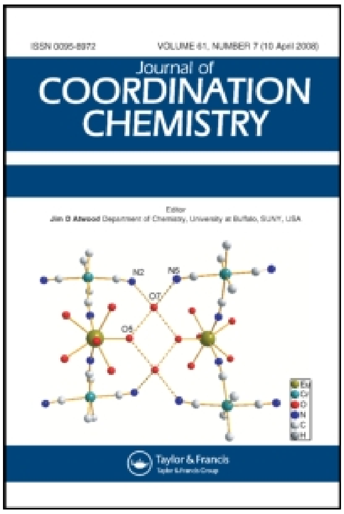

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Ping Che[a]; Daqing Fang[a]; Deping Zhang[a]; Jing Feng[a]; Jingping Wang[a]; Ninghai Hu[a]; Jian[a]
[a] Key Laboratory of Rare Earth Chemistry and Physics, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022

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Hydrothermal synthesis and crystal structure of a new two-dimensional zinc citrate complex

PING CHE*, DAQING FANG, DEPING ZHANG, JING FENG,
JINGPING WANG, NINGHAI HU and JIAN MENG

Key Laboratory of Rare Earth Chemistry and Physics, Changchun Institute
of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022

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A new two-dimensional compound $C_{12}H_{14}O_{16}Zn_3$ (**1**), containing seven-coordinate zinc atoms was prepared by the hydrothermal technique. The compound obtained was characterized by TG-DTA, single crystal X-ray diffraction, elemental analysis and FT-IR analysis. Single-crystal X-ray diffraction analysis shows that compound **1** crystallizes with monoclinic symmetry in the space group $P2_1/c$, $a = 6.1552(13)$ Å, $b = 14.546(3)$ Å, $c = 9.581$ Å, $\beta = 102.66(2)°$, $V = 836.9(4)$ Å^3, $Z = 2$, $R1 = 0.0311$, $wR2 = 0.0830$.

Keywords: Zinc citrate; Crystal structure; Hydrothermal synthesis

1. Introduction

The citrate ligand is widespread in nature. With three carboxylate groups and one hydroxyl group present, citric acid can provide anions ranging from the uni-negative H_3cit^-, to the potential tetradentate cit_4^-. Therefore, it is not surprising that structures of citrate are very complicated. Several papers have been published on coordination of citric acid and transition metals, lead citrate [1], tungsten citrate [2, 3], aluminum citrate [4] and germanium citrate [5]. Few studies focused on the structure of zinc citrate complexes with non-molecular structure. The only compound found is [Zn(II) $(C_6H_5O_7)_2 \cdot 4NH_4^+$] [6], which has a very different structure than compound **1**. Zinc is an essential trace element in the human body; perturbation of the metabolic balance of zinc could lead to diseases [7]. The concentration of zinc is significantly elevated in senile plaques in Alzheimer's disease (AD) brains compared with adjacent neuropil and a significantly increase in AD neuropil compared to control neuropil [8, 9]. The scarcity of crystallographically characterized, low molecular weight, Zn-citrate complex, which could probe the coordination chemistry, has encouraged us to pursue hydrothermal syntheses. Here, we describe the crystal structure of a zinc compound

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*Corresponding author. Email: cheping@buaa.edu.cn

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with a non-molecular structure by hydrothermal technique. The layered trinuclear zinc citrate complex contains an unusual seven-coordinate zinc.

2. Experimental

2.1. *Crystal growth*

Compound **1** was synthesized by the hydrothermal reaction of a mixture of $Zn(NO_3)_2$, citric acid, ethanol and H_2O. All solvents and chemicals were commercial reagent with analysis purity grade and used without further purification. Typically, $Zn(NO_3)_2 \cdot 6H_2O$ was dissolved in a water–ethanol ($v/v = 1:7$) solution containing citric acid (A.R.) as a chelating agent for the metal ions. The pH value of the solution was adjusted to six. The concentration of the zinc ion was 0.1 M. The molar ratio of metal ions to citric acid was 1 : 2. The solution was stirred for 1 h to form a solution, then, it was sealed in a Teflon-lined stainless steel autoclave and heated at 150°C for 20 h under static conditions. Filling volume is 80%. The yellow crystal products were separated and washed by distilled water and ethanol many times. Finally, the products were dried in air at room temperature. The average size of the crystals is about $0.5 \times 0.5 \times 0.5\,\mathrm{mm}^3$ and no other phase was found in the final product.

2.2. *Elemental analysis*

The elemental analysis was carried out on a Perkin–Elmer 2400 elemental analyzer. The results showed that compound **1** contains 23.66 and 1.92 wt% of C and H (Calcd. 23.62 and 1.98 wt%, respectively). Inductively coupled plasma (ICP) analysis performed on a Perkin–Elmer Optima 3300DV spectrometer indicates that it contains 32.19 wt% of Zn (Calcd. 32.14 wt%). The composition analysis is in agreement with calculated values based on the empirical formula of $C_{12}H_{14}O_{16}Zn_3$ given by single-crystal structure analysis. FT-IR spectra were measured on Perkin–Elmer 580B infrared spectrophotometer with the KBr pellet technique. TGA-DTA was carried out on a TA Instruments with a heating rate of $10^\circ\mathrm{C\,min}^{-1}$.

2.3. *Crystal structure determination*

Single crystal structural analysis was carried out on a Rigaku AFC7R automated diffractometer with graphite monochromated Mo K_α radiation ($\lambda = 0.7107\,\text{Å}$) equipped with an 18 kW rotating anode generator. A suitable single crystal with dimensions $0.48 \times 0.42 \times 0.38\,\mathrm{mm}^3$ was mounted on a glass fiber for single-crystal X-ray diffraction analysis. The unit-cell dimensions were derived from a least-square fit to the setting angles of 19 high-angle reflections with 2θ between 9.47° and 17.37°. The intensity data were corrected for Lorentz and polarization effects and for absorption effects. The structure was solved using heavy-atom methods and refined by full-matrix least-squares on F^2 using the SHELXL 97 program [10]. All non-hydrogen atoms were refined anisotropically, while hydrogen atoms were included in the refinements, but fixed with their isotropic displacement parameters the same as U_{eq} value of the corresponding bonded atoms. The crystal parameters and other experimental details

Table 1. The crystal parameters and other experimental details of data collection and refinement for **1**.

Empirical formula	$C_{12}H_{14}O_{16}Zn_3$
Formula weight	610.34
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
a	6.1552 (13) Å
b	14.546 (3) Å
c	9.581 (4) Å
Beta	102.66 (2)°
Volume	836.9 (4) Å^3
Z	2
Density (calculated)	2.422 mg/m^3
Absorption coefficient	4.360 mm^{-1}
Goodness-of-fit on F^2	0.986
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0311$, $wR2 = 0.0830$

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

Zn(1)–O(5)#1	2.044(2)	Zn(1)–O(5)	2.044(2)
Zn(1)–O(1)	2.087(2)	Zn(1)–O(1)#1	2.087(2)
Zn(1)–O(7)	2.118(2)	Zn(1)–O(7)#1	2.118(2)
Zn(2)–O(2)#2	1.975(2)	Zn(2)–O(6)	2.014(2)
Zn(2)–OW	2.037(2)	Zn(2)–O(4)#3	2.070(2)
Zn(2)–O(3)#3	2.320(2)	Zn(2)–C(5)#3	2.539(3)
OW–HW1	0.8327	OW–HW2	0.8681
O(5)#1–Zn(1)–O(5)	180.00(11)	O(5)#1–Zn(1)–O(1)	89.28(9)
O(5)–Zn(1)–O(1)	90.72(9)	O(1)–Zn(1)–O(1)#1	180.0
O(5)#1–Zn(1)–O(7)	102.66(8)	O(5)–Zn(1)–O(7)	77.34(8)
O(1)–Zn(1)–O(7)	84.52(8)	O(1)#1–Zn(1)–O(7)	95.48(8)
O(7)–Zn(1)–O(7)#1	180.00(5)	O(2)#2–Zn(2)–O(6)	115.54(9)
O(2)#2–Zn(2)–OW	102.41(9)	O(6)–Zn(2)–OW	102.30(8)
O(2)#2–Zn(2)–O(4)#3	97.19(8)	O(6)–Zn(2)–O(4)#3	124.62(9)
OW–Zn(2)–O(4)#3	113.14(9)	O(2)#2–Zn(2)–O(3)#3	156.14(9)
O(6)–Zn(2)–O(3)#3	83.35(9)	OW–Zn(2)–O(3)#3	86.47(10)
O(4)#3–Zn(2)–O(3)#3	59.08(8)	OW–Zn(2)–C(5)#3	101.80(10)
O(4)#3–Zn(2)–C(5)#3	30.19(9)	O(3)#3–Zn(2)–C(5)#3	28.94(9)
Zn(2)–OW-HW1	107.1	Zn(2)–OW–HW2	111.1

Symmetry transformations used to generate equivalent atoms: #1 $-x+1$, $-y+1$, $-z+1$ #2 $-x$, $-y+1$, $-z+1$ #3 $-x+1$, $-y+1$, $-z+2$.

of data collection and refinement are presented in table 1. The selected bond distances and bond angles are given in table 2.

3. Results and discussion

3.1. *Structural description*

As shown in figure 1, there are two different zinc atoms in the structural unit. Zn(1) is bonded to the citrate ligand via hydroxyl, central carboxyl group and one of the terminal carboxyl groups of the ligand in a distorted octahedral arrangement. This arrangement is based on deviation of 5.5° between the angle O(1)–Zn(1)–O(7)

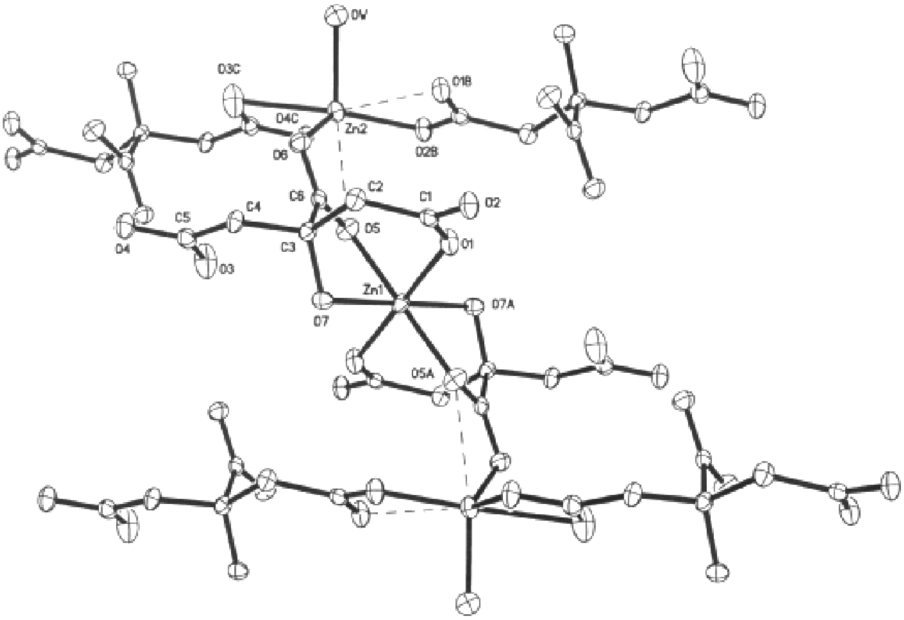

Figure 1. Structure of the complex with the atom labeling scheme. Broken lines denote long coordinated bonds. Thermal ellipsoids represent 50% probability surfaces.

and the ideal value. The apical positions are occupied by O(7) and O(7A). The two metal–oxygen distances are 2.118(2) Å (a symmetry-related pair). The atoms O(5) and O(5A), O(1) and O(1A) (also pairs of symmetry-related bonds) lie in the basal plane at relatively short distances. These distances are 2.044(2) and 2.087(2) Å, respectively (see table 2). The angles around Zn(1) for O(7)–Zn(1)–O(7A), O(5)–Zn(1)–O(5A) and O(1)–Zn(1)–O(1A) are 180.00(5)°, 180.00(11)° and 180.0° respectively. The six oxygen atoms in the coordination sphere belong to hydroxyl groups (O(7) and O(7A)), central carboxyl groups (O(5) and O(5A)) and terminal carboxyl groups (O(1) and O(1A)). The bond lengths of the central carboxyl group to Zn are somewhat shorter than that of the terminal carboxyl group to Zn (2.044 Å *vs.* 2.087 Å). However, the bond lengths of the hydroxyl group to Zn are significantly longer because of the effect of H atoms [9]. There is a strong intermolecular hydrogen-bonding between O(7) and O(4) $(x, 1.5-y, -0.5+z)$ in the structural unit of compound **1**. The bond distance of $H(7)\cdots O(4)$ is 1.779 Å and the angle for $O(7){-}H(7)\cdots O(4)$ is 172.8°.

Zn(2) is coordinated by an oxygen atom of water as well as by six carboxyl oxygen atoms of three carboxyl groups forming seven-coordination. The Zn(2)–Ow distance is 2.037(2) Å. The angle for Zn(2)–Ow–Hw1 is 111.1°. The two hydrogen atoms bond to oxygen atoms of adjacent citrate ligands through H bonds. The Hw–O bond distances are from 2.044 to 2.159 Å. The angle for Hw1–Ow–Hw2 is 64.5°. The Zn(2) atom and four oxygen atoms of two terminal carboxyl groups can be considered as existing in the same plane, but one of the four Zn–O bonds is longer (2.812 Å, dashed in figure 1). The angles for O1B–Zn(2)–O2B, O2B–Zn(2)–O3C and O3C–Zn(2)–O4C are 51.2°, 156.1° and 59.1°, respectively. The two oxygen atoms of the central carboxyl group coordinate with Zn(2) and one of the two Zn–O bond lengths is longer (2.723 Å).

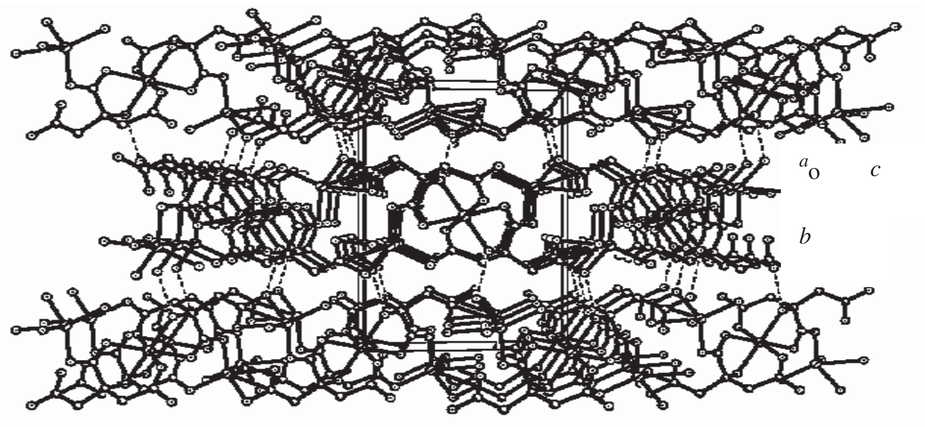

Figure 2. The unit cell of the complex viewed along *a*, showing hydrogen bonds (broken lines).

Each carboxyl group bonded to Zn(2) forms a bidentate structure. The Zn(2)–Ow bond and the bidentate coordinate bond of the central carboxyl group lie on two sides of the plane, giving Zn(2) an irregular geometry. The two zinc atoms (Zn(1) and Zn(2)) share a bridging oxygen atom which belongs to the central carboxyl group. The whole structural unit is exactly symmetrical with the center of Zn(1) atom.

Carboxylic acids (exemplified by citric acid) may be used as reliable building blocks of two-dimensional structures in hydrothermal conditions. In this work, the zinc atom bonds to different citrate ligands and makes adjacent citric acid molecules a chain, then generates a layer structure. Previous work presented Zn complex [6], which was different from this layered structure. Compounds with two-dimensional structure often succeed in the hydrothermal synthesis [11, 12], while layered-structure compounds cannot be formed by traditional methods. The hydrothermal technique facilitates crystal. Hydrothermal synthesis also induced further coordination of the same ligand towards Zn atoms; indicating that compounds with layered structure are more stable in critical-pressure in the hydrothermal process. Moreover, there is an extensive network of hydrogen bonding (HO(7) $\cdots$ O(4)) interactions in the crystal structure of compound **1**. Such interactions may be essential factors contributing to the stability of the assembled complex (see figure 2). The involvement of citrate in hydrogen bonds with water molecule also leads to a much more stable structure.

3.2. *IR spectroscopy*

The FT-IR spectrum of compound **1** is given in figure 3. The IR spectrum demonstrates well-resolved strong and sharp absorption bands for the carboxylate of the coordinated citrates. Antisymmetric stretching vibrations υ_{asym} (COO$^-$) appeared between 1614 and 1562 cm^{-1}. The corresponding symmetric stretches υ_{sym} (COO$^-$) appeared between 1419 and 1406 cm^{-1}. All of the bands are shifted to lower frequencies compared with free citric acid, indicating complexation to zinc. Absence of the typical absorption band of undissociated carboxylic acid group at 1700–1720 cm^{-1} [13, 14] shows that each carboxylic acid group is fully deprotonated. Presence of a broad absorption band at 3048 cm^{-1} shows that the hydroxyl group of the citrate ligand is protonated.

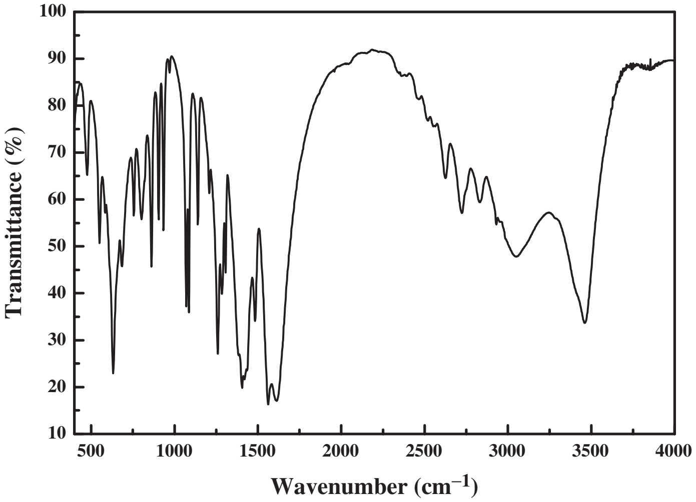

Figure 3. FT-IR spectra of the complex $C_{12}H_{14}O_{16}Zn_3$.

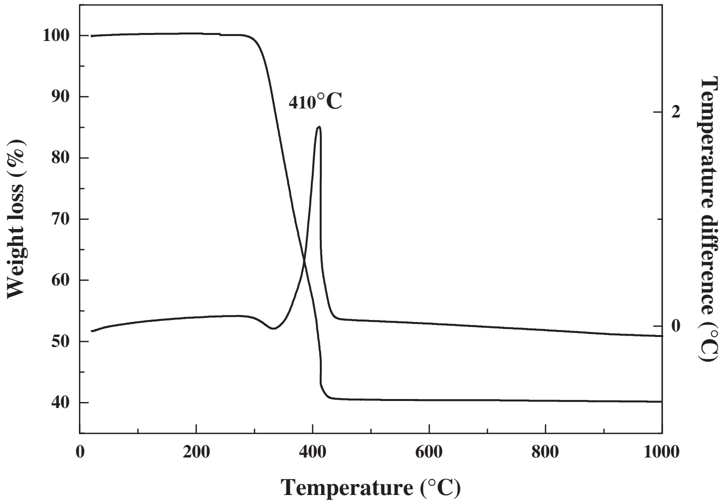

Figure 4. TG-DTA curves of the complex $C_{12}H_{14}O_{16}Zn_3$.

Because of the existing intermolecular H bond, the absorption band is shifted to lower frequency. In addition, the compound gives a strong absorption band at $3461\,\mathrm{cm}^{-1}$, attributed to the vibration of the hydroxyl group of water. These results are in accord with the observed features in the X-ray crystal structure of compound **1**.

3.3. *TG-DTA analysis*

The thermal properties of compound **1** were investigated using TG-DTA (figure 4). Compound **1** was thermally stable up to 300°C and had a weight loss of about 60% in the range 300–450°C. The DTA curve shows a weak endothermic peak at 334°C

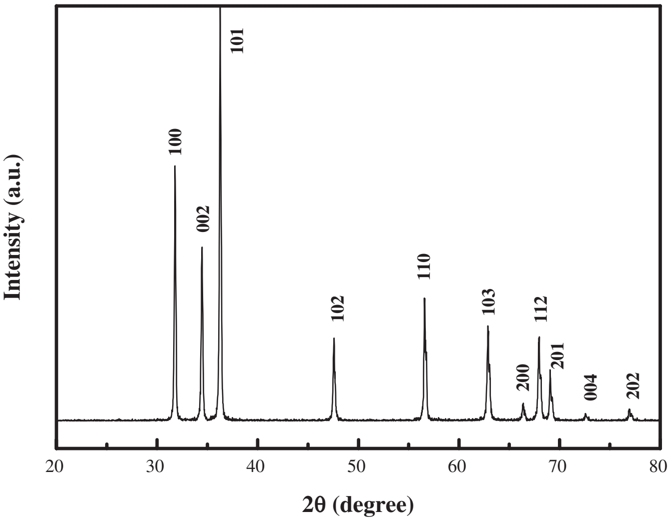

Figure 5. XRD pattern of the complex sintered in 450°C for 10 min.

and a strong exothermic peak at 413°C, perhaps due to dehydration and removal of organic contents, respectively. The observed weight losses agreed well with the calculated value (59.88% *vs*. 60.00%). Compound **1** transfers into zinc oxide above 450°C. The reaction took place according to the following equation:

$$C_{12}H_{14}O_{16}Zn_3 + 9O_2 \rightarrow 3ZnO + 12CO_2 + 7H_2O$$

3.4. *XRD*

Figure 5 shows the XRD pattern of the complex sintered at 450°C for 10 min in air. The XRD result revealed that the structure of the obtained compound is single phase with hexagonal wurtzite structure, indicating complete conversion into ZnO after sintering at 450°C in air.

4. Supporting information

Crystallographic data for $C_{12}H_{14}O_{16}Zn_3$ have been deposited with the Cambridge Crystallographic Data Centre as CCDC 215496. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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