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Structures and standard molar enthalpies of formation of a series of Ln(III)–Cu(II) heteronuclear compounds with pyrazine-2,3-dicarboxylic acid



Qi Yang, Gang Xie, Qing Wei, Sanping Chen^{*}, Shengli Gao

Key Laboratory of Synthetic and Natural Functional Molecule Chemistry of Ministry of Education, College of Chemistry and Materials Science, Northwest University, Xi'an, Shaanxi 710069, China

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ABSTRACT

Fifteen lanthanide–copper heteronuclear compounds, formulated as $[\text{CuLn}_2(\text{pzdc})_4(\text{H}_2\text{O})_6] \cdot x\text{H}_2\text{O}$ (**1–6** ($x=2$), **8** ($x=3$), **9–10** ($x=4$)); $[\text{CuLn}_2(\text{pzdc})_4(\text{H}_2\text{O})_4] \cdot x\text{H}_2\text{O}$ (**7**, **12–13**, **15** ($x=4$), **14** ($x=5$), **11** ($x=8$)) (Ln (III)=La(**1**); Ce(**2**); Pr(**3**); Nd(**4**); Sm(**5**); Eu(**6**); Gd(**7**); Tb(**8**); Dy(**9**); Ho(**10**); Er(**11**); Tm(**12**); Yb(**13**); Lu(**14**); Y(**15**); H_2pzdc ($\text{C}_6\text{H}_4\text{N}_2\text{O}_4$)=pyrazine-2,3-dicarboxylic acid) have been hydrothermally synthesized. All compounds were characterized by element analysis, IR spectroscopy, single-crystal X-ray diffraction and thermal analysis. X-ray diffraction analyses confirm that all compounds are isostructural and feature a 3D brick-like framework structure with $\{4.6^2\}_2\{4^2.6^2.8^2\}\{6^3\}^2\{6^2.8\}_2$ topology. Using 1 mol cm^{-3} HCl (aq) as calorimetric solvent, with an isoperibol solution–reaction calorimeter, the standard molar enthalpies of formation of all compounds were determined by a designed thermochemical cycle. In addition, solid state luminescence properties of compounds **5**, **6**, **8** and **9** were studied in the solid state.

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1. Introduction

In recent years, much research work have been devoted to designing and constructing $3d$ – $4f$ heterometallic coordination polymers based on the notion of crystal engineering, not only due to their fascinating architectures, but also because of their potential applications in magnetism, luminescence, molecular adsorption, ion exchange and separation [1–9]. In these studies, organic ligands containing mixed-donor atoms, such as pyridinecarboxylate, carbonyl, cyanide, amino acid, etc., were often selected to construct discrete, or infinite, structural compounds [10–14]. However, the construction of such frameworks is still a formidable task due to the variable and versatile coordination numbers of the $4f$ metal ions, their low stereochemical preference and also because of competitive reactions between $3d$ and $4f$ metals coordinated to the same organic ligands. Nevertheless, fortunately, according to the hard–soft acid base theory, $3d$ and $4f$ metal ions can easily bind to the ligands containing O- and N-donor atoms, which thus provide the impetus to construct novel heterometallic coordination frameworks with intriguing structural motifs and useful properties [15–18].

We are currently interested in constructing $3d$ – $4f$ heterometallic coordination polymers by solvo-thermal reactions, and have found that

rigid aromatic dicarboxylate ligands containing nitrogen atoms are excellent structural members around which to entrain infinite lattices. Pyrazine-2,3-dicarboxylic acid is such a potential multidentate ligand, which displays diversiform coordination fashions proving by previous essays [19–21]. It is a multifunctional ligand with both nitrogen and oxygen donor atoms; the carboxylate group and the neighboring nitrogen atom can chelate lanthanide ions, while the nitrogen atoms on the opposite site may bond soft transition metal ions.

The datum of the standard molar enthalpy of formation plays an important role in theoretical study, application development and industrial production of a compound as a basis of theoretical analysis. In spite of that, to our best knowledge, there is little reliable experimental data available for the $3d$ – $4f$ compounds.

Herein, we report 15 Ln(III)–Cu(II) coordination compounds with pyrazine-2,3-dicarboxylic acid ligand, which have been characterized by IR spectroscopy, elemental analysis, single crystal diffraction, thermal decomposition and luminescence. Furthermore, the standard molar enthalpies of formation of these compounds have been determined.

2. Experimental section

2.1. Syntheses and characterization of Ln(III)–Cu(II) compounds

All reagents were of reagent grade and used as commercially purchased without further purification. All the compounds were

^{*} Corresponding author. Tel./fax: +86 2988302604.

E-mail addresses: sanpingchen312@gmail.com, sanpingchen@126.com (S. Chen).

synthesized by a similar procedure. Here, compound **1** was employed as a representative. A mixture of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.017 g, 0.1 mmol), $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ (0.074 g, 0.2 mmol) and H_2pzdc (0.067 g, 0.4 mmol) in H_2O (8 mL) was sealed in a 15 mL Teflon-lined stainless autoclave and heated at 433 K under autogenous pressure for 4 days, then cooled at the rate of 5 K h^{-1} to room temperature and blue block crystals were obtained.

Elemental analyses were carried out with an Elementar Vario EL III analyzer. IR spectra were recorded with a Bruker FT-TR instrument as KBr pellets ($4000\text{--}400 \text{ cm}^{-1}$). Thermogravimetric measurements were performed with a Netzsch STA449C apparatus under a static air atmosphere with a heating rate of 10 K min^{-1} from 303 to 773 K. Luminescent spectra were measured using a Hitachi F-4500 fluorescence spectrometer for the solid powder samples under room temperature. UV–visible spectra were recorded with HITACHI U-3010 spectrophotometer.

2.2. X-ray crystallography

Single crystal X-ray experiments were performed on a Bruker Smart Apex CCD diffractometer equipped with graphite monochromatized $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) using ω and φ scan mode. All structures were solved by direct methods and refined with full-matrix least-squares refinements based on F^2 using SHELXS-97 and SHELXL-97 [22,23]. All non-H atoms were located using subsequent Fourier-difference methods. In all cases hydrogen atoms were placed in calculated positions and thereafter allowed to ride on their parent atoms. Other details of crystal data, data collection parameters and refinement statistics are given in Table 1. Selected bond lengths and bond angles of all compounds are listed in Table S1. Hydrogen bond interactions of all compounds are listed in Table S2.

2.3. Calorimetric experiment

The liquid phase reactions of pyrazine-2,3-dicarboxylic acid with $\text{LnCl}_3 \cdot n\text{H}_2\text{O}$ and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ were similar. Here, compound **1**, namely $[\text{CuLa}_2(\text{C}_6\text{H}_2\text{N}_2\text{O}_4)_4(\text{H}_2\text{O})_6] \cdot 2\text{H}_2\text{O}$, was employed as a representative.

The 1 mol dm^{-3} HCl (aq) solvent can dissolve all components of the reaction (6) in the designed thermochemical cycle, as shown in Fig. 1, and its concentration of $1.0004 \text{ mol dm}^{-3}$ was determined by titration with standard sodium carbonate. With the use of its density of 1.019 g cm^{-3} (taken from chemical handbook [24]), its concentration can also be expressed as the form of $\text{HCl} \cdot 54.561\text{H}_2\text{O}$. The molar enthalpies of solution of $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ (s), $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (s), $\text{C}_6\text{H}_4\text{N}_2\text{O}_4$ (s), $[\text{CuLa}_2(\text{C}_6\text{H}_2\text{N}_2\text{O}_4)_4(\text{H}_2\text{O})_6] \cdot 2\text{H}_2\text{O}$ (s) in corresponding solvents were measured, respectively. In all these determinations, strict control of the stoichiometries in each step of the calorimetric cycle must be observed, with the objective that the dissolution of the reactants give the same composition as those of the products.

According to Hess's law, $\Delta_r H_m^\ominus(6)$ can be calculated according to the following equation:

$$\Delta_r H_m^\ominus(6) = \Delta_s H_m^\ominus(1) - \Delta_s H_m^\ominus(2) - \Delta_s H_m^\ominus(3) - \Delta_s H_m^\ominus(4) - \Delta_s H_m^\ominus(5) \quad (1)$$

The standard molar enthalpy of formation of $[\text{CuLa}_2(\text{C}_6\text{H}_2\text{N}_2\text{O}_4)_4(\text{H}_2\text{O})_6] \cdot 2\text{H}_2\text{O}$ can be obtained by the values of $\Delta_r H_m^\ominus(6)$ in combination with the standard molar enthalpies of formation of $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ (s), $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (s), $\text{C}_6\text{H}_4\text{N}_2\text{O}_4$ (s), HCl (aq) and H_2O (l).

All the enthalpies of solution were measured with an RD496-2000 heat conduction microcalorimeter (Mianyang CP Thermal Analysis Instrument Co., Ltd., China), which was a totally automatic instrument by using a computerized control that has been described in detail previously [25]. The total time required for the complete

dissolution reaction was about 0.5 h. There were no solid residues observed after the reactions in each calorimetric experiment.

To check the performance of the calorimeter, the enthalpy of solution of KCl (mass fraction ≥ 0.9999) in deionizer water was determined to be $(17.563 \pm 0.099) \text{ kJ mol}^{-1}$, which was in agreement with that of $(17.524 \pm 0.028) \text{ kJ mol}^{-1}$ reported in the literature [26]. This shows that the device used for measuring the enthalpy of solution in this work is reliable.

3. Results and discussion

3.1. Description of the structure

Single crystal X-ray diffraction analyses reveal that the 15 compounds crystallize in the monoclinic crystal system, space group $P21/c$ and they take on two structural types: I (compounds **1–6** and **8–10**) and II (compounds **7** and **11–15**). The coordination environments of Cu(II) are identical in the two types. As for Ln(III), it presents a tricapped triangular prism configuration in type I, while it shows a dicapped triangular prism configuration in type II. The difference is just caused by the number of coordination waters. All compounds present 3D brick-like structures. Here, compound **1** is employed as a representative to be described in detail and the coordination environment of Cu(II) and La(III) is shown in Fig. 2a.

As shown in Fig. 2a, Cu(II) ion displays a hexacoordinated configuration with distorted octahedral geometry, featuring the contribution of two carboxylate oxygens and two nitrogens from two pzdc^{2-} ligands and two carboxylate oxygens from two pzdc^{2-} ligands. The corresponding bond lengths of Cu–O and Cu–N are $1.979(4)\text{--}2.431(4) \text{ \AA}$ and $1.984(5) \text{ \AA}$, respectively, which are located in the normal range. The coordination environment of La(III) ion is the best described as a tricapped triangular prism (Fig. 2b), featuring the contribution of two oxygen atoms and two nitrogen atoms from two pzdc^{2-} ligands, two oxygen atoms from two pzdc^{2-} ligands and three oxygen atoms from three coordinated waters. The resulting La–O and La–N bond lengths are in the range of $2.419(4)\text{--}2.625(5) \text{ \AA}$ and $2.821(5)\text{--}2.830(5) \text{ \AA}$, respectively, which are consistent with those of reported literature [27].

In compound **1**, the pzdc^{2-} ligand display two coordination modes, as depicted in Scheme 1, which is the same as that of reported Ln(III)–Zn(II) compounds [28]. As shown in Fig. 3, the adjacent La(III) ions are bridged by the pzdc^{2-} ligands in mode I into 2D zigzag layers in ac plane. Meanwhile, every two pzdc^{2-} ligands connect two Cu(II) ions in mode II into 1D chain along a -axis. The distances of $\text{La} \cdots \text{La}$ are in the range of $6.614\text{--}8.317 \text{ \AA}$ and $\text{La} \cdots \text{Cu}$ are 6.995 \AA . Noticeable, there exist face-to-face $\pi\text{--}\pi$ stacking interactions with distance of 3.650 \AA between adjacent pyrazine rings in the 1D chains and 2D layers. As shown in Fig. 4a, the 1D chains link above mentioned 2D layers to form a 3D brick-like structure with a cavity size of $20.663 \times 8.317 \text{ \AA}$ (the distances between the metal centers). Lattice water molecules occupy the cavities and produce hydrogen bonding interactions with oxygen atoms from the carboxyl and the coordinated water molecules, which play an important role in the stability of the entire structure. From the viewpoint of network topology, the 3D structure can be simplified by the Schläfli symbol $\{4.6^2\}_2\{4^2.6^2.8^2\}\{6^3\}^2\{6^5.8\}_2$ based on Cu(II) as a 4-connecting node, La(III) as a 3-connecting node and pzdc^{2-} ligand as a 3-connecting node, as shown in Fig. 4b.

3.2. PXRD, IR and TG of compound **1**

Because of the similarity of all the compounds, a representative example of compound **1** is discussed here. Fig. 5 shows the powder

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