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$[\text{Zn}(\text{H}_2\text{cit})(\text{H}_2\text{O})]_n$

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Synthesis and crystal structure of a zinc citrate complex $[\text{Zn}(\text{H}_2\text{cit})(\text{H}_2\text{O})]_n$

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A zinc citrate coordination complex, $[\text{Zn}(\text{H}_2\text{cit})(\text{H}_2\text{O})]_n$ (**1**), was prepared from $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and citric acid at $\text{pH} = 1.5\text{--}3.0$ in aqueous solution. The complex was characterized by elemental analyses, IR spectroscopy and X-ray crystallography. The Zn(II) ion in complex **1** exists in an octahedral coordination environment. The citrate binds Zn(II) tridentately via its α -hydroxyl, α -carboxylate and one of the β -carboxylate groups. Complex **1** forms a chiral helical chain running along the α axis of the crystal via two bridged oxygens of the α -carboxylate group. The interconversions of different zinc citrate complexes in aqueous solution show their pH-dependent patterns.

Keywords: Citric acid; Crystal structure; pH-dependent; Zinc

1. Introduction

Citric acid, an α -hydroxyl tricarboxylic acid, has diverse physiological roles in bacteria, as well as in higher organisms [1, 2], is central to the citric acid cycle and forms complexes with many metal ions, increasing solubility, bioavailability, and subsequent absorption [3 and references therein]. This function of the citrate ion is directly related to its metal-chelating capacity, with multimodal coordination to various metal ions of biological significance, including Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , and Zn^{2+} . In materials chemistry, as a multidentate ligand, citric acid can circumvent the problem of preferential precipitation of metal ions from aqueous media leading to homogeneous metal citrate precursors, which are technologically important in producing high-tech materials [4, 5].

There has been sustained interest in studying zinc citrate complexes by spectroscopic and structural characterizations [6–10], stemming from their bioavailability and extensive application in preparation zinc-based oxide materials [11, 12]. Efforts have been made to isolate and structurally characterize Zn(II) citrate complexes. However, only three complexes $(\text{NH}_4)_4[\text{Zn}(\text{Hcit})_2]$ [8], $[\text{Zn}(\text{H}_2\text{O})]_{2n}[\text{Zn}(\text{Hcit})_2]_n$ [9], and

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$[\text{C}(\text{NH}_2)_3]_8[\text{Zn}_4(\text{cit})_4] \cdot 8\text{H}_2\text{O}$ [10] were structurally characterized. Formation of metal citrate complexes is frequently influenced by pH, mole ratio, temperature, and concentration of the reactants [13]. By control of the reaction conditions, it is possible to prepare complexes with specific structures. To better understand formation of zinc citrate complexes influenced by pH, we report herein a polymeric zinc citrate complex, $[\text{Zn}(\text{H}_2\text{cit})(\text{H}_2\text{O})_2]_n$ (**1**), at low pH and studied the interconversions of different zinc citrate complexes in aqueous solution.

2. Experimental

All manipulations were carried out in air. Chemicals were analytical reagents and used without purification. $[\text{Zn}(\text{H}_2\text{O})]_{2n}[\text{Zn}(\text{Hcit})_2]_n$ (**2**) [8] and $(\text{NH}_4)_4[\text{Zn}(\text{Hcit})_2]$ (**3**) [7] were prepared according to literature procedures. Infrared spectra were recorded as Nujol mulls between KBr plates using a Nicolet 360 FT-IR spectrometer. Elemental analyses were performed using an EA 1110 elemental analyzer. Luminescent spectra for the solid samples of **1** and **2** were recorded at room temperature on a Hitachi F-4500 spectrometer.

2.1. Preparation of $[\text{Zn}(\text{H}_2\text{cit})(\text{H}_2\text{O})]_n$ (**1**)

$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (3.10 g, 10 mmol) was slowly added to a stirred aqueous solution of citric acid monohydrate (2.10 g, 10 mmol); half an hour later, the pH of the reaction mixture was carefully adjusted to 2.0 by adding sodium hydroxide (4 M) and heated at 60°C. On the following day, colorless crystals precipitated. The products were collected, washed with water three times and air dried to give **1** (1.91 g, 70%). C and H elemental analyses for $\text{C}_6\text{H}_8\text{O}_8\text{Zn}$: Found (Calcd): C, 26.08 (26.33); H, 2.85 (2.95). IR (KBr, cm^{-1}): 3469 s, 3393 s, 1735 s, 1606 vs, 1549 vs, 1475 w, 1419 vs, 1394 s, 1327 m, 1284 m, 1260 m, 1155 w, 1074 s, 890 w, 583 m, 545 m.

2.2. pH-dependent interconversion of **1** and **3**

$[\text{Zn}(\text{H}_2\text{cit})(\text{H}_2\text{O})]_n$ (**1**) (2.73 g, 10 mmol) was suspended in 5 mL water. The pH was maintained at 7.0 with ammonia (1 : 1) until **1** was completely dissolved. The resulting solution was filtered and the filtrate was left at room temperature. Three days later crystalline material came out of the solution and was isolated by filtration and washed with ethanol (95%) three times. Positive identification of the crystalline material as complex **3** came from the IR spectrum. The yield was 30% (1.55 g).

Under similar reaction conditions, **3** (3.07 g, 5 mmol) converts into **1** by adjusting the pH to 2.0 with dilute hydrochloric acid. The IR spectrum of the isolated crystals was identical to that of **1**. The yield was 48% (1.23 g).

2.3. X-ray data collection and structural determination

A crystal of **1** was measured on a Bruker Smart Apex CCD diffractometer with graphite monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 296 K. The data were corrected

for Lorentz and polarization effects. An absorption correction was applied using the SADABS program [14]. The structures were primarily solved by direct methods using SHELXS-97 [15] and refined by full-matrix least-squares procedures with anisotropic thermal parameters for all non-hydrogen atoms. All calculations were performed on a microcomputer using SHELXL-97 [16]. H atoms were located from a difference Fourier map and refined isotropically. Summaries of crystallographic data for **1** are given in table 1. Selected bond distances and angles of the complexes are listed in table 2.

3. Results and discussion

3.1. Syntheses and interconversions

Syntheses of three zinc citrate complexes were carried out in aqueous solutions under slightly different conditions. In these specific reactions, the products do not depend on the ligand-to-metal ratio; despite 1:1 ligand/metal ratio in both reactions, **1** has a 1:1 ligand/metal composition, while a 2:3 ligand/metal complex was achieved for **2**. Scheme 1 illustrates the sensitivity of the reactions toward pH. Compared with the sensitivity to pH, reactions of zinc ions and citric acid toward temperature is not obvious, since **1** and **3** can be isolated from aqueous solution at room temperature or under heat.

To investigate interconversions of the isolated zinc citrate complexes, **1** was suspended in water at 60°C, and the pH was gradually adjusted to 7.0 by ammonia; precipitation with alcohol led to the isolation of **3**. Conversely, when **3** was suspended in

Table 1. Crystal data summary for **1**.

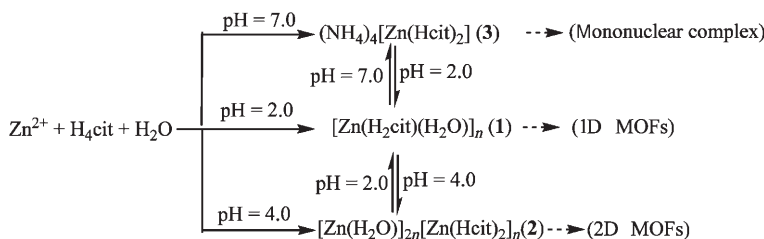
Empirical formula	C ₆ H ₈ O ₈ Zn
Formula weight	273.49
Crystal system	Orthorhombic
Crystal size (mm ³)	0.27 × 0.17 × 0.15
Crystal color	Colorless
Cell constants:	
Unit cells and dimensions (Å)	
<i>a</i>	5.9314(4)
<i>b</i>	10.3966(6)
<i>c</i>	13.4315(8)
<i>V</i> (Å ³)	828.27(9)
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁
Formula units/unit cell	4
<i>D</i> _{Calcd} (g cm ⁻³)	2.193
<i>F</i> (000)	552
Diffractometer/radiation (Å)	0.71073
Reflections collected/unique	4990/1912 [<i>R</i> _(int) = 0.0839]
Data/restraints/parameters	1912/5/148
θ range (°)	2.48–28.16
Goodness-of-fit on <i>F</i> ²	1.065
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.040, 0.093
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.040, 0.093
Largest diff. peak and hole (e Å ⁻³)	1.794, -0.420

Note: $R_1 = \Sigma |F_o| - |F_c| / \Sigma (|F_o|)$, $wR_2 = \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]^{1/2}$.

Table 2. Selected bond distances (Å) and angles (°) for **1**.

Zn(1)–O(1)	2.042(2)	Zn(1)–O(2)	2.288(2)			
Zn(1)–O(4)	2.108(2)	Zn(1)–O(2a)	2.031(2)			
Zn(1)–O(3b)	2.083(3)	Zn(1)–O(1w)	2.079(3)			
O(1)–Zn(1)–O(2)	73.30(9)	O(1)–Zn(1)–O(4)	87.52(9)			
O(1)–Zn(1)–O(1w)	89.4(1)	O(1)–Zn(1)–O(2a)	176.7(1)			
O(1)–Zn(1)–O(3b)	90.79(9)	O(2)–Zn(1)–O(4)	80.57(9)			
O(2)–Zn(1)–O(1w)	91.8(1)	O(2)–Zn(1)–O(2a)	104.78(7)			
O(2)–Zn(1)–O(3b)	163.25(9)	O(2a)–Zn(1)–O(3b)	91.4(1)			
O(4)–Zn(1)–O(1w)	172.3(1)	O(4)–Zn(1)–O(2a)	94.8(1)			
O(4)–Zn(1)–O(3b)	93.8 (1)	O(1w)–Zn(1)–O(2a)	88.0(1)			
O(1w)–Zn(1)–O(3b)	93.26(11)					
Hydrogen bonds	O1...O5c	2.613(3)	179(5)	O6...O5d	2.668(3)	173(4)
	O1w...O4e	2.870(4)	154(4)	O1w...O7f	2.738(4)	174(4)

Notes: Symmetry transformation for **1**: (a) $x + \frac{1}{2}, -y + \frac{1}{2}, -z$; (b) $x + 1, y, z$; (c) $-x + 1, -\frac{1}{2} + y, \frac{1}{2} - z$; (d) $-x + \frac{1}{2}, -y, z + \frac{1}{2}$; (e) $x + \frac{1}{2}, \frac{1}{2} - y, -z$; (f) $x + \frac{1}{2}, -y - \frac{1}{2}, -z$.



water and the pH of the resulting solution was decreased to 2.0 with dilute hydrochloric acid, **3** converted into **1**.

Complex **1** in the crystalline state is almost insoluble in water and common organic solvents such as ethanol and acetone, even after heating. The interconversion of **1** and **3** provided insight into the linkage of Zn(II) citrate complexes in aqueous media, albeit detailed processes of the interconversions are in need of further perusal.

3.2. Description of the crystal structure

Single-crystal X-ray structural analysis revealed that **1** crystallizes in a chiral space group $P2_12_12_1$. On the basis of analysis of the Flack parameter (-0.007), the configuration of **1** is Δ s.

Each Zn(II) in **1** exists in an octahedral environment, surrounded by citrate and a water (figure 1). The six apexes of the coordination octahedron are one citrate that employs both the α -hydroxyl and α -carboxylate oxygens and one β -carboxylate oxygen to bind Zn(II), occupying three coordination positions. Two additional citrate ligands from two adjacent octahedral Zn(II) ions coordinate to Zn(II) through the oxygens of their α -carboxylate groups, occupying two coordination sites. The remaining coordination site is occupied by water. However, the uncoordinated β -carboxylic acid group of the citrate is protonated, participating in hydrogen bonding [O6...O5iv, 2.668(4) Å].

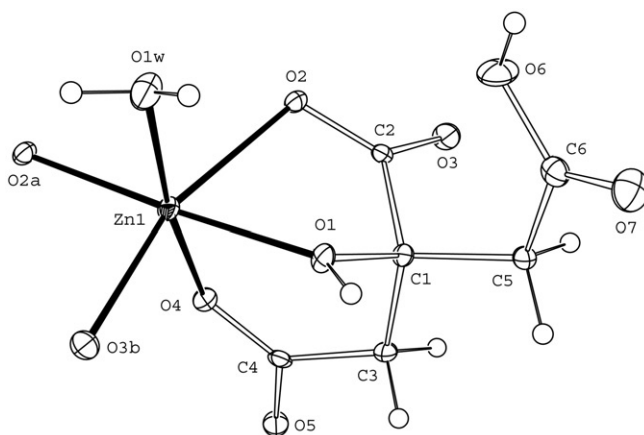


Figure 1. ORTEP plot of the unit in $[\text{Zn}(\text{H}_2\text{cit})(\text{H}_2\text{O})]_n$ (**1**) with 30% probability levels.

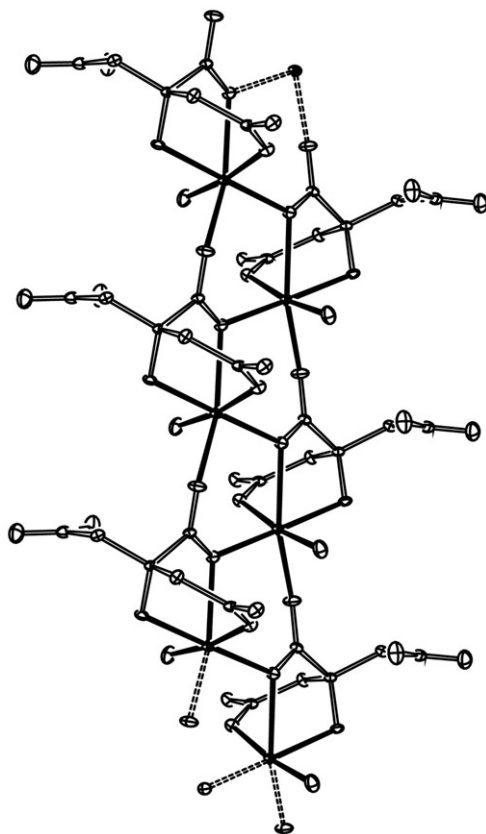


Figure 2. ORTEP plot of **1**, depicting the helical chain propagating along the *a* axis. Hydrogen atoms have been omitted for clarity.

Moreover, the bonded O2 of the α -carboxylate group is further coordinated to an adjacent Zn(II), and O3 of this α -carboxylate group is also bonded to another Zn(II). Adjacent molecules are linked by a screw axis to form a helical chain running along the a axis of the crystal (figure 2). The orientation of the carboxyl groups is remarkably flexible. Neighboring chains are consolidated into a three-dimensional (3-D) structure by hydrogen bonds (as shown in figure 3). This coordination of citrate is also observed in $[\text{Cd}(\text{H}_2\text{cit})(\text{H}_2\text{O})]_n$ [17], $[\text{Mn}(\text{H}_2\text{cit})(\text{H}_2\text{O})]_n$ [18] and $[\text{Co}(\text{H}_2\text{cit})(\text{H}_2\text{O})]_n$ [13(k)].

The Zn–O distances for **1** from 2.031(2) to 2.288(2) Å are very similar to the previously reported zinc citrate complex $(\text{NH}_4)_4[\text{Zn}(\text{Hcit})_2]$ [2.052(2)–2.164(2) Å] [7]. Of the angles in the two octahedral Zn1 ions, the O1–Zn1–O2 angle is 73.30(9) in **1**. This small angle is similar to the corresponding angle in $[\text{Zn}(\text{H}_2\text{O})]_{2n}[\text{Zn}(\text{Hcit})_2]_n$ [77.46(8)°] [8] and is much less than $(\text{NH}_4)_4[\text{Zn}(\text{Hcit})_2]$ [104.9(1)°] [7], indicating distortion of the five-membered ring provided by α -hydroxyl and α -carboxylate groups is larger than that in mononuclear $(\text{NH}_4)_4[\text{Zn}(\text{Hcit})_2]$.

With the structural features of three zinc citrate complexes, some similarities are observed: (i) The citrate in all the complexes is tridentate, coordinating to zinc by α -hydroxyl, α -carboxylate, and one β -carboxylate and (ii) The α -hydroxyl group of the

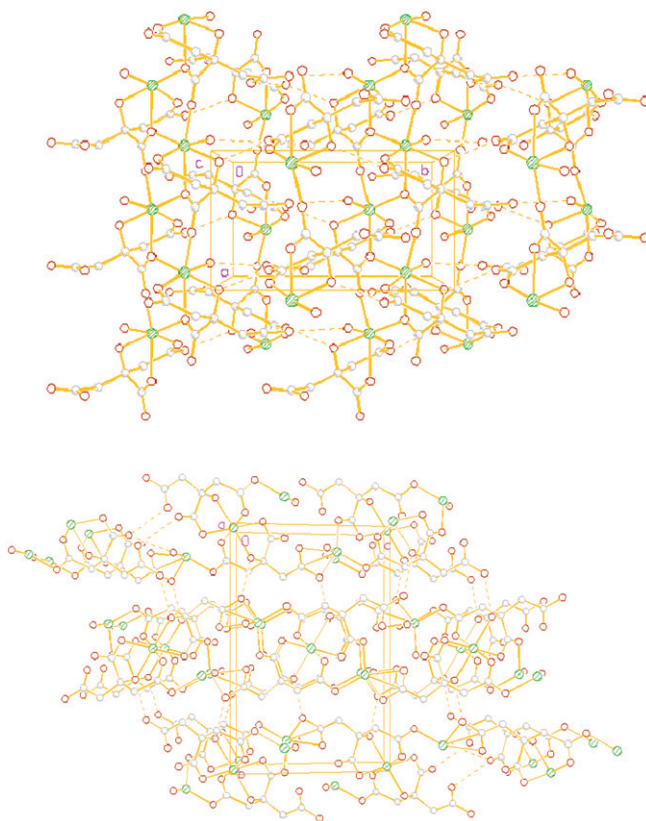


Figure 3. Comparison of the 3-D crystal structures of complexes **1** (1-D \rightarrow 3-D, up) and **2** (2-D \rightarrow 3-D, down). Hydrogen atoms have been omitted for clarity.

citrate ligand retains its proton. The major differences among the complexes are (i) citrate employs its α -carboxylate group as a bridging ligand in **1**; (ii) it employs its α -carboxylate and two β -carboxylate groups simultaneously as bridges in **2** [8]; and (iii) it only employs three oxygens from α -hydroxyl, α -carboxylate, and one β -carboxylate in mononuclear zinc citrate complex [7]. Figure 3 shows the 3-D crystal structures of **1** (built from 1-D MOFs and hydrogen bonds) and **2** (built from 2-D MOFs and hydrogen bonds).

3.3. Photoluminescence properties of the polymeric complexes

The photoluminescence properties of $[\text{Zn}(\text{H}_2\text{cit})(\text{H}_2\text{O})]$ (**1**) and $[\text{Zn}(\text{H}_2\text{O})]_{2n}[\text{Zn}(\text{Hcit})_2]_n$ (**2**) were studied in the solid state at room temperature. The measurements were carried out under the same experimental conditions. The photoluminescence spectrum of **1** is not shown because no clear photoluminescence was observed for **1** at room temperature. Compound **2** displays strong fluorescent emissions at 437 nm (blue fluorescent emission) in the solid state, as shown in figure 4. The fluorescent properties of **2** could have applications in fluorescent materials.

4. Conclusions

In conclusion, we synthesized and characterized a zinc complex with citrate at low pH. The data in this work and previous work [9, 10] confirmed the diversity of citrate as a ligand toward Zn(II); interconversions of different zinc citrate complexes in aqueous solution show their pH-dependency.

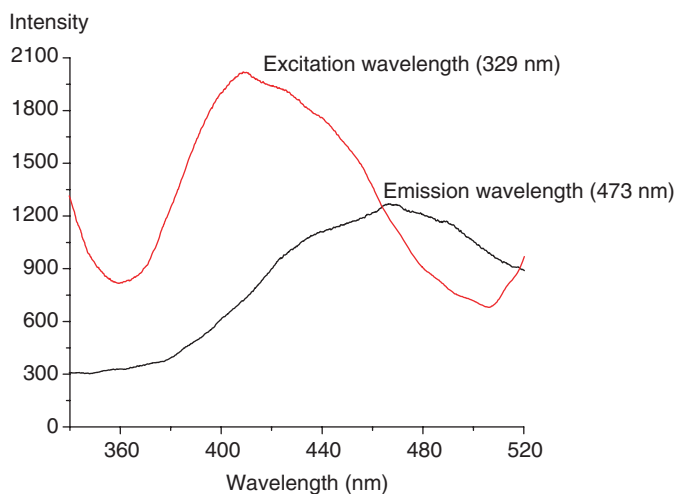


Figure 4. The fluorescent emission spectrum of $[\text{Zn}(\text{H}_2\text{O})]_{2n}[\text{Zn}(\text{Hcit})_2]_n$ in the solid state at room temperature.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 682236 for **1**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; Email: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

Acknowledgments

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