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Metal–organic frameworks constructed from monomeric, dimeric and trimeric phenanthroline citrate zinc building units

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Abstract

Adduct of mononuclear and dinuclear citrate zinc complex $[\text{Zn}(\text{Hcit})(\text{phen})(\text{H}_2\text{O})][\text{Zn}_2(\text{Hcit})(\text{phen})_2(\text{H}_2\text{O})_3] \cdot 13.5\text{H}_2\text{O}$ (**1**) and its aggregate $[\text{Zn}_3(\text{Hcit})_2(\text{phen})_4]_n \cdot 14n\text{H}_2\text{O}$ (**2**) (H_4cit = citric acid, phen = 1,10-phenanthroline) were synthesized in weak acidic solutions. The former was obtained from the reaction of zinc nitrate, citric acid and phenanthroline in a molar ratio of 3 : 2 : 3, while a slightly excess of phenanthroline results in the formation of the polymeric product **2** in a molar ratio of 3 : 2 : 4. Transformation of **1** to **2** was finished by the reaction of **1** with an equimolar of phenanthroline in 72% yield. Reverse conversion of **2** to **1** is obtained in 77% yield, showing an equilibrium between **1** and **2**. Neutral compound **1** consists of one monomeric anionic unit $[\text{Zn}(\text{Hcit})(\text{phen})(\text{H}_2\text{O})]^-$ and one dimeric cationic unit $[\text{Zn}_2(\text{Hcit})(\text{phen})_2(\text{H}_2\text{O})_3]^+$ that connect each other by strong hydrogen bonds $[\text{O}6 \cdots \text{O}4_w \text{ } 2.636(2); \text{O}7 \cdots \text{O}3_w \text{ } 2.630(3) \text{ \AA}]$. In **2**, the citrate ligand links each trinuclear unit $[\text{Zn}_3(\text{Hcit})_2(\text{phen})_4]$ to generate an infinite 1D chain that extends into a 3D supramolecular structure by intra- and inter-molecular hydrogen bonds. Moreover, **1** and **2** exhibit strong fluorescence at room temperature.

Keywords

Zinc; Citric acid; Crystal structure; Mixed ligands; Interconversion

Carboxylate–metal complexes have been investigated over the last few years due to their interesting coordination chemistry, unusual structural features, remarkable physical and chemical properties, and potential applications as dyes, extractants, drugs, pesticides, catalysts, [1–4]. The rational design and synthesis of novel metal carboxylates with structural diversity are still of great challenge. Several factors such as the coordination nature of metal ions [5], counteranions [6], solvents [7], metal-to-ligand ratio [8], pH value [9], and reaction temperature [10] have been found to influence the structures of metal–organic coordination compounds. Hydroxypolycarboxylic acids can act not only as hydrogen-bond acceptors, but also as hydrogen-bond donors to form extended structures by means of additional hydrogen-bond interactions. Citric acid, an α -hydroxytricarboxylic acid, has been widely known for its abundance in physiological fluids and its chemical versatility

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toward transition metal ions. The diverse coordination modes of citrate contribute largely to the formation of various structural types for transition metal citrates, such as mononuclear, dinuclear and polynuclear structural units [11–15]. 1,10-Phenanthroline is an example of N-donor chelating bidentate ligand. It can efficiently provide π - π stacking interactions in either intra- or intermolecular mode. This feature contributes the stability of structures as well as the formation of extended supramolecular structures [16]. These two ligands can simultaneously coordinate with metal ions and provide further intermolecular interactions that allow the formation of supramolecular arrays. In addition, d^{10} metal (such as Zn^{II} and Cd^{II}) complexes exhibit not only appealing structures but also photoluminescent properties [17,18]. In this paper, we reported the syntheses, spectroscopic properties, crystal structures and interconversion of two citrate phenanthroline mixed-ligand complexes $[\text{Zn}(\text{Hcit})(\text{phen})(\text{H}_2\text{O})][\text{Zn}_2(\text{Hcit})(\text{phen})_2(\text{H}_2\text{O})_3] \cdot 13.5\text{H}_2\text{O}$ (**1**), $[\text{Zn}_3(\text{Hcit})_2(\text{phen})_4]_n \cdot 14n\text{H}_2\text{O}$ (**2**) with different metal-to-ligand molar ratio.

The syntheses of **1** and **2** were carried out in warm aqueous solutions [19]. The synthetic conditions for **1** and **2** are very similar except for the different metal-to-ligand molar ratio. The reaction with $\text{Zn}(\text{NO}_3)_2/\text{H}_4\text{cit}/\text{phen}$ molar ratio of 3 : 2 : 3 results in the formation of **1**, but the reaction with ratio of 3 : 2 : 4 forms a new coordination polymer **2** with 1D chain. Moreover, polymer **2** could be obtained in 1 : 1 : 1 ratio. Further standing of the reaction mixture will lead to crystallization of **1** on the surface of **2**. Compound **1** also crystallized out from the filtrate after **2** was removed, indicating an equilibrium between the two complexes. Transformation of **1** to **2** could be finished by the reaction of **1** with an equimolar of phenanthroline in 72% yield at pH 5.1. Meanwhile, **2** could be transformed to **1** with the addition of zinc nitrate and citric acid at pH 5.3, as shown in Scheme 1. The interconversion between **1** and **2** showed that the metal-to-ligand molar ratio plays a key role in the formations of citrate phenanthroline zinc complexes [19].

The crystal structure of **1** [20] consists of a monomeric anionic unit $[\text{Zn}(\text{Hcit})(\text{phen})(\text{H}_2\text{O})]^-$ (**1a**), a dimeric cationic unit $[\text{Zn}_2(\text{Hcit})(\text{phen})_2(\text{H}_2\text{O})_3]^+$ (**1b**) and crystallized water molecules, as shown in Figures 1a and 1b. Zinc ions are six-coordinated and show similar distorted octahedral coordination geometries $[\text{ZnO}_4\text{N}_2]$. Zn1 and Zn2 are surrounded by three oxygen atoms from α -hydroxy, α -carboxy and β -carboxy groups of citrate, two nitrogen atoms from phenanthroline and one water molecule. Zn3 ion is surrounded by two nitrogen atoms from phenanthroline and two water molecules, and the two oxygen atoms from one β -carboxy group of citrate, containing a weak coordinated Zn3–O14 bond [2.747(2) Å]. The other Zn–O distances range from 2.006(2) to 2.263(2) Å, and the Zn–N distances vary from 2.112(2) to 2.158(2) Å (Table S1). These bond distances around Zn ions are comparable to those previously reported for zinc(II) complexes of α -hydroxycarboxylate and N-donor ligands (Table S3) [13,21–25]. Careful comparisons show that zinc complex $[\text{Zn}_2(\text{Hmal})(\text{phen})\text{Cl}]_n$ (H_3mal = malic acid) reported recently contains an unusual coordination of malate with α -alkoxy, α -carboxy and β -carboxy groups, in which the α -hydroxy group is deprotonated [13].

The Zn2 and Zn3 cations in **1** are connected by citrate ligand to form a dimeric unit $[\text{Zn}_2(\text{Hcit})(\text{phen})_2(\text{H}_2\text{O})_3]^+$ (**1b**). The discrete monomeric unit $[\text{Zn}(\text{Hcit})(\text{phen})(\text{H}_2\text{O})]^-$ (**1a**) and dimeric unit $[\text{Zn}_2(\text{Hcit})(\text{phen})_2(\text{H}_2\text{O})_3]^+$ (**1b**) are linked together by strong double hydrogen bonds between the uncoordinated β -carboxy group in **1a** and the coordinated water molecules O3w and O4w in **1b** [O6...O4w 2.636(2), O7...O3w 2.630(3) Å]. The monomeric unit **1a** is connected each other by strong interlaced hydrogen bonds between the uncoordinated water molecule O1w and the oxygen atom O2 of coordinated α -carboxy group [O1w...O2a 2.678(2) Å, $a-x, 1-y, 1-z$], which forms a hexameric zinc unit. The oxygen atom O5 of β -carboxy group in **1a** further forms strong hydrogen bond with the

uncoordinated water molecule O2w in **1b** [O5...O2w 2.727(3) Å, $b \perp x, y, z$]. This results in the formation of an infinite chain along b-axis (Fig. S1).

Structural analysis [20] reveals that **2** is a one-dimensional coordination polymer with trinuclear subunits. In the asymmetric unit of **2**, there are three zinc atoms, two citrate ligands, and four phenanthroline ligands (Fig. 2a). The Zn1 atom is six-coordinated by four oxygen atoms and two nitrogen atoms in a distorted octahedral coordination geometry. Among the above-mentioned oxygen atoms, three are from α -hydroxy, α -carboxy and β -carboxy groups of one citrate anion, and one is from β -carboxy groups of the other citrate ligand, with Zn–O distances ranging from 2.009(2) to 2.230(2) Å. The two nitrogen atoms are from one phenanthroline ligand with Zn–N distances ranging from 2.126(2) to 2.170(2) Å. The Zn2 center is five-coordinated by two nitrogen atoms from one phenanthroline ligand [Zn–N 2.081(2)–2.126(2) Å], two oxygen atoms from hydroxy and α -carboxy groups of one citrate ligand [Zn–O 2.001(2)–2.143(2) Å], and one oxygen atom from the bridging β -carboxy group of the other citrate ligand [Zn2–O5 = 1.970(2) Å] in a distorted trigonal bipyramidal geometry. Interestingly, there exists a strong intramolecular hydrogen bond between the coordinated hydroxy oxygen atom O8 and the oxygen atom O13 of uncoordinated β -carboxy group in the citrate ligand [O8...O13 2.533(3) Å]. The Zn3 center is six-coordinated by four nitrogen atoms from two chelate phenanthroline [Zn–N, 2.120(2) to 2.170(2) Å] and two oxygen atoms from the β -carboxy group of one citrate ligand [Zn–O, 2.155(2) to 2.240(2) Å] in a distorted octahedron. Especially, two oxygen atoms of one β -carboxy group coordinate to Zn(II) ion forming a four-member ring with a O11–Zn3–O12 angle of 59.50(7)°. The trinuclear units are further expanded to form a 1D chain by the linkage of monodentate β -carboxy groups of the citrate (Fig. 2b). The bond distances around all zinc atoms are comparable to those of zinc(II) complexes with α -hydroxycarboxylate and N-donor ligands previously reported (Table S3) [22,24,26,27]. The citrate ligand exhibits an interesting connection mode with zinc ions. One citrate group acts as a tridentate-monodentate ligand bridging three Zn ions, while the other acts as a bidentate-bidentate ligand bridging to the two Zn ions. In addition, the 1D chains are connected by intermolecular hydrogen bonds to generate a 3D supramolecular structure (Fig. S2).

The IR spectra of **1** and **2** (Fig. S3) show characteristic bands of carboxylate groups. The peaks at 1624, 1604, 1585 and 1428, 1412, 1386 cm⁻¹ for **1**, 1624, 1603, 1587 and 1428, 1394, 1385, 1369 cm⁻¹ for **2** correspond to ν_{asym} and ν_{sym} of the coordinated carboxy groups, respectively. The absence of IR absorption bands around 1700 cm⁻¹, attributed to protonated carboxylic acid group, indicates the full deprotonation of citric acid in **1** and **2**, as revealed by the structural analysis. The IR spectra of **1** and **2** are similar, however, there exist considerable differences in several regions, as shown in Fig. S4. Based on these differences, the reversible transformation between **1** and **2** are traced by IR spectra respectively (Fig. S5 and S6). The results show that the conversion from **1** to **2** processes much quickly than that from **2** to **1**. The adduct of monomer and dimer **1** can be transformed into coordination polymer **2** in 5 hrs at 60 °C, while the reverse conversion from **2** to **1** is finished in more than two days at 60 °C.

Thermogravimetric analysis (TGA) was performed to gauge the thermal stability of the complexes. The experiments were performed on the crystal samples of **1** and **2** under nitrogen atmosphere with a heating rate of 10 °C/min⁻¹ (Fig. S7 and S8). The weight losses of **1** corresponding to the release of the lattice and coordinated water molecules are observed from 35 and 155 °C. The anhydrous composition begins to decompose at 200 °C. The TGA curve of **2** shows it undergoes dehydration between 33 and 135 °C. The decomposition of the anhydrous composition occurs at 225 °C.

The solid-state fluorescent properties of **1** and **2** were investigated at room temperature. The emission spectra are given in Fig. 3. Upon excitation at 335 nm, **1** exhibits strong fluorescent emission bands at 372 and 385 nm. Upon excitation at 338 nm, **2** exhibits strong fluorescent emission bands at 378 and 397 nm. Compared to the free phen ligand (362 and 380 nm, $\lambda_{\text{ex}} = 340$ nm) (Fig. S9), the emission bands of **1** and **2** are red shifted (10 and 5 nm for **1**, 16 and 17 nm for **2**). As reported in the literatures [28,29], these emission bands of **1** and **2** are probably assigned to intraligand fluorescent emission. In addition, the red-shifts of the emissions may be attributed to effect of metal coordination [30].

In summary, two zinc(II) compounds have been synthesized from the reactions of zinc nitrate with citrate and phenanthroline in aqueous solution. The structural analysis displays that slightly changing the metal-to-ligand molar ratio leads to the different structures. **1** is an adduct with a monomeric anionic unit $[\text{Zn}(\text{Hcit})(\text{phen})(\text{H}_2\text{O})]^-$ and a dimeric cationic unit $[\text{Zn}_2(\text{Hcit})(\text{phen})_2(\text{H}_2\text{O})_3]^+$, which are linked by strong hydrogen bonds. **2** exhibits a one-dimensional coordination polymer chain structure with trinuclear subunits, linked by the monodentate β -carboxy groups of citrate ligands. In addition, **1** and **2** can be converted reversably and exhibit strong fluorescence at room temperature in the solid state.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Appendix A. Supplementary material

Supplementary data associated with this article, including view of supramolecular structure, IR spectra, TG plots, solid-state emission spectrum of phenanthroline, can be found, in the online version, at doi:XXX.

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19. Synthesis of **1**: Citric acid (0.42 g, 2.0 mmol) and 1,10-phenanthroline (0.59 g, 3.0 mmol) were added to a stirred solution of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.89 g, 3.0 mmol) in water (50 ml). The pH of the solution was adjusted to 5.1 with dilute ammonium hydroxide. The mixture was heated in a water bath at 60 °C for about four days. During heating, a small amount of white floccule appeared from the solution (IR spectrum of the floccule was identical to the crystal sample of **1**). The mixture was cooled to room temperature and left standing for several days to give colorless transparent prism crystalline product of **1** suitable for X-ray diffraction. The products were isolated by filtration and dried in air. Yield: 1.27 g (89%). IR (KBr, cm^{-1}): 3415_{s,br}, 1624_s, 1604_s, 1585_s, 1519_m, 1428_s, 1412_s, 1386_m, 1346_{vw}, 1306_w, 1272_w, 1225_{vw}, 1201_{vw}, 1146_w, 1105_w, 1076_w, 851_m, 727_s, 643_w, 618_w; *Anal. Calc.* for $\text{C}_{48}\text{H}_{69}\text{N}_6\text{O}_{31.5}\text{Zn}_3$: C, 40.3; H, 4.9; N, 5.9. Found: C, 40.3; H, 4.6; N, 5.7 (%). Synthesis of **2**: Citric acid (0.42 g, 2.0 mmol) and 1,10-phenanthroline (0.79 g, 4.0 mmol) were added to a stirred solution of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.89 g, 3.0 mmol) in water (50 ml). The pH of the solution was adjusted to 5.5 with dilute ammonium hydroxide. The mixture was heated in a water bath at 60 °C for four days, and the blocklike colorless crystals of **2** appeared from the warm solution. The products were isolated by filtration and dried in air. Yield: 1.0 g (65%). IR (KBr, cm^{-1}): 3406_{s,br}, 2923_w, 1624_s, 1603_s, 1587_{vw}, 1519_m, 1428_s, 1394_m, 1385_s, 1369_{vw}, 1342_{vw}, 1285_w, 1257_w, 1225_w, 1196_w, 1145_w, 1105_w, 1084_w, 1065_w, 1047_w, 852_s, 727_s, 670_w, 626_w; *Anal. Calc.* for $\text{C}_{60}\text{H}_{70}\text{N}_8\text{O}_{28}\text{Zn}_3$: C, 46.6; H, 4.6; N, 7.2. Found: C, 47.1; H, 4.4; N, 7.1 (%). Transformation of **1** to **2**: A mixture of **1** (72.0 mg, 0.05 mmol) and 1,10-phenanthroline (9.9 mg, 0.05 mmol) in water (10 ml) was heated in a water bath at 60 °C for four days, and the blocklike colorless crystals of **2** (55.8 mg, 72%) appeared from the warm solution. Positive identification of the crystalline product as **2** came from the IR spectrum and the X-ray unit-cell determinations carried out by single-crystal structural analysis. Transformation of **2** to **1**: A mixture of **2** (77.4 mg, 0.05 mmol), $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (14.9 mg, 0.05 mmol) and citric acid (7.0 mg, 0.033 mmol) in water (10 ml) was stirred for 20 min and the pH of the mixture was adjusted to 5.3 with dilute ammonium hydroxide. The mixture was heated in a water bath at 60 °C for about four days. During heating, a small amount of white floccule appeared from the mixture. The resulting mixture was cooled to room temperature and left standing for a couple of weeks to give colorless transparent prism crystalline product of **1** (73.2 mg, 77%). Positive identification of the crystalline product as **1** came from the IR spectrum and the X-ray unit-cell determinations carried out by single-crystal structural analysis.
20. Crystal data for **1** $\text{C}_{48}\text{H}_{69}\text{N}_6\text{O}_{31.5}\text{Zn}_3$, $M = 1430.20$, triclinic, P , $a = 13.1152(3)$ Å, $b = 15.2828(4)$ Å, $c = 16.6633(5)$ Å, $\alpha = 77.760(2)^\circ$, $\beta = 80.800(2)^\circ$, $\gamma = 67.590(2)^\circ$, $V = 3005.9(1)$ Å³, $T = 173$ K, $Z = 2$, $D_c = 1.580$ g·cm⁻³, $R(000) = 1482$, 34050 reflections collected, 13054 unique ($R_{\text{int}} = 0.0309$), $\text{GOF} = 0.936$, final R indices [$I > 2\sigma(I)$]: $R_1 = 0.037$, $wR_2 = 0.091$; R indices [all data]: $R_1 = 0.058$, $wR_2 = 0.095$. For **2**: $\text{C}_{60}\text{H}_{70}\text{N}_8\text{O}_{28}\text{Zn}_3$, $M = 1547.35$, monoclinic, $P2_1/c$, $a = 17.6782(6)$ Å, $b = 26.370(1)$ Å, $c = 13.6688(4)$ Å, $\beta = 95.370(3)^\circ$, $V = 6344.0(4)$ Å³, $T = 173$ K, $Z = 4$, $D_c = 1.620$ g·cm⁻³, $R(000) = 3200$, 30044 reflections collected, 13621 unique ($R_{\text{int}} = 0.0335$), $\text{GOF} = 0.932$, final R indices [$I > 2\sigma(I)$]: $R_1 = 0.039$, $wR_2 = 0.085$; R indices [all data]: $R_1 = 0.067$, $wR_2 = 0.090$. CCDC deposition numbers for **1** and **2** are CCDC 710611 and 710612.
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Fig. 1a. ORTEP plot of the monomeric anionic unit $[\text{Zn}(\text{Hcit})(\text{phen})(\text{H}_2\text{O})]^-$ (**1a**) at the 30% probability level.

Fig. 1b.
ORTEP plot of the dimeric cationic unit $[Zn_2(Hcit)(phen)_2(H_2O)_3]^+$ (**1b**) at the 30% probability level.

Fig. 2a.
ORTEP plot of the unit in $[\text{Zn}_3(\text{Hcit})_2(\text{phen})_4]_n \cdot 14n\text{H}_2\text{O}$ (**2**) at the 30% probability level.

Fig. 2b.
View of the helical chains in **2** along *b*-axis.

Fig. 3.
Solid-state emission spectra of **1** and **2** at room temperature.

Scheme 1.
Interconversion between **1** to **2**.