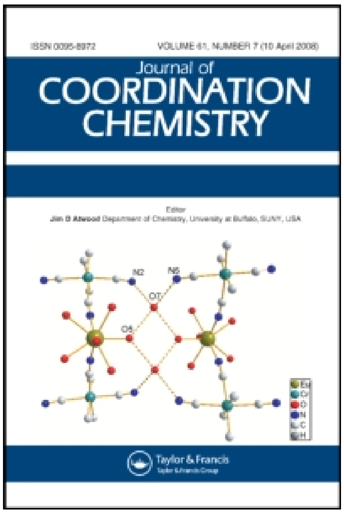

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Synthesis, characterization, crystal structure and non-isothermal dehydration kinetics of a copper(II) complex

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A three-dimensional complex, $[CuL_2(H_2O)]_2$ ($HL = 3$-hydroxy-1-adamantanecarboxylic acid), $C_{44}H_{64}Cu_2O_{14}$, was synthesized under hydrothermal conditions from $CuCO_3 \cdot Cu(OH)_2$ and HL. The crystal structure of the complex was determined by X-ray crystallography and its thermal behavior and IR spectra examined. The non-isothermal dehydration kinetics of the complex were investigated using the Achar differential method.

Keywords: Copper(II) complex; 3-Hydroxy-1-adamantanecarboxylic acid; Crystal structure; Non-isothermal dehydration kinetics

1. Introduction

Complexes of copper and biological ligands play an important role during the life process of enzymatic catalyze, the storage and transport of materials, the transfer of copper(II), and so on [1–5]. In addition, copper(II) complexes are of great significance to study molecular magnets [6–9].

Adamantane has an extensive application in medicine and derivatives of adamantane have pharmaceutical activities. For instance, adamantaneamine has an effect on controlling the exuviating of influenza A virus and can alleviate Parkinson symptoms [10]. Recently, we reported that transition metal and lanthanide complexes with derivatives of adamantane have some antibacterial activities [11–14].

The carboxylate complexes have various structural types and potential use as materials in magnetism, catalysis, adsorption, and luminescent probes [15–19]. Carboxylate complexes of copper(II) serve as models for metallopeptidases in life systems [20–22]. Herein, we choose 3-hydroxy-1-adamantanecarboxylic acid, an important intermediate in production of adamantaneamine, as a carboxylate ligand to coordinate with copper(II). The complex was characterized by FT-IR and

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thermogravimetry analysis, and its crystal structure was obtained by X-ray diffraction. Non-isothermal dehydration kinetics of the copper(II) complex was determined by the Achar differential method.

2. Experimental

2.1. *Materials and measurements*

Basic copper(II) carbonate, 3-hydroxy-1-adamantanecarboxylic acid, the other chemicals and solvents used were of analytical grade. The IR spectra were recorded on a Nicolet NEXUS 670 FT-IR spectrometer (4000–400 cm^{-1}) with KBr discs. Thermogravimetric analysis was carried out on a Mettler-Toledo TGA/SDTA851^e thermal analyzer in the range 30–900°C at a heating rate of $10^\circ C \cdot min^{-1}$ under air.

2.2. *Syntheses*

Basic copper(II) carbonate (0.2211 g, 1 mmol) and 3-hydroxy-1-adamantanecarboxylic acid (HL) (0.7200 g, 4 mmol) in H_2O (20 mL) were stirred at room temperature. Then, the mixture was sealed in a 25 mL Teflon-lined stainless steel reactor and heated to 433 K for 48 h. After cooling, the final mixture was filtered and placed at ambient temperature to slowly evaporate. Glaucous crystals suitable for X-ray structure analysis were obtained after 40 days. Anal. Calcd for $C_{44}H_{64}Cu_2O_{14}$ (%): Cu, 13.46; C, 55.98; H, 6.83. Found: Cu, 13.28; C, 55.79; H, 6.76.

2.3. *X-ray crystallography*

Diffraction data were collected on a Bruker APEXII CCD diffractometer by using graphite-monochromated Mo-Kα (0.71073 Å) radiation and ω scans in the 2.0 to 27.7° θ range. The structure was solved by direct methods with SHELXS-97 [23] and refined on the F^2 by full-matrix least-squares method with SHELXL-97 [24]. The hydrogens on carbon were placed in calculated positions in the riding model approximation, and the H atoms of water were located in difference Fourier synthesis maps. Details of crystal analysis, data collection and structure refinement are summarized in table 1, together with the final values for the unit cell. Selected bond distances and angles are listed in table 2.

3. Results and discussion

3.1. *IR spectra*

Characteristic IR data for the free acid and complex are listed in table 3. The appearance of two medium bands at 3390 cm^{-1} for $\nu(OH)$ and 892 cm^{-1} for $\delta(OH)$ suggest the presence of coordinated water in the complexes [25, 26]. Bands at 2910 and

Table 1. Crystallographic data for the title complex.

Empirical formula	$C_{44}H_{64}Cu_2O_{14}$
Formula weight	944.03
Temperature (K)	296(2)
Wavelength (nm)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions (Å, °)	
a	10.6348(8)
b	1.0492(9)
c	11.1419(8)
α	79.497(4)
β	61.779(4)
γ	64.355(3)
V(Å^3)	1039.56(14)
Z	1
D_{Calcd} (mg m^{-3})	1.508
Absorption coefficient (mm^{-1})	0.487
Crystal size (mm^3)	$0.36 \times 0.18 \times 0.15$
$F(000)$	498
θ range for data collection (°)	2.05 to 27.66
Limiting indices	$-13 \le h \le 13$, $-14 \le k \le 13$, $-14 \le l \le 12$
Reflections collected/unique	14403/4607
Completeness (θ to 25°)/%	94.90%
Max. and min. transmission (mm^{-1})	0.795, 0.853
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4607/3/279
Goodness-of-fit on F^2	1.129
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0826$ $wR_2 = 0.2155$
R indices (all data)	$R_1 = 0.0868$ $wR_2 = 0.2190$
Largest diff. peak and hole (e Å^{-3})	5.692 and −0.726

Table 2. The data of selected bond distances (Å) and angles (°).

Cu1—O5	1.955(4)	C11—O3	1.252(6)
Cu1—O3^i	1.960(3)	C11—O2	1.269(6)
Cu1—O2	1.985(3)	C15—O4	1.439(6)
Cu1—O6^i	1.987(4)	C22—O5	1.255(6)
Cu1—O1W	2.172(3)	C22—O6	1.272(6)
Cu1—Cu1^i	2.6143(10)	O3—Cu1^i	1.960(3)
C10—O1	1.456(7)	O6—Cu1^i	1.987(4)
O3^i—Cu1—O2	168.81(14)	O5—Cu1—O3^i	90.11(17)
O5—Cu1—O6^i	168.76(14)	O5—Cu1—O2	90.12(17)
O3^i—Cu1—O6^i	87.89(17)	O3—C11—O2	125.0(4)
O2—Cu1—O1W	95.24(13)	O3—C11—C4	118.5(4)
O5—Cu1—O1W	94.59(14)	O2—C11—C4	116.5(4)
O3^i—Cu1—O1W	95.89(14)	O5—C22—O6	124.0(5)

^{i}Symmetry code i:1 − x, 1 − y, 1 − z.

2860 cm^{-1} indicate the existence of the adamantine ring [11–14]. The stretching vibrations of the hydroxyl disappear in spectra of the complexes and the absorption frequency of carbonyl significantly decreases. The characteristic frequencies of the $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ are at 1611 and 1402 cm^{-1}, respectively. The value of $\Delta\nu$ ($\Delta\nu = [\nu_{as}(COO^-) - \nu_s(COO^-)]$) is 208 cm^{-1}, smaller than the value observed in sodium

Table 3. Characteristic IR data for the free acid and the complex (cm^{-1}).

Compound	ν(C=O)	ν(O–H)	ν(C–H)	$\nu_{as}(COO^-)$	$\nu_s(COO^-)$	$\Delta\nu$	ν(Cu–O)
HL	1709(s)	3443(s)	2910(s), 2860(m)				
NaL			2909(s), 2855(m)	1623(m)	1389(s)	243	
$[CuL_2(H_2O)]_2$		3390(m)	2905(m), 2852(w)	1611(m)	1403(s)	208	509(w)

3-hydroxy-1-adamantanecarboxylate ($\Delta\nu = 243\,cm^{-1}$), implying weak bidentate chelated coordination mode in the compound [27], consistent with the results of the X-ray crystallography analyses.

3.2. *Crystal structure of the complex*

The crystal structure consists of four 3-hydroxy-1-adamantanecarboxylic acidic anions, two copper(II) cations and two coordinated waters (figure 1). It is a center symmetrical bimetallic complex which has a paddle wheel $[Cu_2O_8]$ unit [28]. The two Cu atoms are bridged by four carboxylate groups and the $Cu \cdots Cu^i$ distance is 2.614 Å (symmetry code i: $-x+1$, $-y+1$, $-z+1$). The four oxygens coordinated to Cu are approximately coplanar, with the Cu 0.153 Å out of the basal plane. The Cu–O bond lengths are 1.955(4) Å and 1.985(3) Å. One water is coordinated to Cu out of the square plane, so the coordination environment is a distorted square-pyramidal structure which can also be seen in the value of the trigonality index [29], $\tau = 0.09$. The coordination geometry of Cu(II) shown in figure 2 has Cu1–O1w bond length of 2.172(3) Å, which is shorter than the corresponding distance of 2.2296(2) Å in $[Cu(ada)_2(py)_2(H_2O)]$ [30], much shorter than the distance of 2.2508(3) Å in the similar dinuclear complex $[Cu(H_2O)_3][Cu(mal)_2(H_2O)]$ [31]. Intermolecular hydrogen bonds, $O1W–H1WB \cdots O1^i$, $O1–H1C \cdots O1W^i$, $O1W–H1WA \cdots O4^{ii}$, $O4–H4A \cdots O1W^{iii}$ (symmetry code i: x, $1+y$, z; $1-x$, $1-y$, $2-z$; x, $-1+y$, z), are formed by coordinated water and the oxygen atoms of the carboxylate and hydroxyl group. There are also weak intermolecular hydrogen bonds $C9–H9A \cdots O4^{iv}$ (symmetry code i: $1-x$, $-y$, $2-z$).

3.3. *Thermal behavior and non-isothermal dehydration kinetics*

The TG curve of the complex indicates that thermal decompositon occurs in two steps in air (figure 3). The first step is dehydration with a weight loss of 3.83%, which corresponds to the loss of two water molecules in the temperature range 136–168°C (Calcd 3.81%); the second step has a decomposition temperature range of 257–329°C with a weight loss of 81.05% corresponding to the loss of four ligands (Calcd 81.46%). A value of 15.12% of the original sample remained with its calculated weight percentage of 14.73%, with CuO as the residue. The non-isothermal dehydration kinetics of the complex was studied as follows.

Non-isothermal decomposition of solid-state material is subjected to the following equation:

$$\frac{d\alpha}{dT} = \frac{A}{\beta\left[\exp\left(-\frac{E}{RT}\right)\right]} f(\alpha), \quad \beta = \frac{dT}{dt} \tag{1}$$

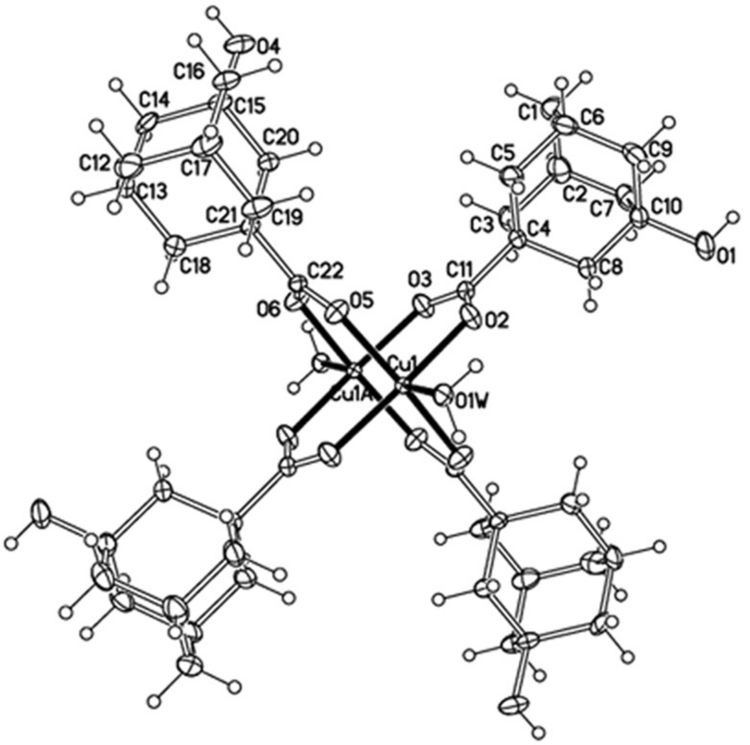

Figure 1. Molecular structure of $[Cu(C_{11}H_{16}O_3)_2(H_2O)]_2$.

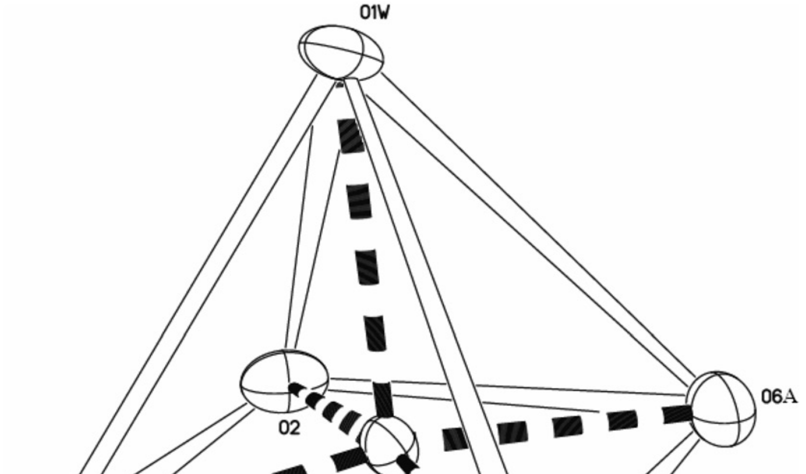

Figure 2. The coordination geometry of Cu(II).

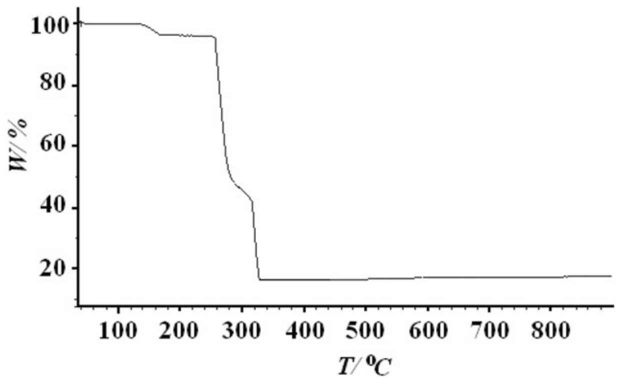

Figure 3. The TG curve of the complex.

From equation (1), a differential rate expression, which is usually known as the Achar equation [32], can be written

$$\ln\left[\frac{(\mathrm{d}\alpha/\mathrm{d}t)}{f(\alpha)}\right] = \ln A - \frac{E}{RT}\left(\frac{\mathrm{d}a}{\mathrm{d}t} = \frac{\beta \mathrm{d}\alpha}{\mathrm{d}T}\right) \tag{2}$$

where α is the reaction of decomposition, $\mathrm{d}\alpha/\mathrm{d}t$ is the rate of conversion, β is the linear heating rate, T is the absolute temperature, A is the pre-exponential factor, R is the gas constant, E is the apparent activitation energy, and $f(\alpha)$ is the differential mechanism functions.

The basic parameters of α, T and $\mathrm{d}\alpha/\mathrm{d}T$ and other data related to the thermal decomposition are listed in supplementary data. The algebraic expression of differential $f(\alpha)$ functions [33] for the most common mechanism used in kinetics of solid-state decomposition tested in this work are listed in supplementary data. On substitution of basic parameters and the 19 types of mechanism functions $f(\alpha)$ into equation (1), the values of E, $\ln A$ and the linear correlation coefficients r of different mechanism functions were calculated.

The kinetic parameters for the dehydration suggest that the possible mechanism is function NO.4 (supplementary data) based on the data. The decomposition reaction was governed by three-dimensional diffusion (cylindrical symmetry, 1D3). The kinetic equation of this process is $3/2[(1-\alpha)^{-1/3}-1]^{-1}$.

According to the customary mathematical expression for the kinetic compensation effect, $1\mathrm{n}\,A = aE + b$ [34, 35], where a and b are the compensation constants. The kinetic parameters (E and $1\mathrm{n}\,A$) obtained from the differential method were fitted by linear least-squares. The mathematical expression for the kinetic compensation effect is $\ln A = 3.5343E + 2.0045$ and $r = 0.9994$. Because the compensation constants are not influenced by experimental factors, description of the thermal decomposition with compensation parameters a and b give a better illustration of the internal relationship between E and $\ln A$ of the thermal decomposition.

4. Conclusion

The copper(II) complex was synthesized by $CuCO_3 \cdot Cu(OH)_2$ and HL under hydrothermal conditions and the structure was proposed by elemental analysis, FT-IR, X-ray diffraction and TG analysis. Lastly, the non-isothermal dehydration kinetics of the complex were determined by the Achar differential method and the kinetic equation is expressed as followed: $f(\alpha) = 3/2[(1-\alpha)^{-1/3} - 1]^{-1}$, $E = 149.11\ \mathrm{KJ\,mol^{-1}}$, $\ln A = 40.27$.

Supplementary material

Supplementary crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 666977. 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).

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