



# Five novel lanthanide complexes with 2-chloroquinoline-4-carboxylic acid and 1,10-phenanthroline: Crystal structures, molecular spectra, thermal properties and bacteriostatic activities



Ye Wang<sup>a, b</sup>, Cheng-Wei Jin<sup>a, b</sup>, Shu-Mei He<sup>a</sup>, Ning Ren<sup>c, \*\*</sup>, Jian-Jun Zhang<sup>a, b, \*</sup>

<sup>a</sup> Testing and Analysis Center, Hebei Normal University, Shijiazhuang, 050024, PR China

<sup>b</sup> College of Chemistry & Material Science, Hebei Normal University, Shijiazhuang, 050024, PR China

<sup>c</sup> College of Chemical Engineering & Material, Handan College, Handan, 056005, PR China

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## ABSTRACT

Five novel lanthanide complexes  $[\text{Ln}_2(2\text{-ClQL})_6(\text{phen})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$  ( $\text{Ln} = \text{Pr}(1), \text{Sm}(2), \text{Eu}(3), \text{Ho}(4), \text{Er}(5)$ ); 2-ClQL: 2-chloroquinoline-4-carboxylate; phen: 1,10-phenanthroline; were synthesized by conventional solution method at room temperature and characterized via elemental analysis, powder x-ray diffraction, Infrared spectroscopy and Raman spectrometry. The results indicate that complexes 1–5 are isostructural, and each  $\text{Ln}^{3+}$  ion is eight-coordinated adopting a distorted square antiprismatic molecular geometry. Binuclear complex 1 are stitched together via hydrogen bonding interactions to form 1D chains, and further to form 2D sheets by the  $\pi$ - $\pi$  interactions. Luminescence investigation reveals that complex 3 displays strong red emission. TG/DTG-FTIR, reveal the thermal decomposition processes and products of title complexes. The bacteriostatic activities of the complexes were evaluated against *Candida albicans*, *Escherichia coli*, and *Staphylococcus aureus*.

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## 1. Introduction

The synthesis and study of lanthanide complexes are one of the very active and charming fields, according to their structural diversity as well as their potential properties [1–4]. Lanthanide cations have the unique optical, electrical, and magnetic properties, but the properties can be changed and improved to be applied to more wider fields through the interactions between lanthanide cations and carboxylic acid ligands [5]. The rare earth complexes exert various and select inhibitions against the plant pathogenic fungi [6], and also have good bacteriostatic activity against *Candida albicans* [7]. In addition, magnet [8], catalysis, gas separation and storage [4], electroluminescent materials [9] and sensors [10] properties have been discovered to be utilized as functional materials.

Aromatic carboxylic acids are usually selected as the conjugated organic ligands, given that they have good light absorptivity and

strong coordination capability to the lanthanide cations [11]. Quinoline carboxylic acid and some of its derivatives are known as the effective chelator, and can be chosen as the sensitizing chromophore and linker to incorporate lanthanide cations into the applicative materials [10,12,13]. However, lanthanide complexes with quinoline carboxylic acid have been fewer reported [14]. So there is a good chance for us to examine the reaction product of lanthanide cations and quinoline carboxylic acid. The bidentate N-donor phen is a rigid, planar, and electron-poor heteroaromatic system [15], and is also an excellent antenna unit for lanthanide luminescence [16], performing the good coordination ability as the second ligand.

Herein we choose 2-chloroquinoline-4-carboxylic as the carboxylic acid ligand, and 1,10-phenanthroline as auxiliary ligand to validly sensitize the lanthanide metal cations to assemble five novel hybrid compounds  $[\text{Ln}_2(2\text{-ClQL})_6(\text{phen})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$  ( $\text{Ln} = \text{Pr}(1), \text{Sm}(2), \text{Eu}(3), \text{Ho}(4), \text{Er}(5)$ ); 2-ClQL = 2-chloroquinoline-4-carboxylate; phen = 1,10-phenanthroline). The 2-chloroquinoline-4-carboxylic has never been used to coordinate with lanthanide cations as the first ligand in previous reports, and that maybe is a new trial for us. There are the 1D, 2D supramolecular structures between the units of lanthanide complexes and uncoordinated water molecules, which has been hardly reported. Previously,

\* Corresponding author. Testing and Analysis Center, Hebei Normal University, Shijiazhuang, 050024, PR China.

\*\* Corresponding author.

E-mail address: [jjzhang@mail.hebtu.edu.cn](mailto:jjzhang@mail.hebtu.edu.cn) (J.-J. Zhang).

binary lanthanide complex  $[\text{Eu}_2(\text{hq})_6(\text{H}_2\text{O})_4] \cdot 8\text{H}_2\text{O}$  with the hydroxyquinoline carboxylate has been reported, and more water molecules were coordinated with the  $\text{Eu}^{3+}$ , resulting the less luminescence property and weak heat stability [10]. In addition, the thermal decomposition processes were studied by the TG/DTG-FTIR technology. The Raman spectra, luminescence spectrum for complex 3 and bacteriostatic activities of the title complexes against *Candida albicans*, *Escherichia coli*, and *Staphylococcus aureus* were also studied.

## 2. Experimental

### 2.1. Materials and methods

$\text{LnCl}_3 \cdot 6\text{H}_2\text{O}$  were acquired by the reaction of  $\text{Ln}_2\text{O}_3$  ( $\text{Ln} = \text{Pr}, \text{Sm}, \text{Eu}, \text{Ho}, \text{Er}$ , Beijing Lanthanide Innovation Technology Co., Ltd, 99.9%) and hydrochloric acid aqueous solution in the condition of water bath heating at a constant temperature of 353.15 K, followed by evaporation of the liquid. The other analytically pure chemicals were purchased and used without further purification.

### 2.2. Equipment and conditions of the experiment

Analyses for C, H, N in the corresponding complexes were carried out via Vario-EL II element analyzer and the percentage of the lanthanide cations were obtained by EDTA titrimetric analysis. The data of single crystal X-ray diffraction were collected on a Smart-1000 diffractometer with graphite-monochromatic  $\text{Mo K}\alpha$  ( $\lambda = 0.71073 \text{ \AA}$ ) at the temperature of 298(2) K. The structures were solved using the SHELXS-97 program (direct methods) and refined by the full-matrix least-squares on  $F^2$  using the SHELXL-97 program. Powder X-ray diffraction identification was carried out by a Bruker D8 ADVANCE X-ray diffractometer in a scanning range of  $5\text{--}50^\circ$  ( $2\theta$ ) with graphite-monochromatic  $\text{Cu K}\alpha$  ( $\lambda = 1.54178 \text{ \AA}$ ) at 298(2) K. IR spectra was measured on a Bruker TENSOR27 spectrometer at a resolution of  $4 \text{ cm}^{-1}$  with KBr medium pellets in the range of  $4000\text{--}400 \text{ cm}^{-1}$ , and scanned 32 times. The Raman spectra were measured by a Bruker VERTEX-70 FTIR-RAMANII equipped with a liquid nitrogen cooling-InGaAs with Nd:YAG laser ( $k = 1.064 \text{ lm}$ ) with 400 mW power operating at a resolution of  $4 \text{ cm}^{-1}$  over the range of  $50\text{--}4000 \text{ cm}^{-1}$ , and scanned 100 times. TG/DTG-FTIR analyses were performed with a heating rate of  $10 \text{ K min}^{-1}$  using a NETZSCH STA 449 F3 instrument under a simulated air atmosphere (There are three flow rate tubes:  $\text{N}_2$  flow rate:  $30 \text{ mL min}^{-1}$ ;  $\text{N}_2$  flow rate:  $20 \text{ mL min}^{-1}$ ;  $\text{O}_2$  flow rate:  $10 \text{ mL min}^{-1}$ ) with a Bruker TENSOR27 Fourier transform infrared spectrometer. The ETZSCH STA 449 F3 instrument was linked to the heated gas cell of the FTIR instrument by means of a heated transfer line kept at 473 K. The bacteriostatic activity of  $\text{LnCl}_3 \cdot 6\text{H}_2\text{O}$ , ligands and title complexes on *Candida albicans*, *Escherichia coli*, and *Staphylococcus aureus* have been determined at the temperature of 303.15 K with three respective concentrations:  $8 \times 10^{-3} \text{ mol L}^{-1}$ ,  $16 \times 10^{-3} \text{ mol L}^{-1}$  and  $32 \times 10^{-3} \text{ mol L}^{-1}$ , and the filter diameter is 6 mm, the sample volume of the complexes is  $5 \mu\text{L}$ . Luminescence spectra were measured on an F-4600 Hitachi Spectrophotometer.

### 2.3. Synthesis

Dissolve 2-ClQL (0.6 mmol) and phen (0.2 mmol) in ethanol (95%) and adjust the solution at the pH of 5–7 with the prepared NaOH solution (1 mol/L). Add the mixed ligands solution to  $\text{LnCl}_3 \cdot 6\text{H}_2\text{O}$  (0.2 mmol) aqueous solution under stirring. Make it stirring for 6 h and deposit it for 12 h. Then filter out precipitates and wash it with 95% ethanol. Make it dried in a far infrared dryer. At last, the powders of target complexes were obtained and the

green platy single crystals were acquired through the method of solvent extraction at room temperature after about two weeks. Element analysis: calcd (%) for  $\text{C}_{84}\text{H}_{54}\text{Cl}_6\text{N}_{10}\text{O}_{16}\text{Pr}_2$ : C, 51.63; H, 2.786; N, 7.065; Pr, 14.42. Found: C, 51.37; H, 2.731; N, 7.169; Pr, 14.15. calcd (%) for  $\text{C}_{84}\text{H}_{54}\text{Cl}_6\text{N}_{10}\text{O}_{16}\text{Sm}_2$ : C, 51.14; H, 2.759; N, 7.099; Sm, 15.24. Found: C, 51.06; H, 2.742; N, 7.104; Sm, 15.13. calcd (%) for  $\text{C}_{84}\text{H}_{54}\text{Cl}_6\text{N}_{10}\text{O}_{16}\text{Eu}_2$ : C, 51.06; H, 2.754; N, 7.088; Eu, 15.38. Found: C, 50.97; H, 2.681; N, 7.075; Eu, 15.33. calcd (%) for  $\text{C}_{84}\text{H}_{54}\text{Cl}_6\text{N}_{10}\text{O}_{16}\text{Ho}_2$ : C, 50.39; H, 2.719; N, 6.997; Ho, 16.47. Found: C, 50.65; H, 2.686; N, 7.205; Ho, 16.50. calcd (%) for  $\text{C}_{84}\text{H}_{54}\text{Cl}_6\text{N}_{10}\text{O}_{16}\text{Er}_2$ : C, 50.28; H, 2.712; N, 6.980; Er, 16.67. Found: C, 50.20; H, 2.670; N, 7.149; Er, 16.58.

## 3. Results and discussion

### 3.1. Crystal structure

Single crystal X-ray diffraction analysis reveals that complex 1 is binuclear with the  $\text{Pr}\cdots\text{Pr}$  distance is  $4.2264(10) \text{ \AA}$  and crystallizes in the monoclinic space group  $P2(1)/c$  (Table 1). The asymmetric unit contains one unique  $\text{Pr}^{3+}$ , which is coordinated by one bidentate phen, one water molecule and three 2-chloroquinoline-4-carboxylate ligands adopting the coordination of bridging bidentate and monodentate models, as showing in Fig. 1a. Each  $\text{Pr}^{3+}$  cation is coordinated with eight atoms adopting a distorted square antiprismatic molecular geometry (Fig. 1b). The bond distances of  $\text{Pr1-O}$  for monodentate 2-chloroquinoline-4-carboxylate (O5) and coordinated water (O7) are  $2.381(9) \text{ \AA}$  and  $2.487(8) \text{ \AA}$ , respectively. Four oxygen atoms (O2, O3, O4, O5) from bridging bidentate 2-chloroquinoline-4-carboxylate are coordinated with praseodymium at the distance of  $2.412(10)$ ,  $2.493(9)$ ,  $2.416(9)$  and  $2.415(9) \text{ \AA}$ . The average  $\text{Pr-N}$  bond distance for the phen molecule is  $2.633 \text{ \AA}$ , which is obviously to found that the distance of  $\text{Pr-N}$  is longer than the distances of  $\text{Pr-O}$ , which is also according with the process of thermal decomposition (Table 2).

As shown in Fig. 2a, the binuclear units are stitched together via two independent and moderate  $\text{OH}\cdots\text{O}$  hydrogen bonding interactions [17–19] (Table 3) to form a supramolecular 1D chain along the z axis direction. One is between uncoordinated water molecules and the neighboring uncoordinated water molecules at the distance of  $3.141 \text{ \AA}$ , and the other is between binuclear structures and uncoordinated water molecules at the distance of  $2.100 \text{ \AA}$ , respectively. These chains are further extended to 2D sheet in the yz plane (Fig. 2b) through slightly offset  $\pi\text{--}\pi$  interactions [15,20] between the centroid of the moiety of phen on one unit and the edge of the quinoline carboxylic acid ring on the neighboring unit with the relevant distances and angles:  $\text{Cg}\cdots\text{Cg}\cdots 3.6255(2) \text{ \AA}$ ;  $\text{Cg1}\cdots\text{Cg1}\cdots 3.6728(3) \text{ \AA}$ ;  $\beta = 77.643^\circ$ . In brief, hydrogen bonding interactions are the main forces responsible for the solid state crystal in the 1D chain. The hydrogen bonding interactions and  $\pi\text{--}\pi$  interactions exist in 2D structures and the centroid-centroid distances of  $\pi\text{--}\pi$  interactions are present.

At 2012, Junwei Ye et al. have reported the structure of  $[\text{Pr}_2(\text{QUIN})_4(\text{phen})_2(\text{NO}_3)_2(\text{H}_2\text{O})_2]$  (QUIN: quinoline-2-carboxylic acid; phen: 1,10-phenanthroline) [19]. It is binuclear with the  $\text{Pr}\cdots\text{Pr}$  distance of  $5.872 \text{ \AA}$  and crystallizes in the triclinic space group  $P\bar{1}$ , which is different from the complex 1. Each  $\text{Pr}^{3+}$  cation of complex  $[\text{Pr}_2(\text{QUIN})_4(\text{phen})_2(\text{NO}_3)_2(\text{H}_2\text{O})_2]$  is nine-coordinated and the  $\text{Pr-N}$  bonds distances are in the range of  $2.697\text{--}2.804 \text{ \AA}$ , which is longer than the  $\text{Pr-N}$   $2.618 \text{ \AA}$  and  $2.648 \text{ \AA}$ . The QUIN adopts two kinds coordination models: bidentate and bridging bidentate and the complex form 1D, 3D supramolecular structures via  $\text{OH}\cdots\text{N}$ ,  $\text{OH}\cdots\text{O}$  and  $\text{OH}\cdots\text{C}$  hydrogen bonding interactions. The difference of the two complexes may be the influence of  $\text{NO}_3^-$  negative ions and the difference of substitution position of carboxylic acid. Xiao-

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