimensional networks, we obtained, via hydrothermal reactions, four novel 4d–4f coordination polymers, namely $[Ag_2Ln(nic)_4(H_2O)_4 \cdot (ClO_4) \cdot H_2O]$ [Ln = Eu (**1**), Gd (**2**)] and $[AgLn(nic)_2(ox)_{0.5}(H_2O)_2 \cdot (ClO_4) \cdot H_2O]$ [Ln = Tb (**3**), Yb (**4**)].

2. Experimental

2.1. General remarks

All materials and reagents were obtained commercially and were used without further purification. Elemental (C, H, N) analyses were performed on a Perkin–Elmer 2400 element analyzer. Infrared (IR) samples were recorded using KBr pellets, and spectra were obtained in the 400–4000 cm^{-1} range using a Nicolet Avatar 360 FT-IR spectrophotometer. Fluorescence spectra were recorded with an Edinburgh F900 FL Spectrophotometer analyzer.

2.2. Synthesis

2.2.1. $[Ag_2Eu(nic)_4(H_2O)_4 \cdot (ClO_4) \cdot H_2O]$ (**1**)

A mixture of nicotinic acid (0.123 g; 1 mmol), $AgNO_3$ (0.100 g; 0.59 mmol), Eu_2O_3 (0.100 g; 0.284 mmol), $HClO_4$ (0.385 mmol)

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and H_2O (10 mL) was heated to 150 °C for 50 h in a 23 mL Teflon-lined stainless-steel autoclave and then it was cooled to room temperature at 10 °C h^{-1} to obtain colorless plate-like single crystals of **1** (yield: 52% based on Eu). *Anal.* Calc. for $Ag_2EuC_{24}H_{26}N_4O_{17}Cl$: C, 27.57; H, 2.51; N, 5.36. Found: C, 27.53; H, 2.53; N, 5.38%. IR frequencies (KBr, cm^{-1}): 3431, 1612, 1560, 1411, 1203, 1099, 840, 756, 692, 538, 420.

2.2.2. $[Ag_2Gd(nic)_4(H_2O)_4 \cdot (ClO_4) \cdot H_2O]$ (**2**)

An identical procedure as for **1** was used to prepare **2** except that Eu_2O_3 was replaced by Gd_2O_3. Colorless plate-like single crystals of (**2**) were obtained (yield: 57% based on Gd) *Anal. Calc.* for $Ag_2GdC_{24}H_{26}N_4O_{17}Cl$: C, 27.43; H, 2.49; N, 5.33. Found: C, 27.40; H, 2.50; N, 5.35%. IR frequencies (KBr, cm^{-1}): 3437, 1614, 1560, 1411, 1203, 1097, 840, 756, 696, 534, 420.

2.2.3. $[AgTb(nic)_2(ox)_{0.5}(H_2O)_2 \cdot (ClO_4) \cdot H_2O]$ (**3**)

A mixture of nicotinic acid (0.123 g; 1 mmol), $Na_2C_2O_4$ (0.0335 g; 0.25 mmol); $AgNO_3$ (0.100 g; 0.59 mmol), Tb_4O_7 (0.100 g, 0.284 mmol), $HClO_4$ (0.385 mmol) and H_2O (10 mL) was heated to 150 °C for 50 h in a 23 mL Teflon-lined stainless-steel autoclave. Colorless plate-like single crystals (**3**) were obtained (yield: 48% based on Tb) on cooling the solution to room temperature at 10 °C h^{-1}. *Anal. Calc.* for $AgTbC_{13}H_{12}N_2O_{12}Cl$: C, 22.61; H, 1.75; N, 4.06. Found: C, 22.62; H, 1.73; N, 4.07%. IR frequencies (KBr, cm^{-1}): 3423, 1612, 1568, 1421, 1201, 1072, 864, 756, 692, 623, 551, 424.

2.2.4. $[AgYb(nic)_2(ox)_{0.5}(H_2O)_2 \cdot (ClO_4) \cdot H_2O]$ (**4**)

An identical procedure as for **3** was used to prepare **4** except that Tb_4O_7 was replaced by Yb_2O_3. Colorless plate-like single crystals (**4**) were obtained (yield: 41% based on Yb) *Anal. Calc.* for $AgYbC_{13}H_{12}N_2O_{12}Cl$: C, 22.16; H, 1.72; N, 3.98. Found: C, 22.12; H, 1.75; N, 3.94%. IR frequencies (KBr, cm^{-1}): 3423, 1612, 1568, 1421, 1201, 1064, 864, 759, 696, 623, 557, 418.

2.3. Crystal structure determination

Single-crystal X-ray diffraction data collections of **1–4** were performed on a Bruker Apex II CCD diffractometer operating at 50 kV and 30 mA using Mo Kα radiation (λ = 0.71073 Å). Data collection and reduction were performed using the APEX II software [9]. Multi-scan absorption corrections were applied for all data sets using the algorithms implemented in APEX II [9]. All four structures were solved by direct methods and refined by full-matrix least squares on F^2 using the SHELXTL program package [9]. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms attached to carbon were placed in geometrically idealized positions and refined using a riding model. Hydrogen atoms on water molecules were located from difference Fourier maps and were also refined using a riding model. Crystallographic data for **1–4** are listed in Table 1 and selected bond lengths and angles for all compounds are given in Table 2. Hydrogen bonding parameters for **1** and **3** are given in Table 3.

3. Results and discussion

3.1. Synthesis and characterization

We initially tried to isolate single crystals of the target compounds by the reactions of lanthanide salts with a mixture of $AgNO_3$, nicotinic acid and/or oxalate salt using conventional solution methods; however, only white precipitates were obtained. Hydrothermal synthesis has been proven to be a powerful method for the construction of organic–inorganic hybrid compounds [10]. By introducing hydrothermal techniques, we obtained a small quantity of microlite unsuitable for single-crystal X-ray diffraction when lanthanide salts were used as the lanthanide source. In our previous work, lanthanide oxides and perchloric acid have been proven to play an important role in the formation of unusual Ln–M coordination polymers [11]. Therefore, we tried lanthanide oxides as the lanthanide source and perchloric acid to synthesize new Ln–M coordination frameworks under hydrothermal conditions.

3.1.1. Structures of $[Ag_2Ln(nic)_4(H_2O)_4 \cdot (ClO_4) \cdot H_2O]$ (Ln = Eu **1**; Gd **2**)

Single-crystal X-ray diffraction studies revealed that compounds **1** and **2** are isostructural, and only the structure of **1** is representatively described here in detail. It exhibits novel 2D wave-like heterometallic coordination frameworks constructed from 1D zigzag chains and perchlorate anions, and crystallizes in the orthorhombic space group *Cmca*. The asymmetric unit of **1** exhibits half a europium ion, one silver ion, half a perchlorate anion, two crystallographically unique nicotinate ligands, and two coordinated and half a non-coordinated water molecule (Fig. 1). Each Eu(III) center lies on an inversion center and is bonded to four oxygen atoms from monodentate nicotinate ligands, and to four

Table 1
Crystal data details of the structure determination for complexes **1**–**4**

Complex	1	2	3	4
Formula	$Ag_2EuC_{24}H_{26}N_4O_{17}Cl$	$Ag_2GdC_{24}H_{26}N_4O_{17}Cl$	$AgTbC_{13}H_{12}N_2O_{12}Cl$	$AgYbC_{13}H_{12}N_2O_{12}Cl$
Formula weight	1045.64	1050.93	690.49	704.61
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	orthorhombic	orthorhombic	monoclinic	monoclinic
Space group	*Cmca*	*Cmca*	$P2_1/c$	$P2_1/c$
a (Å)	35.2066(12)	35.2066(12)	14.8129(4)	14.6528(4)
b (Å)	12.3551(3)	12.3551(3)	12.7377(3)	12.6997(5)
c (Å)	15.0970(4)	15.0970(4)	9.8903(2)	9.8257(4)
β (°)	90	90	93.269(2)	92.838(2)
V (Å^3)	6566.9(3)	6566.9(3)	1863.09(8)	1826.18(11)
Z	8	8	4	4
D_{calc} (g/cm^3)	2.115	2.126	2.462	2.563
μ (mm^{-1})	3.231	3.341	5.029	6.379
F(000)	4064	4072	1316	1336
Parameters	236	236	296	271
Goodness-of-fit (F^2)	0.997	1.133	1.157	1.043
R_1 $[I > 2\sigma(I)]$[a]	0.0644	0.0457	0.0409	0.0383
wR_2 (all data)[b]	0.1752	0.1369	0.1037	0.0838

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$.
[B] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum(F_o^2)^2\}^{1/2}$.