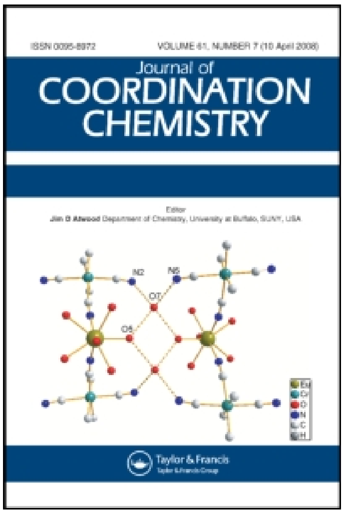

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Tetranuclear cobalt(II) complex and trinuclear copper(II) complex with the ligand 2-hydroxy-3-[(2-sulfoethylimino)-methyl]-benzoic acid: synthesis, structure and properties

Shu-Hua Zhang[a][b]; Yi-Min Jiang[a]; Zhi Min Liu[a]
[a] College of Chemistry and Chemical Engineering, Guangxi Normal University, People's Republic of China [b] Key Laboratory of Nonferrous Metal Materials and Processing Technology, Guilin, 541004, People's Republic of China

To cite this Article Zhang, Shu-Hua , Jiang, Yi-Min and Liu, Zhi Min(2008) 'Tetranuclear cobalt(II) complex and trinuclear copper(II) complex with the ligand 2-hydroxy-3-[(2-sulfoethylimino)-methyl]-benzoic acid: synthesis, structure and properties', Journal of Coordination Chemistry, 61: 12, 1927 — 1934

To link to this Article: DOI: 10.1080/00958970701793628

URL: http://dx.doi.org/10.1080/00958970701793628

Journal of Coordination Chemistry
Vol. 61, No. 12, 20 June 2008, 1927–1934

Taylor & Francis
Taylor & Francis Group

Tetranuclear cobalt(II) complex and trinuclear copper(II) complex with the ligand 2-hydroxy-3-[(2-sulfoethylimino)-methyl]-benzoic acid: synthesis, structure and properties

SHU-HUA ZHANG†‡, YI-MIN JIANG*† and ZHI MIN LIU†

†College of Chemistry and Chemical Engineering,
Guangxi Normal University, 541004, People's Republic of China
‡Key Laboratory of Nonferrous Metal Materials and Processing Technology,
(Department of Material and Chemical Engineering, Guilin University of Technology),
Ministry of Education, Guilin, 541004, People's Republic of China

(*Received 18 June 2007; in final form 20 July 2007*)

A cobalt(II) compound, $[Co_4(L)_2(OH)_2(phen)_2(H_2O)_4] \cdot 6H_2O$ (**1**), and a copper(II) compound, $[Cu_2(L)_2(H_2O)_2][Cu(H_2O)_6] \cdot 6H_2O$ (**2**) [where H_3L is 2-hydroxy-3-[(2-sulfoethylimino)-methyl]-benzoic acid and phen is O-phenanthroline], were prepared and characterized. The tetranuclear cobalt complex **1**, $C_{44}H_{62}N_6O_{28}S_2Co_4$, crystallizes in the monoclinic space group $P2_1/c$, with $a = 11.847(10)$ Å, $b = 19.061(15)$ Å, $c = 12.635(10)$ Å, $\beta = 105.483(9)^\circ$, and $Z = 2$; R_1 for 4821 observed reflections $[I > 2\sigma(I)]$ was 0.0679. Complex **1** is a centrosymmetric tetranuclear cobalt complex with all cobalts having distorted octahedral geometry. The molecule can be viewed as two planar $[Co_2(OH)(L)(Phen)H_2O]$ units tied together by two terminal water molecules. The framework of **1** has the appearance of two connected face-sharing cubes, each with one vertex missing. The trinuclear copper complex **2**, $C_{20}H_{44}Cu_3N_2O_{26}S_2$, crystallizes in the triclinic space group $P1$, with $a = 7.524(\mathbf{1})$ Å, $b = 7.902(2)$ Å, $c = 16.885(4)$ Å, $\alpha = 88.993(6)^\circ$, $\beta = 80.725(7)^\circ$, $\gamma = 66.725(4)^\circ$ and $Z = 1$; R_1 for 4298 observed reflections $[I > 2\sigma(I)]$ was 0.0360. Complex **2** is an ionic compound, in which the three Cu(II) centers have two coordination modes. The molecule has a centrosymmetric dinuclear copper coordinated anion and a hexa-aqua-copper cation. The sulfonic acid group has less coordination ability than carboxylate oxygen.

Keywords: 2-Hydroxy-3-[(2-sulfoethylimino)-methyl]-benzoic acid; Crystal structure; Coordination ability

1. Introduction

Schiff-base complexes containing amino acid have been studied for many years, arousing interest because of their antiviral, anticancer and antibacterial activities [1–3]. Taurine, an amino acid containing sulfur, is indispensable to human beings with important physiologic functions. Recently, we reported many compounds containing taurine Schiff base [1, 3].

---

*Corresponding author. Email: zsh720108@21cn.com

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2008 Taylor & Francis
DOI: 10.1080/00958970701793628

Schiff-base complexes containing taurine are widely used in the assembly of one-, two- and three-dimensional compounds because of the diverse coordination modes and bridging ability [1–3]. For example, [(2-hydroxyphenyl)methylene]-amino-1-ethanesulfonic acid (H_2tssb) can function in six coordination modes [1–3]. Tssb^{2-}, as a multidentate ligand with six coordination sites, might be utilized as a versatile linker in the construction of interesting multi-dimensional complexes with the capability of participating in hydrogen bonding with multi-proton acceptor or donor sites, is a candidate for construction of multi-dimensional complexes [2, 3]. In the present work, in order to contrast coordination ability of sulfonic acid and carboxylate groups, we chose L^{3-} to construct two new supramolecular complexes **1** and **2**.

2. Experimental

All reagents were commercial grade materials and used without further purification. Elemental analyses (C, H, N) were performed by a PE 1700 CHN auto elemental analyzer. IR spectra were recorded on a Spectrum One Perkin-Elmer FT-IR spectrophotometer (KBr disc) between 4000–400 cm^{-1}. Crystal structures were determined by single-crystal X-ray diffraction and SHELXL crystallographic software. The TG analysis was performed on a TG209.

2.1. *Preparation of* $[Co_4(L)_2(OH)_2(phen)_2(H_2O)_4] \cdot 6H_2O$ *(1)*

The ligand (2-hydroxy-3-[(2-sulfo-ethylimino)-methyl]-benzoic acid (H_3L)) was prepared according to a literature procedure [4].

A solution of H_3L (0.261 g, 1 mmol) in ethanol (15 mL) was slowly added to a solution of $Co(OAc)_2 \cdot 4H_2O$ (0.249 g, 1 mmol) in distilled water (15 mL). The mixture was stirred for 30 min at 333 K, and then slowly added to a solution of Phen (0.198 g, 1 mmol) in ethanol (15 mL). The mixture was stirred and refluxed for 4 h at 333 K, and filtered. The filtrate was left to stand at room temperature and red crystals were obtained in a yield of 52% (based on Co). Found: C, 37.29; H, 3.96; N, 3.96. $C_{44}H_{62}Co_4N_6O_{28}S_2$ requires C, 37.30; H, 3.98; N, 5.93.

2.2. *Preparation of* $[Cu_2(L)_2(H_2O)_2][Cu(H_2O)_6] \cdot 6H_2O$ *(2)*

A solution of H_3L (0.261 g, 1 mmol) in ethanol (15 mL) was slowly added to a solution of $Cu(OAc)_2 \cdot 4H_2O$ (0.249 g, 1 mmol) in distilled water (15 mL). The mixture was stirred for 30 min at 333 K, with slow evaporation of the reaction mixture. Good quality blue crystals were obtained in a yield of 63% (based on Cu). Found: C, 24.45; H, 4.54; N, 2.86. $C_{20}H_{44}Cu_3N_2O_{26}S_2$ requires C, 24.43; H, 4.51; N, 2.85.

2.3. *X-ray crystallography*

Intensity data for complexes **1** and **2** were collected at 293 K on a Bruker SMART CCD area-detector diffractometer using graphite-monochromated Mo-Kα radiation

Table 1. Crystal data and refinement details for **1** and **2**.

Formula	$C_{44}H_{62}Co_4N_6O_{28}S_2$	$C_{20}H_{44}Cu_3N_2O_{26}S_2$
CCDC deposit no.	644096	644097
Formula weight	1422.86	983.36
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
a (Å)	11.847(10)	7.524(1)
b (Å)	19.061(15)	7.902(2)
c (Å)	12.635(10)	16.885(4)
a (°)	105.483(9)	88.993(6)
β (°)	2	80.725(7)
γ (°)	2750(4)	66.725(4)
Z	2	1
Volume (Å^3)	2750(4)	908.9(3)
D_{calc} (g cm^{-3})	1.718	1.797
Absorption coefficient (mm^{-1})	1.358	1.952
F(000)	1464	505
Crystal size (mm^3)	$0.15 \times 0.40 \times 1.00$	$0.10 \times 0.32 \times 0.55$
$\theta_{\min}$, $\theta_{\max}$ (deg)	3.0, 25.1	2.5, 25.1
Index ranges	$-14 \le h \le 14$	$-8 \le h \le 8$
	$-22 \le k \le 18$	$-9 \le k \le 9$
	$-15 \le l \le 14$	$-19 \le l \le 20$
Total data	15013	5778
Total unique data	4821	4298
Completeness $\theta = 25.10°$	98.5	98.7
Absorption correction	None	None
Max. and min. transmission	0.816, 0.526	0.823, 0.413
Data/restraints/parameters	4821/0/379	4298/321/478
Goodness-of-fit on F^2	1.073	1.071
Final R indices [$I > 2\sigma$(I)]	0.0679	0.0360
R indices (all data)	0.1870	0.0997
Largest diff. Peak and hole (eÅ^{-3})	1.201, −0.839	0.645, −0.891

($\lambda = 0.71073$ Å) using the ω–θ scan mode in the range $3.0 \le \theta \le 25.1°$ (**1**), $2.5 \le \theta \le 25.1°$ (**2**). Raw frame data were integrated with the SAINT [5] program. The structures were solved by direct methods using SHELXS-97 and refined by full-matrix least-squares on F^2 using SHELXS-97 [6]. An empirical absorption correction was applied with SADABS [7]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were set in calculated positions and refined by a riding mode, with a common thermal parameter. All calculations and graphics were performed with SHELXTL [6]. Crystal data and details of the structure determination are given in table 1. Selected bond lengths and angles are given in table 2. Figures 1 and 2 illustrate the structures of **1** and **2**, respectively.

3. Results and discussion

As shown in figure 1, **1** is a centrosymmetric tetranuclear complex with four cobalt(II) ions with distorted octahedral geometry. The molecule can be viewed as two planar $[Co_2(OH)(L)(Phen)H_2O]$ units connected by two terminal water molecules. The framework of **1** has the appearance of two connected face-sharing cubes, each with

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

Compound **1**			
Co1–O6	1.913(4)	Co1–O7	1.914(4)
Co1–O8	1.873(4)	Co1–N1	1.920(4)
Co1–N2	1.967(5)	Co1–N3	1.933(5)
Co2–O1W	2.162(4)	Co2–O5	1.995(5)
Co2–O6	2.134(4)	Co2–O7	2.061(4)
Co2–O7a	2.171(4)	Co2–O8a	2.016(4)
O6–Co1–O7	82.55(16)	O6–Co1–O8	94.44(16)
O6–Co1–N1	94.28(18)	O6–Co1–N2	91.07(18)
O6–Co1–N3	170.14(17)	O7–Co1–O8	84.55(16)
O7–Co1–N1	173.48(19)	O7–Co1–N2	93.70(16)
O7–Co1–N3	89.27(16)	O8–Co1–N1	90.03(19)
O8–Co1–N2	173.95(19)	O8–Co1–N3	90.25(19)
N1–Co1–N2	92.06(19)	N1–Co1–N3	94.39(19)
N2–Co1–N3	83.9(2)	O1W–Co2–O5	85.96(19)
O1W–Co2–O6	100.76(15)	O1W–Co2–O7	93.20(17)
O1W–Co2–O7a	164.21(15)	O1W–Co2–O8a	90.68(15)
O5–Co2–O6	84.87(15)	O5–Co2–O7	158.30(16)
O5–Co2–O7a	102.38(17)	O5–Co2–O8a	99.29(16)
O6–Co2–O7	73.97(14)	O6–Co2–O7a	93.40(14)
O6–Co2–O8a	168.11(15)	O7–Co2–O7a	83.95(14)
O7a–Co2–O8a	74.86(14)	O7–Co2–O8a	102.41(15)
Compound **2**			
Cu1–O3	1.947(10)	Cu1–O7	1.902(10)
Cu1–O9	1.954(8)	Cu1–O14	2.309(9)
Cu1–N1	1.938(10)	Cu2–O1	1.906(9)
Cu2–O3	1.947(8)	Cu2–O9	1.952(10)
Cu2–O13	2.307(9)	Cu2–N2	1.963(11)
Cu3–O20	2.056(9)	Cu3–O16	2.038(8)
Cu3–O17	2.051(11)	Cu3–O15	2.062(8)
Cu3–O19	2.048(9)	Cu3–O18	2.070(11)
O3–Cu1–O7	169.0(4)	O3–Cu1–O9	78.0(4)
O3–Cu1–O14	93.4(4)	O3–Cu1–N1	93.2(4)
O7–Cu1–O9	92.4(4)	O7–Cu1–O14	92.9(4)
O7–Cu1–N1	94.9(4)	O9–Cu1–O14	95.8(3)
O9–Cu1–N1	164.6(4)	O14–Cu1–N1	97.4(4)
O1–Cu2–O3	92.7(4)	O1–Cu2–O9	168.9(4)
O1–Cu2–O13	94.6(4)	O1–Cu2–N2	95.5(4)
O3–Cu2–O9	78.1(4)	O3–Cu2–O13	94.1(3)
O3–Cu2–N2	164.2(4)	O9–Cu2–O13	92.3(4)
O9–Cu2–N2	92.1(4)	O13–Cu2–N2	98.6(4)
O16–Cu3–O17	91.8(4)	O16–Cu3–O18	88.0(4)
O16–Cu3–O19	87.7(4)	O16–Cu3–O20	91.1(4)
O17–Cu3–O18	179.6(5)	O17–Cu3–O19	89.3(4)
O17–Cu3–O20	94.0(4)	O18–Cu3–O19	91.1(4)
O18–Cu3–O20	85.7(4)	O19–Cu3–O20	176.6(4)
O15–Cu3–O16	178.3(4)	O15–Cu3–O17	86.5(4)
O15–Cu3–O18	93.6(4)	O15–Cu3–O19	92.3(3)
O15–Cu3–O20	89.0(3)		

Symmetry codes: Compound **1**, a: $1-x$, $-y$, $1-z$.

one vertex missing. Four cobalt(II) ions form a plane [plane equation: $-2.746x-12.050y+9.784z=3.591$] with the other atoms distributed up and down from the plane. Complex **1** further constructed a 3-D supramolecular network through strong hydrogen bonds (table 3 and figure 3).

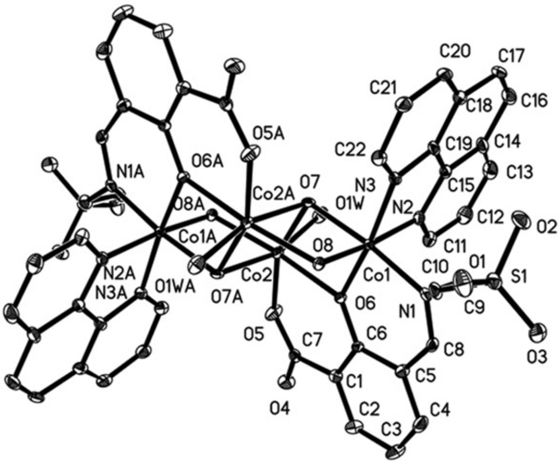

Figure 1. Molecular structure of **1** in the crystal. Hydrogen atoms and noncoordinated solvent water molecules have been omitted.

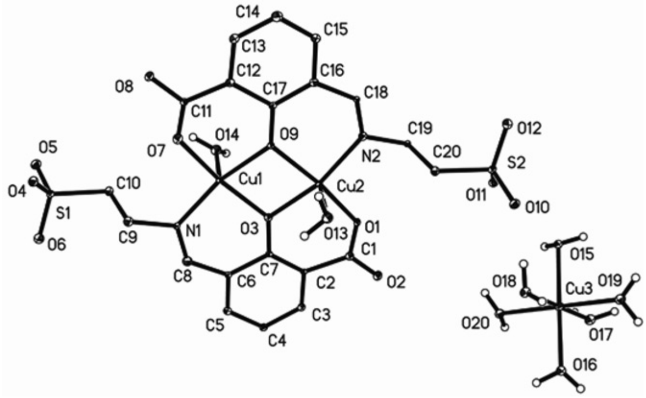

Figure 2. Molecular structure of **2** in the crystal. Non-solvent hydrogen atoms and non-coordinated solvent water molecules have been omitted.

Table 3. Hydrogen-bond geometry (Å, °) for **1**.

D–H···A	D–H	H···A	D···A	∠DHA
O7–H7A···O3[a]	0.85	1.98	2.790(6)	159.0
O8–H8B···O7	0.85	2.41	3.177(5)	149.8
O8–H8C···O2[b]	0.85	2.01	2.746(6)	144.4
O1W–H1WB···O3W	0.85	1.92	2.766(7)	172.3
O1W–H1WA···O1[a]	0.85	2.12	2.934(7)	160.9
O2W–H2WA···O3W[c]	0.85	2.47	2.923(10)	113.8
O2W–H2WB···O5W[d]	0.85	2.06	2.809(9)	146.9
O3W–H3WB···O6W[e]	0.85	2.09	2.759(9)	135.5
O4W–H4WA···O5W[f]	0.85	2.15	2.796(8)	132.2
O4W–H4WB···O4	0.85	1.95	2.795(7)	170.6
O5W–H5WA···O4W	0.85	2.22	2.796(8)	125.3
O6W–H6WA···O3W	0.85	2.34	2.759(9)	111.1
O6W–H6WB···O1	0.85	2.00	2.803(8)	158.0

Symmetry codes, a: $1-x$, $-1/2+y$, $3/2-z$; b: x, $1/2-y$, $-1/2+z$; c: $1-x$, $1/2+y$, $3/2-z$; d: $1+x$, $1/2-y$, $1/2+z$; e: $1-x$, $-y$, $1-z$; f: $-x$, $-1/2+y$, $1/2-z$.

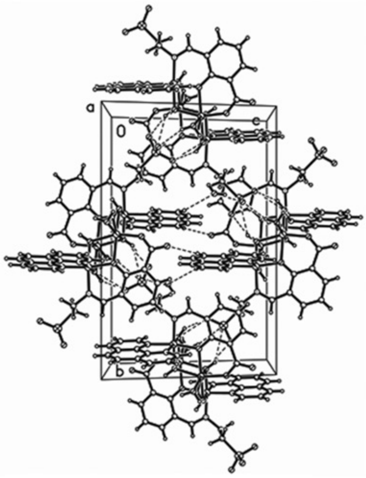

Figure 3. 3-D network of **1**.

The molecule of **2** is shown in figure 2. Complex **2** is an ionic compound, with $[Cu_2(L)_2(H_2O)_2]^{2-}$ a centrosymmetric dinuclear copper coordinated anion in which Cu(II) is coordinated by three oxygens and one nitrogen from two different L^{3-} ligands and one terminal water molecule forming a distorted CuO_4N square pyramid. The other Cu(II) has six water molecules in a distorted CuO6 octahedral cation. Besides the electrostatic force, there are abundant hydrogen bonds between anions and cations. The compound was assembled into a 3D supramolecular network through strong hydrogen bonds (figure 4 and table 4).

In **1** and **2**, the sulfonic acid groups do not coordinate in contrast to the literature [1–3], where $tssb^{-2}$ is tridentate, coordinating through the phenolato oxygen, imine nitrogen, and sulfonic acid oxygen forming five- and six-membered rings. In **1** and **2**, the L^{3-} is also tridentate, coordinating through the phenolato oxygen, imine nitrogen, and carboxylate oxygen forming two five-membered rings. Complex **2** shows that coordination ability of sulfonic acid is weaker than carboxylate for Cu^{2+} [8].

3.1. *Thermal and spectroscopic properties*

IR bands for **1** and **2** at 1638(1630) and 1405(1418) cm^{-1} are assigned to ν_sCOO^- and $\nu_{as}COO^-$, respectively. The shifts suggest that the carboxylate groups are monodentate [9]. IR spectra of the ligand show strong imine bands at 1648 cm^{-1} which shift to 1624 and 1622 cm^{-1} in **1** and **2**, respectively. The shifts are consistent with coordination of the N of C=N of the ligand [3e]. The complex gives a broad band between 3500 and 3000 cm^{-1}, attributable to –OH groups involved in hydrogen bonding [10]. In-plane and out-of-plane vibrations of water associated with coordinated water were observed in the spectrum of the complex at 764(**1**), 774(**2**) and 604(**1**), 581(**2**) cm^{-1} [11]. The sulfonic acid group IR bands at 1206, 1179 and 1035(1039) cm^{-1} do not shift in the complexes, suggesting sulfonic acid group does not coordinate.

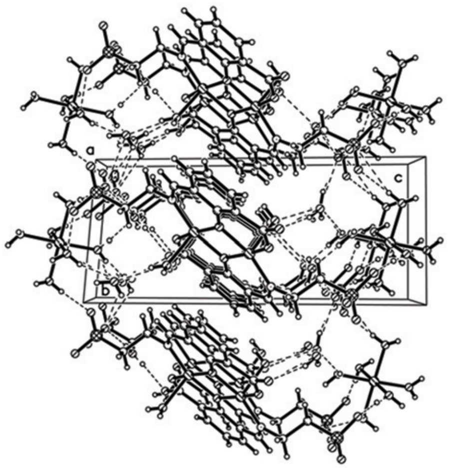

Figure 4. 3-D network of **2**.

Table 4. Hydrogen-bond geometry (Å, °) for **2**.

D–H···A	D–H	H···A	D···A	∠DHA
O3W–H1#···O11$^{\mathrm{i}}$	0.85	2.0156	2.848(12)	166.22
O1W–H1A···O2	0.85	2.0828	2.901(11)	161.32
O1W–H1B···O3W	0.85	2.0720	2.714(14)	131.95
O2W–H2A···O11	0.85	2.0384	2.792(14)	147.23
O5W–H3#···O8$^{\mathrm{ii}}$	0.85	1.9219	2.756(13)	167.06
O3W–H3B···O1W	0.85	1.8714	2.714(14)	171.06
O5W–H5B···O4$^{\mathrm{ii}}$	0.85	1.9706	2.810(14)	169.19
O6W–H6A···O8$^{\mathrm{ii}}$	0.85	2.0148	2.854(11)	168.98
O6W–H6B···O17$^{\mathrm{iii}}$	0.85	2.3749	3.132(12)	148.82
O13–H13B···O2$^{\mathrm{iv}}$	0.85	1.9550	2.787(15)	165.64
O14–H14B···O4W	0.85	1.9975	2.821(12)	163.30
O14–H14C···O8$^{\mathrm{ii}}$	0.85	2.1154	2.793(15)	136.42
O15–H15B···O6$^{\mathrm{v}}$	0.85	1.8569	2.686(11)	164.69
O16–H16A···O12$^{\mathrm{vi}}$	0.85	1.9412	2.733(13)	154.52
O16–H16B···O4$^{\mathrm{vii}}$	0.85	2.0146	2.865(14)	178.69
O17–H17A···O6W$^{\mathrm{viii}}$	0.85	2.3192	3.132(12)	160.14
O17–H17B···O10$^{\mathrm{ii}}$	0.85	1.9391	2.750(14)	159.13
O18–H18B···O5$^{\mathrm{viii}}$	0.85	1.9612	2.753(13)	154.41
O18–H18C···O10	0.85	1.8855	2.718(13)	166.02
O19–H19C···O5W$^{\mathrm{viii}}$	0.85	1.8634	2.710(13)	174.96
O19–H19D···O4W$^{\mathrm{viii}}$	0.85	1.9899	2.818(14)	164.60
O20–H20C···O2W	0.85	1.8502	2.686(12)	167.83

Symmetry codes, i: $x, -1+y, z$; ii: $1+x, y, z$; iii: $x, y, -1+z$; iv: $-1+x, y, z$; v: $x, 1+y, 1+z$; vi: $1+x, -1+y, z$; vii: $1+x, y, 1+z$; viii: $x, y, 1+z$.

Upon heating under nitrogen, **2** undergoes three major stages of weight loss. The first occurs at 80–120°C. The DTA curve shows one narrow endothermic peak between 85 and 120°C. Associated weight losses (10.4%) are consistent with values calculated for the removal of six lattice water molecules. In the second stage, $[Cu_2(L)_2(H_2O)_2][Cu(H_2O)_6]$ is decomposed at 120–185°C, with the mass loss of 15.2%, the theoretical value being 14.6%, corresponding to the loss of eight coordinated water molecules. In the third stage, $Cu_3(L)_2$ is completely decomposed at 350–800°C with formation of CuO. From the above analysis, the thermal decomposition of $[Cu_2(L)_2(H_2O)_2][Cu(H_2O)_6]\cdot 6H_2O$ may be expressed by the following scheme:

$$[Cu_2(L)_2(H_2O)_2][Cu(H_2O)_2]\cdot 6H_2O\,\frac{80-120^\circ C}{-6H_2O}\rightarrow [Cu_2(L_2)(H_2O)_2]$$

$$[Cu(H_2O)_6]\,\frac{120-185^\circ C}{-8H_2O}\rightarrow Cu_3(L)_2\,\frac{350-800^\circ C}{-3L}\rightarrow 3CuO$$

Supplementary data

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 644096 and 644097 for **1** and **2**, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: 44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgements

We acknowledge financial support by the Key Laboratory of Non-ferrous Metal Material and New Processing Technology, Ministry of Education, P. R. China.

References

[1] S.H. Zhang, Y.M. Jiang, Z. Liu, K.B. Yu. *Acta Cryst.*, **E61**, m446 (2005).

[2] B. Sreenivasulu, M. Vetrichelvan, F. Zhao, S. Gao, J.J. Vittal. *Eur. J. Inorg. Chem.*, 4635 (2005).

[3] (a)S.H. Zhang, Y.M. Jiang, Y. Xiao, Z.Y. Zhou. *Chin. J. Inorg. Chem.*, **19**(5), 517 (2003); (b) S.H. Zhang, Y.M. Jiang, Z.Y. Zhou. *Chin. J. Chem.*, **11**, 1303 (2004); (c) H.F. Xu, S.H. Zhang, Y.M. Jiang, X.X. Zhong, F. Gao. *Chin. J. Struct. Chem.*, **23**(7), 808 (2004); (d) M. Xing, S.H. Zhang, R.B. Du, Y.M. Jiang, W.N. Sun, S.M. Liao. *Chin. J. Inorg. Chem.*, **22**(1), 179 (2006); (e) S.H. Zhang, Y.M. Jiang, X.X. Zhong. *Chin. J. Inorg. Chem.*, **20**(8), 959 (2004).

[4] Z.M. Liu, Y.M. Jiang. *Chin. Inorg. Chem.*, **21**(5), 733 (2005).

[5] Siemens. *SAINT: Area Detector Control and Integration Software*, Siemens Analytical X-ray Instruments Inc., Madison, WI, USA (1996).

[6] G.M. Sheldrick. *SHELXL97 and SHELXTL Software Reference Manual*, Version 5.1, Brucker AXS Inc., Madison, WI, USA (1997).

[7] G.M. Sheldrick. *SADABS. Program for Empirical Absorption Correction of Area Detector Data*, University of Göttingen, Germany (1996).

[8] J.W. Cai, C.H. Chen, J.H. Yao, X.P. Hu, X.M. Chen. *J. Chem. Soc., Dalton Trans.*, 1137 (2001).

[9] S. Gao, Z. Shi, J. Hua, S.H. Feng, R.R. Xu, S.X. Liu, L.H. Huo, P.G. Chen. *Chem. J. Chin. Univ.*, **21**, 177 (2000).

[10] G. Singh, P.S.S.J. Shastry, R.K. Lonibala, T.R. Rao. *Synth. React. Inorg. Met.-Org. Chem.*, **22**, 1041 (1992).

[11] K. Nakamoto. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Part B, 5th Edn, Wiley, New York (1997).