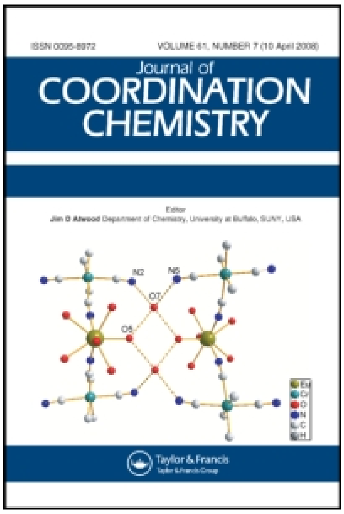

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis, structure and characterization of copper(II) and zinc(II) complexes based on 3-carboxyl-1,2,4-triazole

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To cite this Article Liu, Yuan-Yuan(2007) 'Synthesis, structure and characterization of copper(II) and zinc(II) complexes based on 3-carboxyl-1,2,4-triazole', Journal of Coordination Chemistry, 60: 23, 2597 — 2605
To link to this Article: DOI: 10.1080/00958970701286359
URL: http://dx.doi.org/10.1080/00958970701286359

Journal of Coordination Chemistry
Vol. 60, No. 23, 1 December 2007, 2597–2605

Synthesis, structure and characterization of copper(II) and zinc(II) complexes based on 3-carboxyl-1,2,4-triazole

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(*Received 13 August 2006; in final form 16 October 2006*)

Two complexes $[CuL_2(H_2O)_2]$ (**1**) and $[ZnL_2(H_2O)_2]$ (**2**) (L = 3-carboxyl-1,2,4-triazole (L)) have been synthesized and characterized by single-crystal X-ray diffraction analysis. Compound **1** crystallizes in the monoclinic space group $P_2(1)/n$, $a = 8.632(8)$ Å, $b = 9.153(8)$ Å, $c = 6.991(7)$ Å, $\beta = 94.279(12)^\circ$, $Z = 2$, $R_1 = 0.0296$, $wR_2 = 0.0918$. Compound **2** also crystallizes in the monoclinic space group $P_2(1)/n$, $a = 4.937(3)$ Å, $b = 18.107(10)$ Å, $c = 6.344(4)$ Å, $\beta = 106.839(7)^\circ$, $Z = 2$, $R_1 = 0.0230$, $wR_2 = 0.0556$. Extensive intermolecular hydrogen bonds assemble **1** and **2** into three-dimensional (3D) supramolecular architectures, with eight-member H-bonded synthons. Compounds **1** and **2** were also characterized by element analysis, FT–IR, luminescence and EPR studies.

Keywords: Cu(II); Zn(II); 3-Carboxyl-1,2,4-triazole; Supramolecular network; H-bonded synthons

1. Introduction

Construction of functional supramolecular coordination polymers is of interest due to their intriguing network topologies and interesting electric, magnetic, catalytic and optical properties [1]. Many N-containing carboxylic acid ligands such as pyridine 2,6-carboxylic acid, imidazole acid etc. exhibit rich coordination modes and have been used to construct supramolecular compounds [2–6]. 3-Carboxyl-4H-1,2,4-triazole (L) is also a rigid multidentate N-containing carboxylic acid ligand, which simultaneously contains carboxylate and 1,2,4-triazole groups [7]. Due to many potential coordination sites L is expected to exhibit diverse coordination modes (scheme 1) and produce functional supramolecular materials. Only one previous report deals with coordination compounds based on 3-carboxyl-4H-1,2,4-triazole [8].

In this work, using 3-carboxyl-4H-1,2,4-triazole (L), two new complexes $[CuL_2(H_2O)_2]$ (**1**) and $[ZnL_2(H_2O)_2]$ (**2**) have been synthesized and determined by

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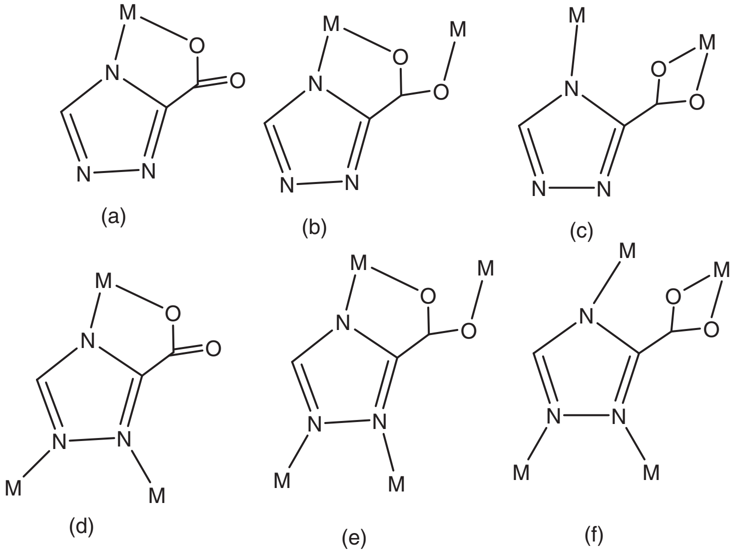
Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958970701286359



Scheme 1. Several possible coordination modes for L based on widely used N-containing carboxylates such as pyridine acid and imidazole acid.

single-crystal X-ray diffraction analysis, element analysis and FT–IR spectra. The EPR spectrum of **1** was also determined and analyzed.

2. Experimental section

2.1. *General considerations*

All solvents and chemicals were reagent grade and used without further purification. The ligand was prepared by the method described in the literature [9]. Deionized water was used for the synthesis. Elemental analyses of carbon, hydrogen and nitrogen were carried out with a Perkin-Elmer analyzer model 240. The FT–IR spectra were recorded from KBr pellets in the range 400–4000 cm^{-1} on a Bio-Rad FTS 135 spectrometer. The X-band EPR spectra of crystal samples were recorded on a Bruker ER 200 D-SRC ESR spectrometer. The photoluminescence spectrum was measured by a MPF-4 fluorescence spectrophotometer with a xenon arc lamp as the light source.

2.2. *Synthesis of 1 and 2*

To a solution of L in EtOH was added an equivalent of $Cu(NO_3)_2 \cdot 3H_2O$ aqueous solution under stirring at room temperature. The resulting solution was stirred for 3 h and the filtrate was allowed to stand at room temperature. Blue block crystals of **1** suitable for X-ray analysis were obtained by slow evaporation of the solvent at room temperature for a couple of weeks. Yield: 35%. Anal. Calcd (%) for $C_6H_6CuN_6O_6$: C, 22.40; H, 1.88; N, 26.13. Found (%): C, 22.65; H, 1.92; N, 26.42. Important IR

Table 1. Crystal data and structure refinement parameters for **1** and **2**.

	1	**2**
Empirical formula	$C_6H_6N_6O_6Cu$	$C_6H6N_6O_6Zn$
Formula weight	321.71	323.55
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group (Å, °)	$P_2(1)/c$	$P_2(1)/n$
a	8.632(8)	4.937(3)
b	9.153(8)	18.107(10)
c	6.991(7)	6.344(4)
α	90	90
β	94.279(12)	106.839(7)
γ	90	90
Volume (Å^3)	550.8(9)	542.8(5)
Z	2	2
Density (g cm^{-3})	1.940	1.992
Absorption coefficient (mm^{-1})	2.021	2.301
$F(000)$	322	328
Crystal size (mm^3)	$0.22 \times 0.20 \times 0.14$	$0.22 \times 0.16 \times 0.10$
θ Range for data collection	2.37–25.01	2.25–25.01
Limiting indices	$-8 \le h \le 10$, $-10 \le k \le 10$, $-8 \le l \le 8$	$-3 \le h \le 5$, $-18 \le k \le 21$, $-7 \le l \le 7$
Reflections collected/unique	2855/969	2789/954
Data/restraints/parameters	969/3/88	954/3/88
Goodness-of-fit on F^2	1.088	1.081
Final R indices ($I > 2\sigma(I)$)	0.0296, 0.0890	0.0230, 0.0541
R indices (all data)	0.0351, 0.0918	0.0281, 0.0556
Largest diff. peak and hole (e Å^{-3})	0.636 and −0.274	0.252 and −0.206

absorption (KBr, cm^{-1}): 3431.1bm, 3033.2m, 1671.4m, 1639.4s, 1492.7m, 1411.7vs, 1375.4m, 1051.6w, 852.5w, 790.7m and 664.3. Complex **2** was prepared similar to **1** except using $Zn(ClO_4)_2 \cdot 6H_2O$ instead of $Cu(NO_3)_2 \cdot 3H_2O$. Yield: 42%. Anal. Calcd (%) for $C_6H_6ZnN_6O_6$: C, 22.27; H, 1.86; N, 25.97. Found (%): C, 22.43; H, 1.98; N, 25.82. Important IR absorption (KBr, cm^{-1}): 3396.3br, 3007.1m, 1663.4m, 1644.4s, 1453.7m, 1416.7s, 1397.1s, 1053.8s, 962.7w, 795.5w, and 664.6 m.

2.3. *X-ray crystallography*

Structure measurements of both complexes were performed on a computer controlled Bruker SMART 1000 CCD diffractometer equipped with graphite-monochromated Mo-Kα radiation with radiation wavelength 0.71073 Å by using the ω-scan technique. Lorentz polarization and absorption corrections were applied. The structures were solved by direct methods and refined with full-matrix least-squares using the SHELX-97 and SHELXL-97 programs [10, 11]. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The organic hydrogen atoms were generated geometrically; the hydrogen atoms of the water molecules were located from difference maps and refined with isotropic temperature factors. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated. The crystallographic data and selected bond lengths and angles are listed in tables 1 and 2, respectively.

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

1		**2**	
Cu(1)–N(1)	1.988(3)	Zn(1)–N(1)	2.108(2)
Cu(1)–O(1)	2.004(2)	Zn(1)–O(3)	2.1336(19)
Cu(1)–O(3)	2.400(3)	Zn(1)–O(2)	2.1171(17)
N(1)#1–Cu(1)–N(1)	180.0	N(1)#1–Zn(1)–N(1)	180.00(3)
N(1)–Cu(1)–O(1)	82.52(9)	N(1)–Zn(1)–O(2)#1	100.54(7)
N(1)–Cu(1)–O(3)#1	92.62(11)	N(1)#1–Zn(1)–O(3)	94.17(8)
O(1)–Cu(1)–O(3)	94.02(8)	O(2)–Zn(1)–O(3)	89.62(8)
N(1)#1–Cu(1)–O(1)	97.48(9)	O(2)–Zn(1)–O(3)#1	90.38(8)
N(1)–Cu(1)–O(3)	87.38(11)	O(2)#1–Zn(1)–O(3)	90.38(8)
O(1)–Cu(1)–O(3)#1	85.98(8)	N(1)–Zn(1)–O(2)	79.46(7)
N(1)#1–Cu(1)–O(3)#1	87.38(11)	N(1)–Zn(1)–O(3)	85.83(8)
O(3)#1–Cu(1)–O(3)	180.000(1)	O(3)–Zn(1)–O(3)#1	180.00(9)

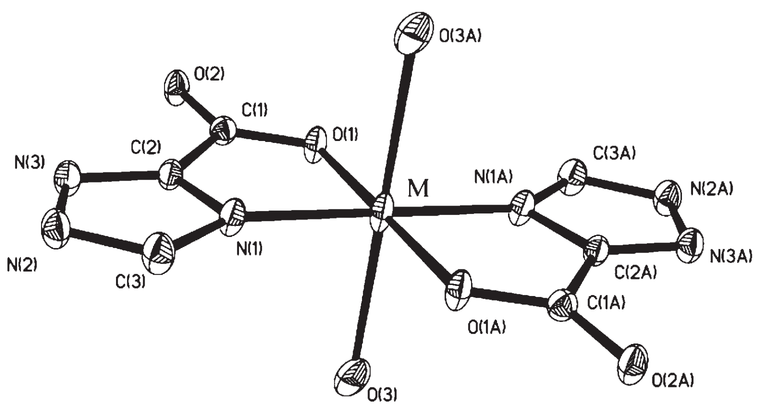


Figure 1. ORTEP drawing of title complexes (M = Cu, Zn) with 30% thermal ellipsoids.

3. Results and discussion

3.1. *Structure of 1 and 2*

Compounds **1** and **2** have similar fundamental structural units and herein only the fundamental structural unit of **1** is described. An ORTEP drawing of the title complexes $[M(L)_2(H_2O)_2]$ (M = Cu, Zn) is shown in figure 1. In **1** and **2**, L adopts a chelating coordination mode via one nitrogen atom N(1) and one oxygen atom O(1). Copper(II) and zinc(II) centers, both lying on the inversion center, are six-coordinate to two nitrogens, two oxygens from two chelating ligands in the equatorial plane and two oxygens from two aqua molecules in the axial sites. In **1**, Cu–O(3) distance (2.400(3) Å) is much longer than that of Cu–N(1) and Cu–O(1) (1.988(3) and 2.004(2) Å), which can be attributed to Jahn–Teller effect of copper. For **2** the axial Zn–O(3) distance (2.133(6) Å) is close to that of Zn–N(1) and Zn–O2(2.117(1) and 2.108(2) Å). The triazole ring in **1** makes an angle of 3.1° with the basal plane of Cu(II), while in **2** it makes an angle of 9.6°.

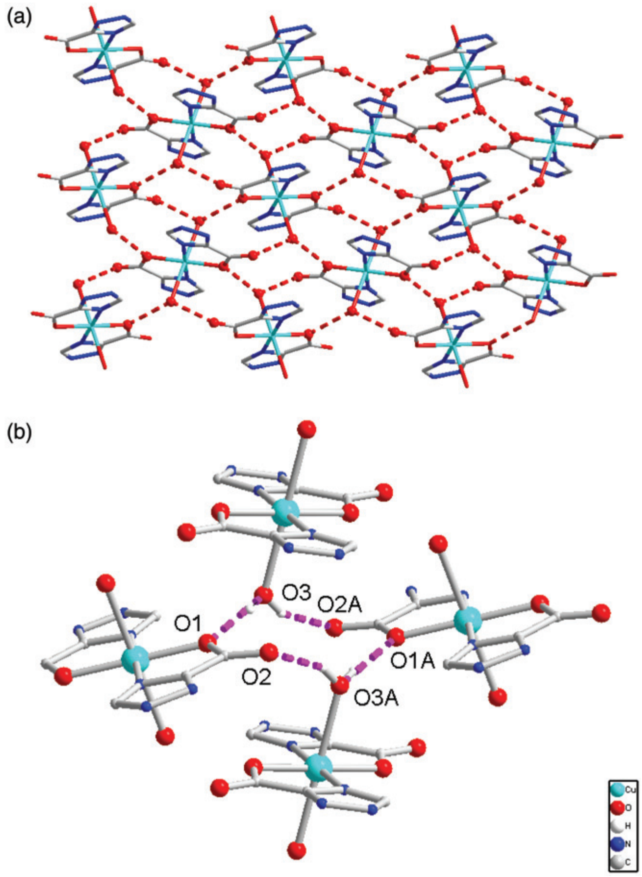


Figure 2. (a) 2D supramolecular layer structure of **1** and **2**, (b) eight-member H-bonded synthons in the 2D supramolecular layer structure (Cyan: M (Cu, Zn); Red: O; Grey: C; Blue: N).

As shown in figure 2(a), in **1** O3 from coordinated water and O1, O2 from ligand carboxylate groups generate intermolecular hydrogen-bonds, which assemble the basic $[M(L)_2(H_2O)_2]$ ($M = Cu$, Zn) structural unit into 2D hydrogen layer structures. Hydrogen bonds distances are 2.774(6) Å (O(3)–H(3A)$\cdots$O(2)) and 2.801(2) Å (O(3)–H(3B)$\cdots$O(1)). As shown in figure 2(b), O(3) acts as hydrogen donor and O(1), O(2) as hydrogen acceptors, forming eight-member H-bonded synthons. Furthermore triazole nitrogen atom N(3) and carboxylate O(2) atom from two neighboring layers also have the strong interactions (N(3)$\cdots$O(2), 2.710(1) Å), which assemble 2D supramolecular layers into a 3D supramolecular architecture (figure 3). The strong hydrogen bonds may prevent triazole 1- and 2-position nitrogens from coordinating to metal(II) even though triazole nitrogens are strong donors.

The 3D supramolecular architecture of **2** is similar to that of **1**. Because of the Jahn–Teller effect of copper(II) and van der Waals radii difference of metal(II), the corresponding hydrogen bond distances for **2** are slightly shorter than those of **1**. The hydrogen bond lengths and angles of **1** and **2** are listed in table 3.

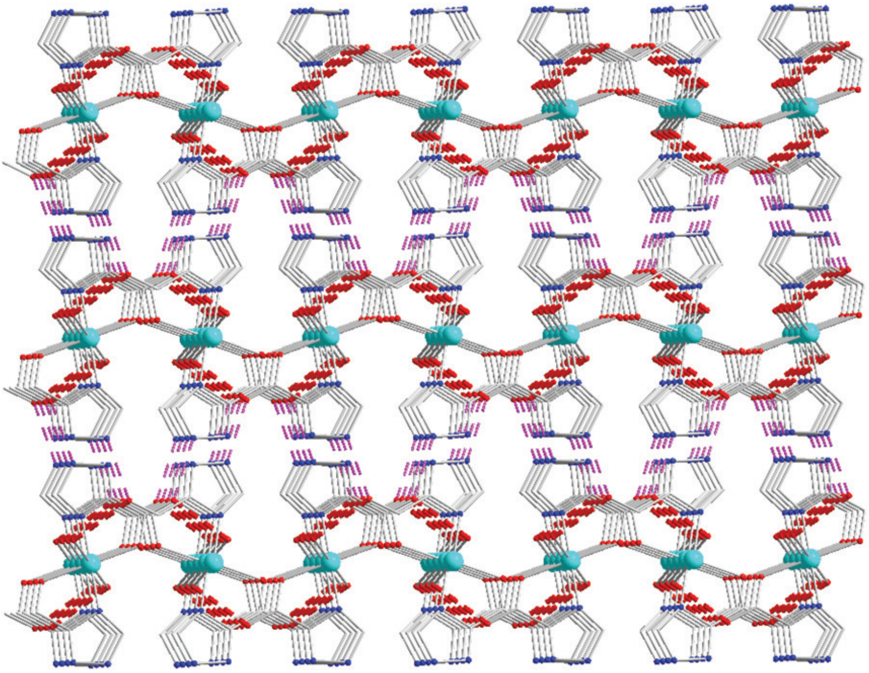


Figure 3. 3D Packing arrangement of **1** and **2** showing extensive hydrogen-bonding interactions along the *b* axis (cyan lines represent N(3) ⋯ O(2) strong interactions which assemble 2D supramolecular planes into 3D supramolecular architectures).

Table 3. Hydrogen bond lengths (Å) and bond angles (°) for **1** and **2**.

1				
D–H ⋯ A	d(D–H)	d(H ⋯ A)	d(D ⋯ A)	∠DHA
O(3)–H(3A) ⋯ (O1)^{a}	0.85	1.975	2.7746	156.26
O(3)–H(3B) ⋯ (O2)^{b}	0.85	1.961	2.8012	169.41
2				
O(3)–H(3A) ⋯ (O1)^{a}	0.850	1.888	2.721	166.28
O(3)–H(3B) ⋯ (O2)^{b}	0.850	1.888	2.705	160.64

Symmetry codes for **1**: a: $-x+2$, $y+1/2$, $-z+5/2$; b: x, $-y+3/2$, $z+1/2$. **2**: a: x, y, $z-1$; b: $-x$, $-y$, $-z$.

From structural considerations L is somewhat similar to imidazole 4,5-carboxylic acid, in that both contain five-member N-containing heterocycle and carboxylic groups. Therefore 3D supramolecular structural motifs of **1** and **2** can be compared with previously reported 3D supramolecular compound $[Cd(imdc)_2(H_2O)]H_2O$ (imdc = imidazole-4,5-dicarboxylic acid) [12], which contains a similar structural unit to **1** but a different 3D hydrogen bonding network because the carboxylic acids participate in intramolecular hydrogen bonding. L and imidazole 4,5-carboxylic acid construct 3D supramolecular networks slightly differently.

A series of Cd-imdc compounds have been prepared via changing solvent and M/L molar ratio exhibiting seven different coordination motifs for imdc; compound framework structures vary from mononuclear, 1D chain, 2D layer to 3D [13].

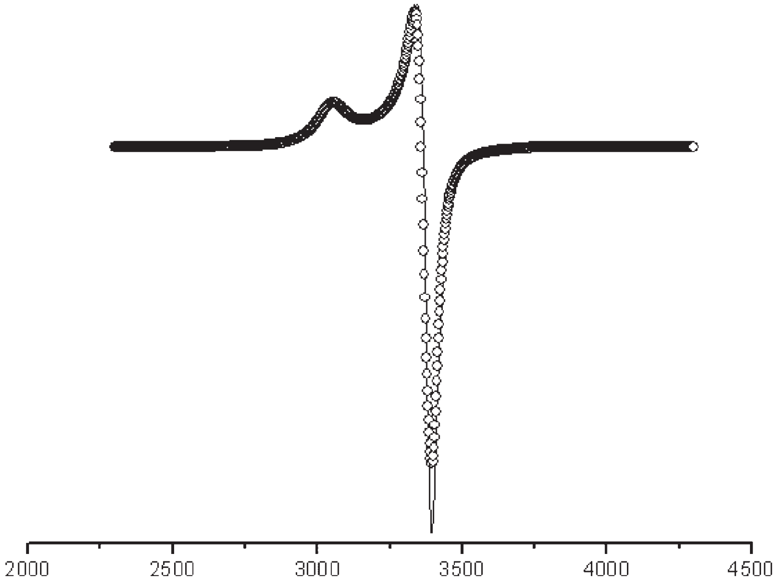


Figure 4. X-band EPR spectrum of **1** at 110 K (line) and computer simulation results (scatter). The Brucker winepr simfonia is used as simulation software.

Slight differences in **1** and **2** in solvent and M/L molar ratio may effectively tune structural motifs of coordination polymers with L and generate further functional materials.

3.2. *FT–IR and TGA spectra of 1 and 2*

For **1**, absorption peaks at 3431.1 and 3033.2 cm^{-1} are assigned to $\nu_{\mathrm{O\text{–}H}}$ of coordinated water. The FT–IR spectrum of **1** also shows characteristic bands of carboxyl at 1671.4, 1639.4 cm^{-1} for the antisymmetric stretching and at 1492.7, 1411.7 cm^{-1} for symmetric stretching. The separations between $\nu_{\mathrm{asym}}(\mathrm{CO_2})$ and $\nu_{\mathrm{sym}}(\mathrm{CO_2})$ indicate unidentate coordination, consistent with the crystal structure of **1** [14]. FT–IR spectrum of **2** is similar to **1** and may be assigned similarly.

Thermal analyses (TGA) of **1** and **2** show very similar TGA curves which may be derived from similar structural units and supramolecular architectures. The TGA curve of **1**, shown in figure 5, shows two decomposition steps. The weight loss from 160 to 200°C for **1** can be attributed to loss of two coordinated water molecules (found: 10.71%; Calcd: 11.19%). The second step from 200 to 600°C corresponds to loss of two ligand molecules. The remaining residue at 600°C should be metal oxide.

3.3. *EPR spectra of 1*

The X-band powder ESR spectrum of **1** at room temperature displays an asymmetric broad absorption (figure 4). ESR spectra at 110 K show three different *g* tensors with a

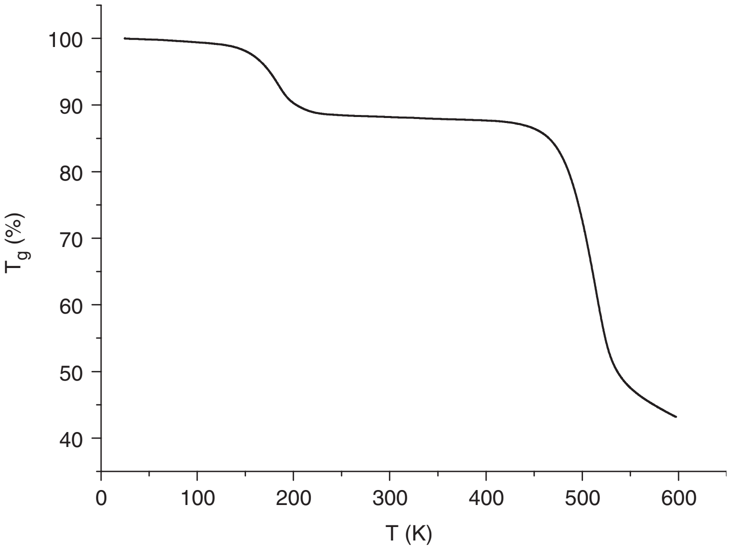


Figure 5. TGA curve of **1**.

hyperfine structure in the g_z signal. Computer simulation gave the ESR parameters $g_x = 2.055$, $g_y = 2.077$, $g_z = 2.29$, indicating a d_{z^2} ground state for Cu(II) of complex **1**.

4. Conclusion

Two new complexes $[CuL_2(H_2O)_2]$ (**1**) and $[ZnL_2(H_2O)_2]$ (**2**) (L = 3-carboxyl-1,2,4-triazole) have been synthesized and characterized by single-crystal X-ray diffraction analysis. Intermolecular hydrogen bonds assemble **1** and **2** into 3D supramolecular architectures, with eight-membered H-bonded synthons. Furthermore investigation on 3-carboxyl-4H-1,2,4-triazole via changing solvent and M/L molar ratio to form a variety of supramolecular coordination frameworks are under way.

Supplementary material

CCDC-216005 **1** and CCDC-216006 **2** contain the supplementary crystallographic data for this article. These data can be obtained free of charge via www.ccdc.can.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Centre, 12 Union Road, Cambridge CB21EZ, UK; Fax: (+44) 1223-336033; or deposit@ccdc.cam.ac.uk).

Acknowledgment

This present work was supported by Tianjin Normal University Foundation of China.

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