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Synthesis, Structure and Luminescence of Lanthanide Coordination Polymers Based on the 1,3-Bis(carboxymethyl) Imidazolium Salt

Li-Xin You,^a Yang Guo,^a Shi-Yu Xie,^a Shu-Ju Wang,^a Gang Xiong,^a Ileana Dragutan,^{*b} Valerian Dragutan,^b Fu Ding^a and Ya-Guang Sun^{*a}

^a Key Laboratory of Inorganic Molecule-Based Chemistry of Liaoning Province, Shenyang University of Chemical Technology, Shenyang, 110142, China.

^b Institute of Organic Chemistry, Romanian Academy, Bucharest, 060023, Romania.

*Corresponding authors.

E-mail addresses: sunyaguang@syuct.edu.cn (Y.-G. Sun); idragutan@yahoo.com (I. Dragutan)

ABSTRACT

The 1,3-bis(carboxymethyl)imidazolium salt (zwitterion) (HBCI) was reacted, under solvothermal conditions, with rare earth chlorides to provide a series of new two-dimensional (2D) coordination polymers, namely [LnBCI)(HCOO)(H₂O)₂Cl]_n [Ln = Sm (1); Eu (2); Gd (3); Tb (4); Dy (5)]. The complexes were characterized by X-ray single crystal diffraction, powder X-ray diffraction, infrared spectroscopy, elemental analysis and thermogravimetric analysis. Compounds of 1, 2, 4 and 5 exhibit the characteristic luminescence of the corresponding lanthanide ions, due to the 4fⁿ-4fⁿ transition. Furthermore, the fluorescence lifetime of 2 and the phosphorescence spectrum of 5 at 77k are discussed.

Keywords: lanthanide coordination polymers; 1,3-bis(carboxymethyl) imidazolium salt; crystal structure; luminescence.

1. Introduction

Chemical researchers have a strong interest in the study of coordination polymers (CPs) mainly due to the diversity of their structures and wide applications in various fields, such as luminescence,¹⁻⁷ chemical sensing,⁸⁻¹⁰ catalysis,¹¹⁻¹⁵ magnetism,¹⁶⁻¹⁸ gas storage and separation,^{19,20} and drug delivery.^{21,22} Therefore, the synthesis and application of functionalized CPs has become a hot research topic in recent years.²³⁻²⁵ However, the synthesis process of CPs is affected by many factors, such as the structural characteristics of the ligand, the coordination mode of the lanthanide, the ratio ligand to the metal, the reaction temperature, the nature of the solvent, and the pH of the solution.²⁶⁻³¹ Most trivalent lanthanide ions have excellent luminescent properties produced by the 4fⁿ electronic configuration and electronic transitions from the visible to near infrared region of the spectrum. So far, many CPs of lanthanides have been extensively studied and applied.³²⁻³⁶ However, due to the high and variable coordination number of the lanthanide ions and their flexible coordination environment, synthesizing CPs of lanthanides with predictable and controlled geometries still remains challenging.³⁷⁻⁴¹ Therefore, the rational selection of organic ligands is particularly important because it has strong effect on the arrangement of the molecular packing in the formed CPs.³¹⁻³³

As a polycarboxylate, the 1,3-bis(carboxymethyl) imidazolium salt (zwitterion) (HBCI) endowed with two carboxylic groups, may provide, under suitable synthetic conditions, various coordination modes to construct the CPs. In view of the above, we selected the HBCI ligand to react with different lanthanide ions and yield under hydrothermal conditions a series of new 2D CPs, *i. e.* {[Ln(BCI)(HCOO)(H₂O)₂Cl]_n; [Ln = Sm (1); Eu (2); Gd (3); Tb (4); Dy (5)]}. The structures were characterized by single crystal X-ray diffraction analysis, elemental analysis, infrared (IR) spectroscopy and thermogravimetric analysis (TGA). The luminescent properties of 1, 2, 3, 4 and 5 were studied in detail.

2. Experimental section

2.1 Materials

All the chemicals used were of reagent grade and were used without further purification. All syntheses were carried out in 25 mL teflon-lined autoclaves under autogenous pressure. The reaction vessels were filled to approximately 50% volume capacity. The water used in the synthesis was distilled before use.

2.2 Physical measurements

Elemental analyses (C, H, and N) were carried out with a Perkin-Elmer 240C elemental analyzer. FT-IR spectra were recorded on a Nicolet IR-470 spectrometer using KBr pellets. Powder X-ray diffraction (PXRD) patterns of the samples were recorded using an X-ray diffractometer (BRUKER D8 ADVANCE) with Cu K α radiation. Thermogravimetric analysis (TGA) experiments were performed on a NETZSCH TG 209 instrument applying a heating rate of 10 °C min⁻¹. Luminescence spectra were recorded on a FS920 steady state fluorescence spectrometer (Edinburgh Instruments) equipped with a Hamamatsu R928P red-sensitive photomultiplier for the visible range and a germanium detector for the near infrared range. Luminescence decay measurements were taken with a pulsed nitrogen laser (excitation wavelength of 337 nm, pulse length of 800 ps, repetition rate of 1 Hz) and a 1024-channel Intensified CCD (Andor Technology) attached to a 0.5 m monochromator. At 298 K, the luminescence decay curve was obtained using a FLSP920 fluorescence spectrophotometer, and an NF900 lamp was used as an excitation source. For low temperature (77K) measurements, samples were cooled in a liquid nitrogen cryostat (Oxford Instruments), and quantum efficiency (QE) was measured by an integrating sphere at low temperatures by a FLSP920 photoluminescence quantum yield measurement system. Then, the QE was calculated according to the method of the software provided by the manufacturer. The phosphorescence spectrum was measured by FLSP 920 at a low temperature of 77K.

2.3 Synthesis of the 1,3-bis(carboxymethyl)imidazolium ligand (HBCI)

The 1,3-bis(carboxymethyl)imidazolium ligand (HBCI) was prepared according to the reported method.^{42,43} Glycine (3.75 g, 50 mmol), 40% aqueous glyoxal (2.8 mL, 25 mmol), formaldehyde solution (40%; 2.5 mL, 25 mmol) and 20 mL water were placed in a 100 mL round bottom flask and heated at 95 °C for 2h. The resulting solution was left to dry at room temperature to yield colourless crystals. The impurities were removed by washing with water and methanol and dried in the air to obtain colourless, transparent, bulk crystals; yield 77.5%. The crystal data are shown in Table S1. 2.4 Synthesis of complexes 1-5

Compounds 1-5 are synthesized in a similar way, and thus the synthesis method of 1 is taken as a representative example. $SmCl_3 \cdot 6H_2O$ (0.1 mmol, 36.48 mg), HBCI (0.1 mmol, 18.62 mg), DMF (3.0 mL), ethyl alcohol (7.0 mL) and H_2O (2.0 mL) were placed in a 25 mL teflon-lined stainless steel vessel, stirred and heated to 110 °C for 72 h. The reactor was then cooled to room temperature. The impurities were removed by washing with DMF and dried in the air to obtain colorless, transparent, bulk crystals. Anal. Calcd. (%) for 1: C 21.31; H 2.66; N 6.21. Found: C 21.30; H 2.64; N 6.18. Calcd. for 2: C 21.26; H 2.66; N 6.20. Found: C 21.22; H 2.64; N 6.18. Calcd. for 3: C 21.0; H 2.63; N 6.13. Found: C 20.98; H 2.62; N 6.09. Calcd. for 4: C 21.06; H 2.63; N 6.14. Found: C 21.05; H 2.61; N 6.11. Calcd. for 5: C 20.88; H 2.6; N 6.09. Found: C 20.86; H 2.58; N 6.06.

2.5 Single crystal X-ray crystallographic study

The collection of single crystal crystallographic data was carried out on a Bruker SMART Apex CCD diffractometer using graphite-monochromated Mo K α radiation (0.71073 Å) at 293 K in the ω -2 θ scan mode. An empirical absorption correction was applied to the data using the SADABS program.⁴⁴ The structures were solved by direct methods and refined by full matrix least-squares methods on F^2 using the SHELXTL crystallographic software package.^{45,46} All non-H atoms were refined anisotropically. The H atoms were placed in calculated positions and refined using a riding mode. Crystallographic data and structural refinement parameters are shown in Table 1.

Complex	1	2	3	4	5
Formula	$C_8H_{12}SmN_2O_8Cl$	C ₈ H ₁₂ EuN ₂ O ₈ Cl	$C_8H_{12}GdN_2O_8Cl$	$C_8H_{12}TbN_2O_8Cl$	$C_8H_{12}DyN_2O_8Cl$
Fw	450.56	451.61	456.90	455.89	459.72
Temp. (K)	298.15	298.15	298.15	298.15	298.15
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	Cmca	Cmca	Cmca	Cmca	Cmca
<i>a</i> (Å)	17.198(9)	17.204(18)	9.062(9)	17.153(13)	17.100(6)
<i>b</i> (Å)	9.123(5)	9.090(9)	17.183(17)	9.055(7)	9.0295(15)
<i>c</i> (Å)	16.628(8)	16.599(17)	16.490(16)	16.486(13)	16.403(4)
$V(\text{\AA})^3$	2609.0(2)	2596.0(5)	2568.0(4)	2561.0(3)	2532.7(11)
Ζ	8	8	8	8	8
$\rho_c (\mathrm{g \ cm}^{-3})$	2.203	2.287	2.364	2.379	2.128
μ/mm^{-1}	4.549	4.906	5.414	5.118	5.917
<i>F</i> (000)	1680.0	1737.0	1752.0	1956.2	1552.0
Rec/unique	11896/1538	12290/1551	12154/1511	12240/1523	11539/1500
GOF on F^2	1.105	1.112	1.087	1.006	1.089
$R_1^a [I > 2\sigma(I)]$	0.0253	0.0255	0.0261	0.0604	0.0311
$wR_2^b [I > 2\sigma(I)]$	0.0644	0.0658	0.0635	0.1720	0.0773

Table 1. Crystal data and structure refinement of compounds1-5

 $\overline{{}^{a}R_{1}=\Sigma||F_{o}|-|F_{c}||/\Sigma|F_{o}|} \cdot {}^{b}wR_{2} = \{\Sigma[w(F_{o}^{2}-F_{c}^{2})^{2}]/\Sigma[w(F_{o}^{2})^{2}]\}^{1/2}$

3. Results and discussion

3.1 Structure description

X-ray crystal structure analysis showed that **1-5** are isomorphous, and **1** was taken as an example to describe the structural details. Compound **1** belongs to the orthorhombic system, *C*mca space group. As shown in Fig. 1, around the Sm^{3+} ion in **1** there are four BCT ligands, two formate ions and two coordinating water molecules. Each Sm^{3+} ion is coordinated by eight oxygen atoms, four from four different BCT ligands (O3, O3D, O4A and O4B), two from coordinating water molecules (O5 and O5D) and two from the formate ions (O1 and O2C). The formate ions derive from decomposition of the DMF solvent at the high temperature of the hydrothermal synthesis.⁴⁷ Therefore, centering on the Sm^{3+} ion, the coordination environment can be considered as the geometry of a twisted double-capped triangular prism. The length of the Sm-O bonds is 2.388(5)-2.561(7) Å, the average bond length is 2.452(1) Å, and the O-Sm-O bond angle range is 69.43(2)°-144.5 (2)°.



Fig. 1. The coordination environment of the Sm(III) ion in **1** (hydrogen atoms and free ions are omitted for clarity). Symmetry codes: (A) 1-*x*, 1-*y*, 1-*z*; (B) 1-*x*, *y*, *z*; (C) 1-*x*, 1.5-*y*, 0.5+*z*, (D) *x*, 1-*y*, 1-*z*.



Fig. 2. (a) Schematic illustration of the 1D chain structure in 1; (b) 2D network of 1; (c) Sm dimers in 1 are represented by purple balls; (d) The topology of 1.

Each BCI⁻ ligand links to four Sm³⁺ ions in the coordination mode of $[(\kappa_1-\kappa_1-\mu_2)-(\kappa_1-\kappa_1-\mu_2)-\mu_4]$. Two adjacent Sm³⁺ ions are connected by the carboxyl group to form a binuclear structure. The distance between two Sm³⁺ ions is 4.6124(2) Å. The Sm dimers were linked by the BCI⁻ ligands to form one-dimensional (1D) chain, as shown in Fig. 2(a). The 1D chains are connected by formate ions to form a two-dimensional (2D) network, as shown in Fig. 2(b). In addition, the Sm dimers are considered as nodes (purple balls), while the BCI ligands (blue lines) and formate ions (yellow lines) are considered as connectors, as shown in Fig. 2(c). The TOPOS 4.0 software was used to describe the topology of **1** as a 2D network with the Schläfli symbol $\{3^6.4^6.5^3\}$, as shown in Fig. 2(d). 3.2 Infrared Spectroscopy

Infrared spectra were collected in order to detect and characterize the functional groups of HBCI, NaBCl and compounds 1-5 (Fig. S1 in ESI). Since the results for 1-5 are similar, the infrared absorption spectra characteristics of these compounds are illustrated taking compound 1 as an example. The broadband centered at v = 3432 cm⁻¹ can be assigned to the -OH stretching vibration, indicating the presence of water molecules in the structure of 1. As expected, the (C=O) and (C-OH) absorption bands of HBCI, at 1690 and 1253 cm⁻¹, are not found in the spectrum of 1; the absence of the (C-OH) absorption indicates that the ligand is completely deprotonated when it is coordinated to the lanthanide ions. The absorption bands at 1630 cm⁻¹ and 1312 cm⁻¹ are due to the tensile modes of v_{asym}(COO⁻) and v_{sym}(COO⁻) with the difference of $\Delta v = 318$ cm⁻¹. The Δv value of 1 was greater than that of the ionic NaBCI ($\Delta v = 240$ cm⁻¹). This indicates that the compound 1 adopts the monodentate coordination mode. All results are consistent with the coordination mode of the carboxyl group given by the single crystal test.

3.3 Powder X-ray diffraction (PXRD) and thermogravimetric analysis (TGA)

Powder X-ray diffraction (PXRD) analyses of **1-5** have been performed at room temperature (Fig. S2, ESI). The patterns for **1-5** are in good agreement with the calculated ones, obtained from the single-crystal structures, thus confirming that purities equal those of the single crystal samples.

Compounds 1-5 were subjected to thermogravimetric analysis (TGA) in a N₂ atmosphere, at a heating rate of 10 $^{\circ}$ C min⁻¹, aiming to study their structural integrity and stability (Fig. S3, ESI). Compounds 1-5 exhibited a similar thermal behaviour, and thus 1 was used as example. The TGA curve indicates that the process of mass loss of 1 proceeds in two stages. The first weight loss, from 150 to 220 $^{\circ}$ C, was about 6.5% which was assigned to the loss of two coordinating water molecules (calculated value: 7.9%). The second weight loss began to collapse at a heating temperature greater than 310 $^{\circ}$ C, quickly and significantly losing weight due to the destruction of the organic ligands. TGA showed that 1-5 have a certain structural stability.

3.4 Luminescence

The trivalent lanthanides have excellent fluorescent properties, especially the Sm³⁺, Eu³⁺, Tb³⁺ and Dy³⁺ ions. Photoluminescence of solid samples of the compounds **1**, **2**, **4** and **5** was tested with a FL-1000 fluorometer at room temperature. As shown in Fig. 3, compound **1** was excited at 375 nm and peaked at 565 nm, 600 nm, 647 nm and 704 nm. This is due to the transition of the excited state ${}^{4}G_{5/2}$ to the low energy levels ${}^{6}H_{5/2}$, ${}^{4}G_{5/2} \rightarrow {}^{6}H_{7/2}$, ${}^{4}G_{5/2} \rightarrow {}^{6}H_{9/2}$ and ${}^{4}G_{5/2} \rightarrow {}^{6}H_{11/2}$. The emission intensity at 600 nm and 647 nm is slightly stronger. The emission spectrum is dominated by a ${}^{4}G_{5/2} \rightarrow {}^{6}H_{9/2}$ transition with galvanic polarity. When excited at 405 nm compound **2** exhibited the characteristic emission peaks of the three Eu³⁺ ions at 591 nm, 612 nm and 703 nm, assigned to ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ is a magnetic dipole transition, and ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ is a dipole transition, emitting red light. Compound **4**, excited by 365 nm, exhibits typical Tb³⁺ sharp emission peaks at 488 nm, 544 nm, 587 nm, and 623 nm, assigned to ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ transition,

Journal Pre-proof

which emits green light. At 331 nm excitation, compound **5** displayed the typical emission bands of Dy^{3+} at 481 nm, 574 nm, 664 nm, and 750 nm, due to the transition of the excited state ${}^{4}F_{9/2}$ to the low energy levels ${}^{6}H_{15/2}$, ${}^{6}H_{13/2}$, ${}^{6}H_{11/2}$ and ${}^{6}H_{9/2}$.



Fig. 3. Emission spectra of compounds 1, 2, 4 and 5.

In addition to the steady-state emission, we also investigated the fluorescence lifetime and quantum yield of compound **2**. The decay curve of the ${}^{5}D_{0}$ Eu³⁺ complex was studied by monitoring the emission at 368 nm and the result is shown in Fig 4. It was found that the decay curve of Eu³⁺ can be fitted to a double index. The emission decay lifetime was τ_1 =210 µs (11%), τ_2 =540 µs (89%). Barium sulfate was chosen as reference, and the quantum efficiency of **2** was measured to be 6.47%.



Fig. 4. Fit attenuation curve for solid composite **2**. The sample was excited at 365 nm. Fitted by Fit = $A + B1 \times exp(-t/\tau_1) + B2 \times exp(-t/\tau_2)$.

Usually, the emission phosphorescence spectrum for the Gd³⁺complexes allows the identification of the lowest triplet state of the ligand. Obviously, the singlet energy level (S_1) of the HBCI ligand is 32258 cm⁻¹ (310 nm) (Fig. S4, ESI). The lowest triplet excited state (T_1) of HBCI was 22727 cm⁻¹ (440 nm)(Fig. 5), which was significantly higher than ${}^{4}G_{5/2}$ level of Sm³⁺(17900 cm⁻¹), ${}^{5}D_0$ level of Eu³⁺ (17300 cm⁻¹), ${}^{5}D_4$ level of Tb³⁺ (20500 cm⁻¹) and ${}^{4}F_{9/2}$ level of Dy³⁺ (21000 cm⁻¹). This phenomenon indicates that HBCI can act as an antenna for the photosensitization of trivalent lanthanides, transferring energy through T_1 state to the excited states of lanthanide ions. The energy gap $\Delta E(S_1-T_1)$ for HBCI is 9531 cm⁻¹. It shows that the intersystem crossing is effective in HBCI.



Fig 5. Phosphorescence spectra of compound **5** in the solid-state, at low-temperature (77 K). The excitation spectra monitored the emission at 440 nm while the emission spectra were recorded upon excitation at 310 nm.

4. Conclusions

Five new two-dimensional lanthanide coordination polymers based on the 1,3-bis(carboxymethyl) imidazolium salt (zwitterion) were prepared under solvothermal conditions, fully characterized, and their properties studied with emphasis on their luminescence. Compounds **2** and **4** show respectively the typical bright red and green luminescence assigned to the $4f^{n}$ - $4f^{n}$ transition in Eu³⁺ and Tb³⁺. The fluorescence lifetime of **2** is shortened by a non-radiative decay due to the presence of coordinated water molecules. The singlet excited state (32258 cm⁻¹) and the lowest triplet state energy level (22727 cm⁻¹) of HBCI were calculated based on this ligand and the phosphorescence spectrum of its Gd³⁺ complex (**3**) at 77 K, showing an substantial energy transfer from the HBCI ligand to the lanthanide ions. Our coordination polymers integrating lanthanides may find applications in advanced therapies implying antibacterial or anticancer agents.

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Appendix A. Supplementary material

CCDC Nos. 1904893-1904896 and 1915613, contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10......

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Research highlights

- ► Five 2D CPs [LnBCI)(HCOO)(H₂O)₂Cl]_n were prepared and characterized
- ▶ 1,3-Bis(carboxymethyl)imidazolium salt (zwitterion)(HBCI) was used as organic linker
- Compounds 1, 2, 4 and 5 show luminescence of the trivalent lanthanides
- ► The energy transfer processes of the Ln CPs were investigated

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Synthesis, Structure and Luminescence of Lanthanide Coordination

Polymers Based on the 1,3-Bis(carboxymethyl) Imidazolium Salt

Li-Xin You,^a YangGuo,^a Shi-Yu Xie,^a Shu-Ju Wang,^a Gang Xiong,^a Ileana Dragutan,^{*b} Valerian Dragutan,^b Fu Ding^a and Ya-Guang Sun^{*a}

Five 2D coordination polymers, namely $[LnBCI)(HCOO)(H_2O)_2Cl]_n$ [Ln = Sm (1); Eu (2); Gd(3); Tb (4); Dy (5)] [HBCI = 1,3-bis(carboxymethyl)imidazolium salt] were prepared and structurally characterized. Luminescence properties of 1, 2, 4 and 5, fluorescence lifetime of 2 and the phosphorescence spectrum of 5 are discussed.