

Synthesis, Crystal Structure of Zinc Complex with 3-Hydroxy-1-adamantanecarboxylic Acid

GUO-LIANG ZHAO*, XIAO-YONG WU, QUAN-YIN GUAN and JIN-BEI SHEN

College of Chemistry and Life Science, Zhejiang Normal University, Jinhua 321004, P.R. China

*Corresponding author: Fax: +86 579 82282269; Tel: +86 579 82282061; E-mail: sky53@zjnu.cn

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A novel zinc(II) complex, $[\text{Zn}(\text{HOC}_{10}\text{H}_{14}\text{COO})_2(1,10\text{-phen})]\cdot 6\text{H}_2\text{O}$ (**1**) was synthesized by hydrothermal method from zinc hydroxide, 1,10-phenanthroline and 3-hydroxy-1-adamantane acid ($\text{C}_{10}\text{H}_{14}(\text{HO})\text{COOH}$). It was characterized by IR spectrum, elemental analysis and thermogravimetric analysis. Its crystal structure was determined by single crystal diffraction technique. The complex, $\text{C}_{34}\text{H}_{50}\text{N}_2\text{O}_{12}\text{Zn}$, crystallizes in the monoclinic system, space group P21/c with $a = 1.25822(6)$ nm, $b = 0.72825(2)$ nm, $c = 2.63620(6)$ nm, $\beta = 106.067(1)^\circ$, $V = 3.50999(19)$ nm³, $Z = 4$, $M_r = 744.15$, $F(000) = 1576$, $D_c = 1.408$ mg cm⁻³, $\mu(\text{Mo K}\alpha) = 0.765$ mm⁻¹. CCDC: 757154.

Key Words: Zinc(II) complex, 3-Hydroxy-1-adamantanecarboxylic acid, Crystal structure.

INTRODUCTION

Zinc is an important life element and some activity centers of enzyme¹. The coordination ability of aromatic carboxylic acids towards transition metal complexes has received considerable attention, due to the strong coordination ability and varieties of the bridging modes of the carboxylate group with regard to the formation of extended frameworks²⁻⁵.

Adamantane-1-carboxylic acid has a highly-symmetric and steady structure, which is an effective cure for virus. For instance, it has an obvious effect on controlling the exuviating the influenza A virus⁶. The fascinating structures of adamantane-1-carboxylic acid complexes coupled with their special functionality catch a lot of chemists' interests⁷⁻¹⁰. Recently, we have reported copper and cadmium complexes with 3-hydroxyadamantane-1-carboxylic acid and 1,10-phenanthroline^{11,12}. As an extension of our work in this field, we report the synthesis, thermogravimetric analysis and single crystal X-ray diffraction of a new zinc(II) complex $[\text{Zn}(\text{HOC}_{10}\text{H}_{14}\text{COO})_2(1,10\text{-phen})]\cdot 6\text{H}_2\text{O}$ (**1**).

EXPERIMENTAL

3-Hydroxyadamantane-1-carboxylic acid was synthesized as article reported¹³ and recrystallized in water and decoloured with activated carbon before using. Other reagents were of analytical grade quality and were used without further purification. Elemental analyses were carried out on Elementar Vario EL III elemental analyzer. The FTIR spectra were obtained from KBr pellets in the range 4000-400 cm⁻¹ with a Nicolet

NEXUS 670 FTIR spectrometer. Thermal analyses were carried out using Mettler-Toludo TGA/SDTA 851° thermal analyzer at a heating rate of 10 °C min⁻¹ from 30 to 800 °C in air atmosphere. Diffraction data were collected at 296(2) K on a Bruker APEXII CCD diffractometer with graphite monochromated Mo-K α radiation ($\lambda = 0.071073$ nm).

Synthesis of the complex: A mixture of 3-hydroxyadamantane-1-carboxylic acid (0.3925 g, 2 mmol), $\text{Zn}(\text{OH})_2$ (0.0990 g, 1 mmol), 1,10-phenanthroline (0.1980 g, 1 mmol) and water (20 mL) was sealed in a 25 mL stainless steel reactor with a Teflon liner and heated at 433 K for 3 days. On completion of the reaction, the reactor was cooled slowly to room temperature. Then the mixture was filtered, colourless single crystals suitable for X-ray analysis were obtained after 60 days. Yield: 56 % based on metal. Anal. calcd. for $\text{C}_{34}\text{H}_{50}\text{N}_2\text{O}_{12}\text{Zn}$ (%): C, 54.91; H, 6.81; N, 3.75. Found: C, 54.87; H, 6.77; N, 3.77. IR (KBr, cm⁻¹): 3373 (m), 2906 (m), 2851(w), 1691 (s), 1548 (s), 1425 (s), 1518 (s).

Crystal structure determination: A single crystal of the title complex with dimensions of 0.354 mm \times 0.017 mm \times 0.084 mm was selected and mounted on a glass fiber and collected diffraction data on a Bruker Smart APEX II CCD diffractometer with graphite monochromated Mo-K α radiation ($\lambda = 0.071073$ nm). Structure was solved by direct methods using SHELXS-97¹⁴ and refined on the F² by full-matrix least-square method with SHELXL-97¹⁵. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in geometrically calculated positions and refined by using a riding mode. Experimental details for X-ray data collection are

presented in Table-1. The selected bond lengths and angles are listed in Table-2. CCDC No. 757154 of **1** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre.

TABLE-1
CRYSTALLOGRAPHIC DATA FOR COMPOUND **1**

Formula	C ₃₄ H ₅₀ N ₂ O ₁₂ Zn
Formula weight	744.15
Temperature (K)	296(2)
Wavelength (nm)	0.071073
Crystal system	Monoclinic
Space group	P21/c
a (nm)	1.90262(5)
b (nm)	0.72825(2)
c (nm)	2.63620(6)
β (°)	106.067(1)
Volume (nm ³)	3.50999(16)
Z	4
Calculated density (g/cm ³)	1.408
Absorption coefficient (mm ⁻¹)	0.765
F(000)	1576
Crystal size (mm)	0.354 × 0.170 × 0.084
Theta range for data collection (°)	1.61 to 27.66
Limiting indices	-24 ≤ h ≤ 24, -9 ≤ k ≤ 9, -33 ≤ l ≤ 34
Reflections collected / unique	29094 / 8114 [R(int) = 0.0332]
Completeness to theta = 24.04 (%)	98.7
Max. and min. transmission	0.938 and 0.856
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	8114 / 18 / 478
Goodness-of-fit on F ²	1.040
Final R indices [I > 2σ(I)]	R ₁ = 0.0541, wR ₂ = 0.1487
R indices (all data)	R ₁ = 0.0703, wR ₂ = 0.1570
Absolute structure parameter	-0.007(10)
Largest diff. peak and hole (e nm ⁻³)	1239 and -411

TABLE-2
SELECTED BOND LENGTHS (nm) AND ANGLES (°)

Bond	(nm)	Angle	(°)
Zn-O(4)	0.1975(2)	O(4)-Zn-O(2)	124.30(11)
Zn-O(2)	0.1979(2)	O(4)-Zn-N(2)	113.87(11)
Zn-N(2)	0.2101(3)	O(2)-Zn-N(2)	107.15(11)
Zn-N(1)	0.2105(3)	O(4)-Zn-N(1)	107.00(11)
Zn-O(5)	0.2483(3)	O(2)-Zn-N(1)	116.30(11)
Zn-O(1)	0.2497(2)	N(2)-Zn-N(1)	79.58(11)
O(1)-C(1)	0.1236(4)	O(4)-Zn-O(5)	57.36(9)
O(2)-C(1)	0.1269(4)	O(2)-Zn-O(5)	90.48(10)
O(3)-C(6)	0.1445(4)	N(2)-Zn-O(5)	161.42(10)
O(4)-C(12)	0.1269(4)	N(1)-Zn-O(5)	87.45(11)
O(5)-C(12)	0.1246(4)	O(4)-Zn-O(1)	88.45(10)
O(6)-C(17)	0.1438(4)	O(2)-Zn-O(1)	57.02(9)
—	—	N(2)-Zn-O(1)	87.39(10)
—	—	N(1)-Zn-O(1)	162.82(11)
—	—	O(5)-Zn-O(1)	107.66(10)
—	—	O(1)-C(1)-O(2)	121.4(3)
—	—	O(5)-C(12)-O(4)	120.6(3)

RESULTS AND DISCUSSION

FTIR spectra: The FTIR spectra of Zn(II) complex shows absorption bands resulting from the skeletal vibrations of the heteroaromatic rings in 1518 cm⁻¹, which verifies the

presence of 1,10-phen. Comparing to the infrared spectra of free 3-hydroxyadamantane-1-carboxylic acid, the characteristic sharp band centered at about 1708 cm⁻¹ for $\nu(\text{C}=\text{O})$ is vanished and there are two new peaks appear: 1548 cm⁻¹ for $\nu_{\text{as}}(\text{COO}^-)$ and 1425 cm⁻¹ for $\nu_{\text{s}}(\text{COO}^-)$ of bidentate COO⁻. This shift suggests the coordination modes of carbonyl oxygen with zinc(II) ions. And the broad band at about 3373 cm⁻¹ is the characteristic absorption peak of $\nu(\text{OH})$, which proves there are water molecule in this compound¹⁶.

Description of the structure: The crystal structure of the coordination complex is shown in Fig. 1, which reveals that the basic coordination unit of present compound consists of two 3-hydroxyl-1-adamantanecarboxylic acidic anions, one 1,10-phenanthroline molecule, one Zn(II) cation and six uncoordinated waters molecules. The central Zn(II) ion is six coordinated by two bidentate 3-hydroxyl-1-adamantanecarboxylic acidic anions ligands *via* four O atoms and two N atom from one bidentate phen ligand in a distorted octahedral geometry. The four Zn-O bond length range from 0.1975(2)-0.2497(2) nm, two of which are similar with reported adamantanecarboxylic acidic complexes^{17,18}, the other two of which are slightly longer than the reported Zn-O bond of zinc carboxylic acid complexes¹⁹. The two Zn-N bond length are respectively 0.1975(2) nm and 0.2497(2) nm, which approximate related compounds in the literatures¹⁹. The complex consists of six lattice water molecules and each lattice water molecule is respectively bonded to the oxygen atoms of water and hydroxy through relative weak hydrogen bonds. Furthermore, the hydroxy oxygen is bonded to the carboxyl oxygen by a intramolecular hydrogen bonding. It is evident that the abundant hydrogen bonds in lattice water molecules play an important role in cementing the structure together. The hydrogen bonding interactions lead to the formation of a one-dimensional chain along the b axis. The uncoordinated water molecules filling in small void form water network through hydrogen bonding. The stacking plot of the title compound is shown in Fig. 2, showing H-bond interactions and π - π stacking interactions.

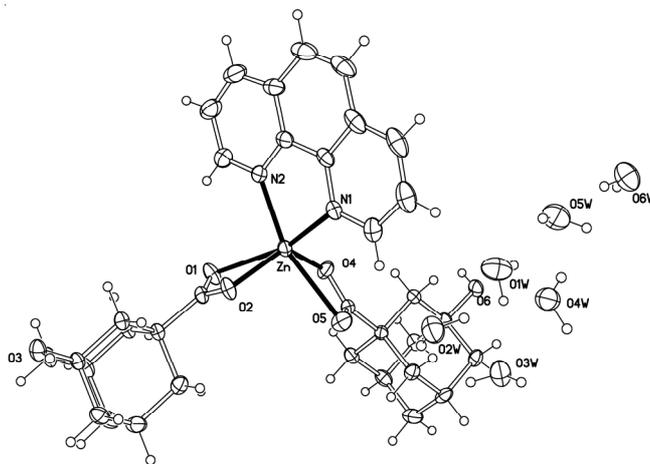


Fig. 1. Molecular structure of the Zn(II) complex

Thermogravimetric analysis: TG-DTG curves were shown in Fig. 3. The TG degradation of the compound reveals two decomposition stages, as predicted by the DTG curve.

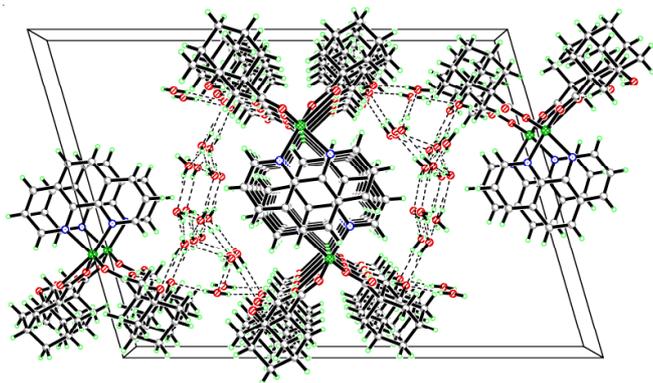


Fig. 2. The packing plot of the present Zn(II) complex

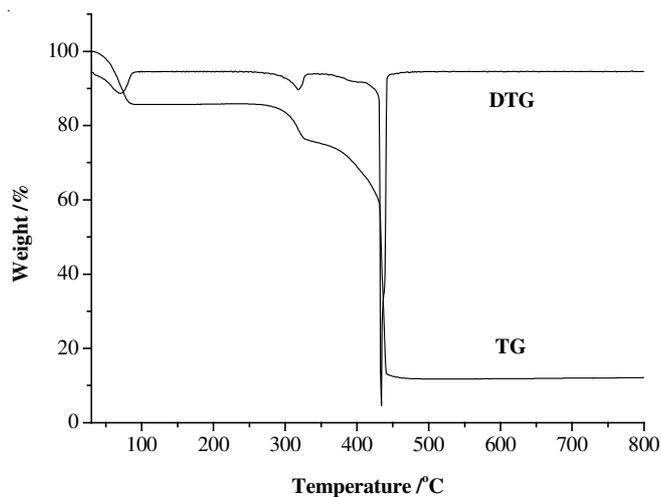


Fig. 3. DG-DTG of the Zn(II) complex

The first stage starts from 35 to 96 °C with a mass loss 14.32 % which corresponds to the loss of 6 mol H₂O of per-mole complex (theoretical loss is 14.55 %). The second stage decomposition temperature is in the range of 273-474 °C with a mass loss 74.82 % which corresponds to the loss of one mol of 1,10-phen and 2 mol of 3-hydroxyadamantane-1-carboxylic

anions (theoretical loss is 74.52 %). The residue weights 10.86 % corresponds to values calculated for ZnO 10.93 %. This result is in good accordance with the composition of the complex.

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