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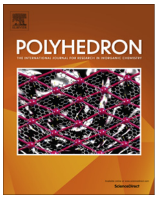

1D and 2D Zn–Ln coordination polymers based on compartment compounds: $[ZnLn(L)(NO_3)_2(4\text{-ppa})(EtOH)]$ and $[ZnLn(L)(NO_3)_2(4\text{-pca})(H_2O)]$ (Ln = Eu, Tb; H_2L = 1,3-bis((3-methoxysalicylidene)amino) propane; 4-Hppa = 4-pyridinepropionic acid; 4-Hpca = 4-pyridinecarboxylic acid)

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ABSTRACT

This paper describes the preparation of four 3*d*–4*f* (3*d* = Zn; 4*f* = Eu, Tb) coordination polymers and their emission quenching of the lanthanide ions. Two dinuclear Zn–Ln compartment compounds, $[ZnLn(L)(NO_3)(CH_3CN)(H_2O)_4](NO_3)_2(H_2O)$ (Ln = Eu, Tb), were prepared at room temperature by stirring an acetonitrile solution containing [Zn(L)] (H_2L = 1,3-bis((3-methoxysalicylidene)amino)propane) and $Ln(NO_3)_3 \cdot n(H_2O)$. When these compounds were treated with 4-pyridinepropionic acid (4-Hppa) under microwave-heating conditions, one-dimensional Zn–Ln coordination polymers were formed: $[ZnLn(L)(NO_3)_2(4\text{-ppa})(EtOH)]$ (Ln = Eu (**1**), Tb (**2**)). By contrast, these compounds reacted with pyridine-4-carboxylic acid (4-Hpca) to give two-dimensional Zn–Ln coordination polymers: $[ZnLn(L)(NO_3)_2(4\text{-pca})(H_2O)]$ (Ln = Eu (**3**), Tb (**4**)). All the compounds (**1**–**4**) exhibited the emission quenching of the Ln^{3+} ion, probably due to the $Ln^{3+} \rightarrow Zn^{2+}$ energy transfer.

1. Introduction

Coordination polymers (CPs), frequently also called metal–organic frameworks (MOFs), consist of both organic and inorganic components connected by external multifunctional linkers [1–7]. CPs continually attract researchers in various fields due to their interesting structures as well as desirable applications, including photoluminescence, sensing, catalysis, molecular magnetism, and gas storage [8–13]. Successful preparation of desired CPs requires a suitable combination of a metal component (net metal ions or secondary building units (SBUs)) and an organic linking ligand with proper terminal groups (*e.g.*, ligands with pyridyl–pyridyl, carboxylate–carboxylate, and pyridyl–carboxylate terminals).

For the past 20 years, compartment ligands with the N_2O_4-donor units, which basically belong to Schiff-base ligands, have been employed to prepare discrete bimetallic (*d*–*d* or *d*–*f* metals) complexes as well as a few CPs [14–26]. Such ligands are readily prepared from ketone and diamine with the aid of template effects of *d*-block metals, and the resulting compartment compounds (complexes and CPs) are primarily used for the study of magnetochemistry.

Our research group previously prepared three-dimensional Ag–Ln CPs, $[AgLn(3\text{-pca})_2(H_2O)_3](NO_3)_2(H_2O)_4$ (3-Hpca = pyridine-3-carboxylic acid; Ln = Eu, Tb, Nd), from $AgNO_3$ and discrete 4*f* complexes ($[Ln_2(3\text{-pca})_6(H_2O)_4] \cdot \{[Ln_2(3\text{-pca})_4(H_2O)_8](NO_3)_2\}$) as SBUs [27]. We could also synthesize one-dimensional 3*d*–4*f* CPs, $[NiLn(L)(NO_3)_2(4\text{-ppa})(EtOH)]$ (Ln = Nd, Eu; H_2L L = 1,3-bis((3-methoxysalicylidene)amino)propane; 4-Hppa = 4-pyridinepropionic acid), as well as two-dimensional 3*d*–4*f* CPs, $[NiLn(L)(NO_3)_2(4\text{-pca})(H_2O)]$ (Ln = Nd, Eu, Tb; 4-Hpca = pyridine-4-carboxylic acid) from $[NiLn(L)(NO_3)(CH_3CN)(H_2O)_4](NO_3)_2(H_2O)$ as SBUs and the corresponding external pyridyl–carboxylate-type linking ligands (for ligands, see Chart 1) [28,29]. The formation of our CPs can be explained rationally on the basis of a universal hard–soft acid–base (HSAB) concept, which forces the harder *O*-donor atoms of the carboxylate terminal to bind to the *f*-block metals and the softer *N*-donor atoms of the pyridyl terminal to coordinate to the *d*-block metals.

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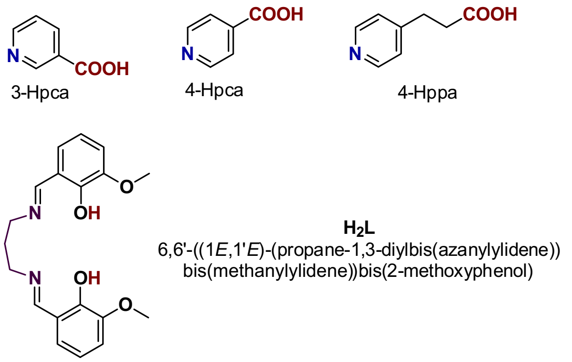

Chart 1. Ligands in this study.

As a continuation of our ongoing study on CPs, we decided to extend the SBU strategy as a synthetic route to prepare Zn–Ln CPs by utilizing two compartment compounds $[ZnLn(L)(NO_3)(CH_3CN)(H_2O)_4](NO_3)_2(H_2O)$ (Ln = Eu, Tb) and pyridyl–carboxylate-type linking ligands (4-Hppa and 4-Hpca). In this paper, we report the synthesis of two 1D and two 2D Zn–Eu and Zn–Tb CPs, together with the emission quenching of the lanthanide ions in these CPs.

2. Experimental

All solvents were distilled, and all solid chemicals were purified by recrystallization. A household microwave oven (Samsung RE-C23RW, 700 W) was used for microwave heating experiments. IR spectra were obtained in the range of 400–4000 cm^{-1} on a Vertex 70 FTIR spectrophotometer. Thermogravimetric analysis (TGA) was performed on a TA4000/SDT 2960 instrument at the Cooperative Center for Research Facilities (CCRF) in Sungkyunkwan University. Elemental analyses were carried out by means of an Elementar Vario EL cube (CCRF). Solid-state luminescent spectra were obtained with a DARSA PRO-5200 SYSTEM (Xenon lamp, 500 W).

Compartment compounds, $[ZnLn(L)(NO_3)(CH_3CN)(H_2O)_4](NO_3)_2(H_2O)$ (Ln = Eu, Tb), were prepared by the literature method, which had been employed to synthesize a dysprosium (Dy) analogue [30,31]. $Ln(NO_3)_3{\cdot}nH_2O$ (2 mmol) was added to [Zn(L)] (0.796 g, 2 mmol) in acetonitrile (10 ml), and the reaction mixture was stirred for 30 min at room temperature. The resulting powder was filtered and air-dried for two days.

2.1. Preparation of $[ZnLn(L)(NO_3)_2(4\text{-}ppa)(EtOH)]$ {Ln = Eu (**1**), Tb (**2**)}

Both compounds were prepared in the same way. An ethanol solution (3 ml) containing 0.016 g (0.106 mmol) of 4-Hppa and 0.096 g of $[ZnLn(L)(NO_3)(CH_3CN)(H_2O)_4](NO_3)_2(H_2O)$ {Ln = Eu (0.110 mmol) or Tb (0.109 mmol)} was microwave-heated (700 W) in a 25 ml Teflon-lined vessel for 1 min. The resulting solution was air-cooled slowly to room temperature, filtered, and allowed to evaporate slowly for four days. The crystals formed were filtered, washed with ethanol (3 ml × 3), and then air-dried.

Data for compound **1** (yellow crystals, 0.026 g, 0.030 mmol, Yield: 28.3%): IR (KBr, cm^{-1}): 813, 1035, 1216, 1299, 1469, 1539, 1635 (C=N). *Anal.* Calc. for $C_{29}H_{34}N_5O_{13}ZnEu$: C, 39.67; H, 3.90; N, 7.98. Found: C, 39.46; H, 3.64; N, 7.92%.

Data for compound **2** (colorless crystals, 0.047 g, 0.053 mmol, Yield: 50.0%): IR (KBr, cm^{-1}): 815, 1066, 1218, 1299, 1471, 1635 (C=N). *Anal.* Calc. for $C_{29}H_{34}N_5O_{13}ZnTb$: C, 39.36; H, 3.87; N, 7.91. Found: C, 38.98; H, 3.90; N, 7.69%.

2.2. Preparation of $[ZnLn(L)(NO_3)_2(4\text{-}pca)(H_2O)]$ {Ln = Tb(**3**), Eu (**4**)}

Both compounds were prepared in the same way. An acetonitrile solution (3 ml) containing 0.096 g of $[ZnLn(L)(NO_3)(CH_3CN)(H_2O)_4](NO_3)_2(H_2O)$ {Ln = Eu (0.110 mmol) or Tb (0.109 mmol)} and 0.015 g (0.122 mmol) of 4-Hpca was microwave-heated for 1 min. The resulting solutions were air-cooled slowly to room temperature, filtered, and then allowed to evaporate slowly for five days for compound **3** and two days for compound **4**. The crystals formed were filtered, washed with ethanol (3 ml × 3), and then air-dried.

Data for compound **3** (yellow crystals, 0.031 g, 0.039 mmol, Yield: 35.5%): IR (KBr, cm^{-1}): 849, 945, 1065, 1223, 1295, 1466, 1626 (C=N). *Anal.* Calc. for $C_{25}H_{24}N_5O_{12}ZnEu$: C, 37.35; H, 3.01; N, 8.71. Found: C, 37.33; H, 2.73; N, 8.59%.

Data for compound **4** (yellow crystals, 0.019 g, 0.023 mmol, Yield: 21.1%): IR (KBr, cm^{-1}): 820, 1224, 1319, 1467, 1639 (C=N). *Anal.* Calc. for $C_{25}H_{24}N_5O_{12}ZnTb$: C, 37.03; H, 2.98; N, 8.64. Found: C, 37.39; H, 2.82; N, 8.69%.

2.3. X-ray structure determination

X-ray data were collected at 296 K for all compounds with a Bruker Smart APEX2 diffractometer (CCRF in Sungkyunkwan University) equipped with a Mo X-ray tube. Collected data were corrected for absorption with the sadabs program based on the Laue symmetry by using equivalent reflections [32]. All calculations were carried out with SHELXTL programs [33]. All four structures were solved by direct methods. All non-hydrogen atoms were refined anisotropically. Details on crystal data, intensity collection, and refinement details are given in Table 1.

A yellow crystal of compound **1** (a block, 0.30 × 0.10 × 0.04 mm), a colorless crystal of compound **2** (a block, 0.25 × 0.12 × 0.06 mm), a yellow crystal of compound **3** (a plate, 0.12 × 0.12 × 0.02 mm), and a yellow crystal of compound **4** (a plate, 0.20 × 0.20 × 0.08 mm) were used for crystal- and intensity-data collection. For compounds **1** and **2**, the OH hydrogen atom in the ethanol ligand was located in difference Fourier maps and refined freely. The remaining hydrogen atoms were generated in idealized positions and refined in a riding mode. In the case of compounds **3** and **4**, the C10 atom in the propylene fragment showed a structural disorder, and the site occupation ratios (C10: C10A) for this disordered atom were best fit to be 0.33:0.67 (**3**) or 0.30:0.70 (**4**). All hydrogen atoms were generated in idealized positions.

3. Results and discussion

3.1. Synthesis of Zn–Eu and Zn–Tb CPs

Scheme 1 summarizes the synthesis of CPs in this study. When Zn–Ln compartment compounds, $[ZnLn(L)(NO_3)(CH_3CN)(H_2O)_4](NO_3)_2(H_2O)$ (Ln = Eu, Tb), were treated with 4-pyridinepropionic acid (4-Hppa) under microwave-heating conditions, the corresponding one-dimensional Zn–Ln CPs were formed: $[ZnLn(L)(NO_3)_2(4\text{-}ppa)(EtOH)]$ (Ln = Eu (**1**), Tb (**2**)). By contrast, the reactions involving pyridine-4-carboxylic acid (4-Hpca) produced two-dimensional CPs, $[ZnLn(L)(NO_3)_2(4\text{-}pca)(H_2O)]$ (Ln = Eu (**3**), Tb (**4**)). Compounds **1** and **2** were prepared in ethanol, whereas compounds **3** and **4** were prepared in acetonitrile. All products were characterized by IR spectroscopy, elemental analysis, TGA, and X-ray diffraction. The C=N (the imine bond in the compartment ligands) stretching frequencies fall in a rather narrow range of 1626–1639 cm^{-1}. As a comparison, C=N absorption bands of