Studies on mono- and dinuclear bisoxime copper complexes with different coordination geometries

Wen-Kui Dong · Jun-Feng Tong · Yin-Xia Sun · Jian-Chao Wu · Jian Yao · Shang-Sheng Gong

Received: 5 January 2010/Accepted: 11 February 2010/Published online: 19 March 2010 © Springer Science+Business Media B.V. 2010

Abstract Two new mono- and dinuclear Cu(II) complexes, namely $[CuL^1] \cdot 0.5H_2O(1)$ and $[(Cu_2(L^2)_2)(DMF)] \cdot$ 0.5DMF (2) $(H_2L^1 = 1, 2\text{-bis}[(Z)-(3\text{-methyl-5-oxo-1-phe-})]$ nyl-1*H*-pyrazolidin-4(4*H*)-yl)(phenyl)]methylene-aminooxy} ethane; $H_2L^2 = 1,3$ -bis{[(Z)-(3-methyl-5-oxo-1-phenyl-1Hpyrazolidin-4(4*H*)-yl)(phenyl)] methyleneaminooxy}propane), have been synthesized and characterized by X-ray crystallography. The unit cell of complex 1 contains two crystallographically independent but chemically identical [CuL¹] molecules and one crystalline water molecule, showing a slightly distorted square-planar coordination geometry and forming a wave-like pattern running along the *a*-axis via hydrogen bonding and $\pi \cdots \pi$ stacking interactions. Complex 2 has a dinuclear structure, comprising two Cu(II) atoms, two completely deprotonated phenolate bisoxime $(L^2)^{2-}$ moieties (in the form of enol), and both coordinated and hemi-crystalline DMF molecules. Complex 2 has square-planar and square-pyramidal geometries around the two copper centers, whose basic coordination planes are almost perpendicular and form an infinite threedimensional supramolecular network structure involving intermolecular C–H···N, C–H···O, and C–H··· π (Ph) hydrogen bonding and $\pi \cdots \pi$ stacking interactions of neighboring pyrazole rings.

W.-K. Dong (⊠) · J.-F. Tong · Y.-X. Sun · J.-C. Wu · J. Yao · S.-S. Gong
School of Chemical and Biological Engineering, Lanzhou Jiaotong University, 730070 Lanzhou,
People's Republic of China
e-mail: dongwk@126.com

Introduction

Bisoxime compounds have received much attention recently, not only because the *O*-alkyloxime groups in these complexes resist metathesis of the C=N bonds [1–4] but also because the large electronegativity of the oxygen atoms is expected to affect strongly the electronic properties of the N₂O₂ coordination sphere, which can lead to different and novel properties and structures of the resulting complexes [5, 6]. Bisoximes are fascinating and versatile chelating ligands, which have been used to form neutral complexes with a number of divalent transition metal ions through the loss of the two hydroxyl protons [4, 7, 8].

In the past years, we have prepared a series of complexes of transition metals with bisoxime ligands and investigated their coordination behavior, solvent effects, supramolecular architectures, and other properties [2, 6, 7, 9-11]. As a part of our comprehensive efforts toward synthesis and structural characterization of these new materials, we now report on two new Cu(II) complexes, namely [CuL¹]·0.5H₂O (1) and $[(Cu_2(L^2)_2)(DMF)] \cdot 0.5DMF$ (2) $(H_2L^1 = 1, 2 \cdot bis \{ [(Z) - (3 - C)(L^2)_2)(DMF) \} \cdot 0.5DMF$ (2) $(H_2L^1 = 1, 2 \cdot bis \} [(Z) - (3 - C)(L^2)_2)(DMF) \}$ methyl-5-oxo-1-phenyl-1*H*-pyrazolidin-4(4*H*)-yl)(phenyl)] methyleneaminooxy}ethane; $H_2L^2 = 1,3$ -bis{[(Z)-(3-methyl-5-oxo-1-phenyl-1H-pyrazolidin-4(4H)-yl)(phenyl)]methyleneaminooxy } propane), obtained by the complexation of two bisoximes with Cu(II) in different solvents (Scheme 1). We discuss their coordination behavior, the influence of solvent, and the effects of variations in ligands in the formation and structure of the complexes.

Experimental

4-Benzoyl-3-methyl-1-phenyl-1*H*-pyrazol-5(4*H*)-one (BMPP) from East China Normal University Chemical Plant was

Scheme 1 Synthesis of H_2L^1 and H_2L^2 (n = 0, $H_2L = H_2L^1$; n = 1, $H_2L = H_2L^2$) and structural formulae of complexes 1 and 2 (S = solvent DMF)



used without further purification. The other reagents and solvents were analytical grade reagents from Tanjin Chemical Reagent Factory.

Carbon, hydrogen, and nitrogen were analyzed with a GmbH VariuoEL V3.00 automatic elemental analyzer. Elemental analyses for Cu were determined with an IRIS ER/S·WP-1 ICP atomic emission spectrometer. FTIR spectra were recorded on a VERTEX70 FT-IR spectrophotometer, with samples prepared as KBr (4,000- 500 cm^{-1}) and CsI (500–100 cm⁻¹) pellets. UV-vis spectra were taken on a Shimadzu UV-240 spectrophotometer. Electrolytic conductance measurements were made with a DDS-11A type conductivity bridge using 1.0×10^{-3} mol L⁻¹ solutions in DMF at room temperature. Melting points were measured by the use of a microscopic melting point apparatus made by the Beijing Taike instrument limited company, and the thermometer was uncorrected. TG-DTA analyses were carried out in an N₂ atmosphere at a heating rate of 5 °C/min in the temperature range 25-900 °C on a ZRY-1P thermoanalyzer, using an Al₂O₃ crucible. X-ray single-crystal structure determination was carried out on a Bruker Smart APEX CCD diffractometer.

Synthesis of H₂L¹

1,2-Bis(aminooxy)ethane was synthesized by a similar method to that reported earlier [12]. ¹H NMR (400 MHz, CDCl₃, δ , ppm): 3.79 (s, 4H), 5.52 (s, 4H). H₂L¹ was synthesized according to a method analogous to that reported earlier [13]. A colorless ethanol solution (4 mL) of 1,2-bis(aminooxy)ethane (43.2 mg, 0.469 mmol) was slowly added to a yellow ethanol solution (4 mL) of BMPP (267.2 mg, 0.961 mmol), and the mixture was stirred for 24 h at 55 °C. After cooling to room temperature, the precipitate was filtered off and washed in succession with

ethanol and ethanol–hexane (1:4) (3 × 4 mL). The product was purified by recrystallization from ethanol and dried under vacuum, yielding a white powder (Yield 0.2035 g, 69%, M.P. 191–193 °C). Found: C, 70.4; H, 5.2; N, 13.8. Calcd. for $C_{36}H_{32}N_6O_4$ (%): C, 70.6; H, 5.3; N, 13.7.

Synthesis of H_2L^2

1,3-Bis(aminooxy)propane was synthesized using an analogous method to that reported earlier [12].

A colorless ethanol solution (4 mL) of 1,3-bis(aminooxy)propane (56.4 mg, 0.531 mmol) was slowly added to a yellow ethanol solution (4 mL) of BMPP (300.5 mg, 1.08 mmol), and the mixture was stirred for 24 h at 55 °C. After cooling to room temperature, the precipitate was filtered off and washed successively with ethanol and ethanol–hexane (1:4) (3 × 4 mL). The product was purified by recrystallization from ethanol and dried under vacuum, yielding a white powder (Yield 0.2617 g, 77%, M.P. 194–195 °C). Found: C, 70.8; H, 5.4; N, 13.5. Calcd. for $C_{37}H_{34}N_6O_4$ (%): C, 70.9; H, 5.5; N, 13.4.

Preparation of complex 1

A pale-blue MeOH solution (2 mL) of copper acetate monohydrate (4.3 mg, 0.022 mmol) was added dropwise to a colorless MeOH solution (4 mL) of H_2L^1 (5.1 mg, 0.0083 mmol) at room temperature. The color of the solution immediately turned brown. The mixture was filtered, and the filtrate was left standing at room temperature to crystallize for about 3 weeks. With evaporation of the solvent, brown needle-like single crystals suitable for X-ray crystallographic analysis were obtained. Found: C, 63.1; H, 4.3; N: 12.5; Cu, 9.2. Calcd. for [CuL¹]·0.5H₂O (C₃₆H₃₁CuN₆O_{4.5}) (%): C, 63.3; H, 4.6; N, 12.3; Cu, 9.3.

Preparation of complex 2

A pale-blue methanol solution (5 mL) of copper chloride dihydrate (2.8 mg, 0.016 mmol) was added dropwise to a colorless DMF solution (5 mL) of H_2L^2 (4.0 mg, 0.006 mmol) at room temperature. The color of the mixing solution immediately turned brown. The mixture was filtered, and the filtrate was allowed to stand at room temperature for about 3 weeks. With evaporation of the mixed solvent, brown block-like single crystals suitable for X-ray crystallographic analysis were gained. Found: C, 63.4; H, 5.0; 12.8; Cu, 8.5. Calcd. for [(Cu₂(L²)₂)(DMF)]·0.5DMF (C_{78.5}H_{74.5}Cu₂N_{13.5}O_{9.5}) (%): C, 63.4; H, 5.1; N, 12.7; Cu, 8.6.

Crystal structure determination and refinement

Single-crystal X-ray diffraction data were collected at 298 K on a BRUKER SMART APEX II CCD diffractometer with graphite monochromated Mo- $K\alpha$ radiation ($\lambda = 0.71073$ Å). The LP factor semi-empirical absorption corrections were applied using the SADABS program [14]. The structure was solved by direct methods and refined by the full-matrix least-squares method on F^2 using the SHELXTL crystallographic software package [15]. The non-hydrogen atoms were refined anisotropically; hydrogen atoms were positioned geometrically (C–H = 0.93, 0.96 and 0.97 Å) and were refined as riding, with U_{iso}(H) = 1.20 or 1.50 U_{eq}(C). The crystal data and experimental parameters relevant to the structure determination are listed in Table 1.

Results and discussion

Complexes 1 and 2 with new tetradentate bisoxime chelating ligands have been synthesized and characterized by molar conductance, IR and UV–vis spectra, TG–DTA and X-ray crystallography analyses. Both complexes are soluble in both DMF and DMSO but not soluble in CHCl₃, DCM, EtOH, MeOH, MeCN, THF, acetone, ethyl acetate, or *n*-hexane. Noticeably, only complex 1 displays good stability in air at room temperature but complex 2 is markedly unstable. The free bisoximes (H₂L¹ and H₂L²) are both soluble in all of the aforementioned solvents. The molar conductance values of complexes 1 and 2 in 1.0×10^{-3} mol L⁻³ DMF solutions are 2.2 and 2.9 Ω^{-1} cm² mol⁻¹, respectively, indicating that these complexes are non-electrolytes.

The FTIR spectra of H_2L^1 and H_2L^2 together with their corresponding complexes **1** and **2** were recorded in the 4,000–400 cm⁻¹ region, and the most important bands are given in Table 2.

As expected, there are no obvious v(O-H) or v(N-H)absorption bands near 3,400 and 3,145 cm^{-1} in the free bisoximes H_2L^1 and H_2L^2 . H_2L^1 and H_2L^2 exhibit characteristic C=N stretching bands at 1,618 and 1,620 cm⁻¹, respectively, assigned to the pyrazole ring, and for complexes 1 and 2, the corresponding bands were observed at 1,597 and 1,608 cm^{-1} , respectively, indicating red shifts of 21 and 12 cm⁻¹. The oxime C=N bands are 1.593 and 1,595 cm⁻¹ for H₂L¹ and H₂L², respectively. Both of these are red shifted by 29 cm^{-1} in complexes 1 and 2 [16]. Hence, the red shift of the oxime C=N of the chain is bigger than that of the ring, owing to coordination of the azomethine nitrogen to the copper center. Bands in the range of 1.535-1.423 cm⁻¹ were attributed to the aromatic C=C skeleton vibrations. The spectrum of complex 1 shows new bands at 3,279 and 1,638 cm^{-1} which could be attributed to crystalline water. A weak band at 1,724 and 1,722 cm⁻¹ for the free bisoximes H_2L^1 and H_2L^2 is absent in the spectra of the corresponding complexes, which is attributed to the carbonyl oxygen coordinating to the copper center. Weak bands at 509 and 441 cm^{-1} for complex 1 and at 538 and 439 cm^{-1} for complex 2 are assigned to v(Cu-N) and v(Cu-O) [17], respectively, consistent with the literature values [18–20].

The UV–vis absorption spectra of H_2L^1 and H_2L^2 and their corresponding complexes **1** and **2** were determined in 1×10^{-4} mol L⁻¹ DMF solution. The spectra of free H_2L^1 and H_2L^2 exhibit absorption peaks at *ca.* 273 and 273 nm, respectively. Complexes **1** and **2** have similar UV–vis spectra, with maxima at *ca.* 272 and 269 nm, respectively. These peaks can all be assigned to the π – π * transitions of the benzene and pyrazole rings. The small hypochromic shifts of ca. 1–4 nm for the complexes are consistent with coordination between Cu(II) and the ligands.

Thermal stability studies were performed for both complexes. The TG curve of complex **1** can be divided into two stages, and the first stage is at 116–167 °C. The weight loss corresponding to this temperature range is 1.5%, which roughly coincides with the value of 1.3% calculated for the loss of a hemi-crystalline water molecule from the outer coordination sphere of complex **1**. The solid remains stable up to 240 °C, and the second weight loss starts at around 255 °C, with decomposition of the compound. The TG curve shows around 87% total mass loss at 800 °C, indicating complete loss of the L¹ unit. The main residual product was CuO, with a value of 12.3% (theoretical value 11.7%).

The TG curve of complex 2 can be divided into three stages. The first stage is at 70–86 °C. The weight loss corresponding to this temperature range is 2.9%, again corresponding to a value of 2.6% calculated for the loss of a hemi-crystalline DMF molecule from the outer coordination sphere. The second stage starts from 101 to 181 °C with a weight loss of 5.5%, which corresponds to the loss

Complex	1	2	
Empirical formula	$C_{36}H_{31}CuN_6O_{4.5}$	$C_{78,50}H_{74,50}Cu_2N_{14}O_{9,50}$	
Formula weight (g mol^{-1})	683.21	1486.10	
Crystal system, space group	Triclinic; $P - 1$	Triclinic; $P - 1$	
Temperature (K)	298(2)	298(2)	
Unit cell dimensions (Å, °)	a = 12.768(1)	a = 13.178(1)	
	b = 13.036(2)	b = 13.980(1)	
	c = 21.811(2)	c = 22.021(2)	
	$\alpha = 80.304(2)$	$\alpha = 72.040(1)$	
	$\beta = 80.155(2)$	$\beta = 75.727(1)$	
	$\gamma = 63.925(1)$	$\gamma = 77.361(2)$	
$V(\text{\AA}^3)$	3194.8(6)	3694.7(6)	
Z, Calculated density (mg/m^3)	4; 1.420	2; 1.336	
Absorption coefficient (mm ⁻¹)	0.736	0.643	
θ range for data collection (°)	1.75–25.02	1.55–25.02	
Limiting indices	$-15 \le h \le 15, -12 \le k \le 15, -21 \le l \le 25$	$-15 \le h \le 15, -16 \le k \le 9, -26 \le l \le 26$	
F (000)	1,416	1,548	
Crystal size (mm)	$0.34 \times 013 \times 0.06$	$0.24 \times 0.14 \times 0.05$	
Reflections collected/unique	16,822/11,066	19,725/12,902	
	[R(int) = 0.0805]	[R(int) = 0.0528]	
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	
Data/restraints/parameters	11,066/0/860	12,902/6/986	
Goodness-of-fit on F^2	1.033	0.912	
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0933, wR_2 = 0.2107^{\rm a}$	$R_1 = 0.0695, wR_2 = 0.1741^{\rm b}$	
R indices (all data)	$R_1 = 0.1757, wR_2 = 0.2408$	$R_1 = 0.1500, wR_2 = 0.2114$	
Max, min $\Delta \rho$ (e Å ⁻³)	1.837 and -0.854	0.783 and -0.513	
CCDC	757702	757711	

Table 1 Crystal data and structure refinement parameters for complexes 1 and 2

^a $w = 1/[\sigma^2(F_o^2) + (0.097P)^2], ^b w = 1/[\sigma^2(F_o^2) + (0.1015P)^2], \text{ where } P = (F_o^2 + 2F_c^2)/3$

Table 2	Principal	FTIR	bands	for	the	bisoximes	and	their	com	plexes	(cm^{-1}))
---------	-----------	------	-------	-----	-----	-----------	-----	-------	-----	--------	-------------	---

Compound	<i>v</i> _(C–H)	v _(C=O)	$v_{(C=N)}$ ring	$v_{(C=N)}$ chain	v _(Cu-N)	v _(Cu–O)	$v_{(C=C)}$ benzene ring skeleton
H_2L^1	3,059	1,724	1,618	1,593	_	_	1,535, 1,499, 1,458
Complex 1	3,063	_	1,597	1,564	509	441	1,525, 1,493, 1,435
H_2L^2	3,061	1,722	1,620	1,595	-	_	1,533, 1,501, 1,458
Complex 2	3,047	-	1,608	1,566	538	439	1,516, 1,456, 1,423

of one coordinated DMF (theoretical mass loss 5.1%). The solid remains stable up to 216 °C, and the third weight loss starts at around 223 °C, with decomposition of the compound. The TG curve shows around 80% total mass loss at 650 °C, indicating complete removal of the L^2 unit. The main residual product was CuO, with a value of 11% (theoretical value 10.8%).

Description of the crystal structures

X-ray crystallographic analysis reveals that complex 1 crystallizes in the triclinic system, space group *P*-1, and the unit cell contains two crystallographically independent but

chemically identical mononuclear $[CuL^1]$ molecules (A and B) and one crystalline water molecule (Fig. 1). Molecules A and B both consist of one Cu(II) atom and one $(L^1)^{2-}$ unit (in the enol tautomeric form). Each Cu(II) center is tetra-coordinated and lies in the *cis*-N₂O₂ donor site of the ligand. Consequently, the coordination environment around the Cu(II) center can be described as a slightly distorted square-planar geometry. Compared with molecule A, molecule B is similar in the overall structure but distinct in some bond distances and angles (Table 3). The Cu1 atom for molecule A is 0.038 Å out of the N₂O₂ coordination plane, while the Cu2 atom for molecule B is 0.031 Å out of the N₂O₂ coordination plane.

Fig. 1 The ORTEP view of the crystal structure with thermal ellipsoids was drawn at the 30% probability for complex 1, and hydrogen atoms have been omitted for clarity



Table 3 Selected bond distances (Å) and bond angles (°) for complexes 1 and 2

Complex 1		Complex 2	
Bond lengths			
Cu(1)–O(4)	1.919(5)	Cu(1)–O(7)	1.894(4)
Cu(1)–O(3)	1.930(5)	Cu(1)–O(3)	1.912(4)
Cu(1)–N(1)	1.952(6)	Cu(1)–N(1)	1.995(5)
Cu(1)–N(2)	2.037(6)	Cu(1)–N(7)	1.999(5)
Cu(2)–O(8)	1.908(5)	Cu(2)–O(8)	1.916(4)
Cu(2)–O(7)	1.938(5)	Cu(2)–O(4)	1.932(4)
Cu(2)–N(7)	1.948(6)	Cu(2)–N(8)	1.973(5)
Cu(2)–N(8)	2.023(6)	Cu(2)–N(2)	1.989(5)
		Cu(2)–O(9)	2.643(9)
Bond angles			
O(4)–Cu(1)–O(3)	82.5(2)	O(7)–Cu(1)–O(3)	170.2(2)
O(3)–Cu(1)–N(1)	91.5(2)	O(7)-Cu(1)-N(1)	88.8(2)
O(3)-Cu(1)-N(2)	161.1(3)	O(3)-Cu(1)-N(1)	90.8(2)
O(8)–Cu(2)–O(7)	83.0(2)	O(7)-Cu(1)-N(7)	92.4(2)
O(7)–Cu(2)–N(7)	92.0(2)	O(3)-Cu(1)-N(7)	91.2(2)
O(7)–Cu(2)–N(8)	161.6(3)	N(1)-Cu(1)-N(7)	160.9(2)
O(4)-Cu(1)-N(1)	164.7(2)	O(8)-Cu(2)-O(4)	87.2(2)
O(4)-Cu(1)-N(2)	91.4(2)	O(8)-Cu(2)-N(8)	91.5(2)
N(1)-Cu(1)-N(2)	98.4(3)	O(4)-Cu(2)-N(8)	148.1(2)
O(8)–Cu(2)–N(7)	165.2(2)	O(8)-Cu(2)-N(2)	162.7(2)
O(8)–Cu(2)–N(8)	90.5(2)	O(4)-Cu(2)-N(2)	92.1(2)
N(7)-Cu(2)-N(8)	98.2(3)	N(8)-Cu(2)-N(2)	98.1(2)
		O(8)-Cu(2)-O(9)	79.8(2)
		O(4)-Cu(2)-O(9)	89.0(2)
		N(8)-Cu(2)-O(9)	122.2(2)
		N(2)-Cu(2)-O(9)	82.9(2)

As shown in Fig. 2, molecules of complex 1 are connected by intramolecular C–H···O hydrogen bonding and C–H··· π (Ph) interactions (Table 4), which play a role in

stabilizing the structure of the crystal. The neighboring units are linked into an infinite one-dimensional chain by intermolecular hydrogen bonding (O9–H9C···O6 and C38– H38A···O9) forming a five-membered ring with a graph motif $R_2^2(5)$, and hydrogen bonding (O9–H9···N10 and C51–H51···O9) that can be described as an $R_2^2(7)$ motif and produces an eight-membered ring. The packing diagram shows that complex **1** forms a wave-like pattern running along the a-axis via weaker $\pi \cdots \pi$ stacking interactions between two neighboring pyrazole rings as well as the benzene and metal chelate rings (Table 5).

X-ray crystal structure analysis shows that complex 2 has a dinuclear structure, consisting of two Cu(II) atoms, two deprotonated $(L^2)^{2-}$ units (in the enol form), one coordinated DMF ligand, and a hemi-crystalline DMF molecule (Fig. 3). The center Cu1 atom is tetra-coordinated in a trans-N₂O₂ plane by two oxime nitrogen (N1, N7) atoms and two oxygen (O3, O7) atoms of two deprotonated $(L^2)^{2-}$ units, displaying a slightly distorted square-planar coordination motif. The center Cu2 atom is penta-coordinated by two oxime nitrogen (N2, N8) atoms and two oxygen (O4, O8) atoms of two $(L^2)^{2-}$ units defining the cis-N₂O₂ basal plane, plus one carbonyl oxygen (O9) atom from a DMF ligand occupying the apical position. Therefore, the coordination environment around Cu2 is best regarded as a slightly distorted square-pyramidal geometry with the distance of the apical oxygen O9 atom to the N_2O_2 basal plane being 2.642. The center atom Cu1 is 0.085 out of the N₂O₂ coordination plane, while the deviation of Cu2 atom from the N₂O₂ basal plane is 0.124. An interesting feature is that the basal plane of Cu1 and the equatorial plane of Cu2 are almost perpendicular, making a dihedral angle of 84.97° to each other, and the long distance (Cu1…Cu2 = 7.082) between two coppers suggests that there is no interaction between these two metal centers.

Fig. 2 Diagram showing hydrogen bonds and $\pi \cdots \pi$ interactions for complex 1. Hydrogen atoms, except those involved in hydrogen bonds, have been omitted for clarity



Table 4 Hydrogen bonding distances (Å) and bond angles (°) for complexes 1 and 2 $\,$

D–H…A	D–H	Н…А	D····A	D–H…A
Complex 1				
C15-H15-···O3	0.93	2.33	2.93(1)	122
C36-H36····O4	0.93	2.32	2.896(9)	120
C38–H38A…O9	0.97	2.58	3.254(3)	127
C51-H51O9	0.93	2.84	3.584(5)	139
C55-H55O7	0.93	2.29	2.866(9)	120
C68–H68…O8	0.93	2.33	2.88(1)	117
O9-H9D…N10	0.85	2.12	2.923(4)	139
O9-H9C…O6	0.85	2.29	3.090(4)	120
C6–H6B…Cg10a	0.93	2.93	3.52(2)	121
C23–H23B…Cg12a	0.96	3.26	3.490(1)	115
C59–H59B…Cg16a	0.96	2.98	3.49(1)	115
Complex 2				
C1-H1B…O7	0.97	2.51	3.107(8)	119
C16-H16…O3	0.93	2.22	2.849(8)	124
C37-H37-04	0.93	2.31	2.903(9)	121
C38-H38BO3	0.97	2.38	2.985(7)	120
C44–H44A \cdots N4 ⁱ	0.96	2.54	3.35(1)	141
С57-Н57…О7	0.93	2.23	2.871(8)	126
C61-H61AN14	0.96	2.54	3.49(4)	173
C70–H70…O8	0.93	2.41	2.938(8)	116
C76-H76C···O9	0.96	2.59	3.41(2)	142
C78–H78····O4 ⁱⁱ	0.93	2.55	3.12(4)	119
C79–H79A…N6 ⁱⁱⁱ	0.95	2.39	3.11(3)	132
C14–H14…Cg8b ^{iv}	0.93	2.93	3.729(7)	145
C44–H44C…Cg11b	0.96	2.82	3.33(1)	114
C66–H66…Cg8b	0.93	2.95	3.592(9)	127

Symmetry codes: (i) x - 1, y, z; (ii) -x + 1, -y + 1, -z + 1; (iii) x + 1, y, z; (iv) 1 - x, 1 - y, 1 - z

Cg10a, Cg12a, and Cg16a for complex **1** are the centroids of atoms C8–C13, C26–C30, and C61–C66, respectively. Cg8b and Cg11b for complex **2** are the centroids of atoms C15–C20 and C46–C51, respectively

Table 5 $\pi \cdots \pi$ stacking interaction (Å, °) for complexes 1 and 2

Ring 1	Ring 2	α	DCC (Å)	CgI-prep (Å)	CgJ-prep (Å)
Comple	x 1				
Cg4	Cg5	1.93(2)	3.654(4)	3.336 (3)	-3.350(3)
Cg9	Cg15	2.3(4)	3.682(5)	-3.469(3)	3.448(4)
Comple	x 2				
Cg1	$Cg1^X$	0	3.303(3)	-3.174(2)	-3.173(2)

Symmetry codes: (*X*) 1 - x, 1 - y, -z. DCC = distance between ring centroids; α = dihedral angle between planes I and J; CgIperp = perpendicular distance of Cg(I) from ring J; CgJ-perp (MeJperp) = perpendicular distance of Cg(J) from ring I (perpendicular distance of Cg(I) from metal J). Cg4, Cg5, Cg9, and Cg15 for complex **1** are the centroids of atoms N5\N6\C20-C22, N9\N10\C39-C41, Cu1\O4\C20\C21\C24\N2, and C50-C55; Cg1 for complex **2** is the centroid of atoms N3\N4\C4-C6

As shown in Fig. 4, there are a large number of intramolecular C–H···O and C–H··· π (Ph) hydrogen bonding interactions (Table 4) in the molecular unit of complex **2** and C–H···O hydrogen bonds form an S(6) motif producing a six-membered ring and stabilizing the molecular structure. Intermolecular hydrogen bonds between C44– H44···N4, 78–H78···O4, and C79–H79···N6 (Table 4) link three neighboring molecules into a three-polymeric structure. Adjacent molecular units are linked together by π ··· π stacking interactions between two neighboring pyrazole rings and intermolecular C–H··· π (Ph) interactions to give an infinite three-dimensional supramolecular network structure.

To sum up, the structure of complex 2 is obviously different from complex 1. Complex 2 is a dinuclear structure with two ligand units, whereas complex 1 is a mononuclear structure with one ligand unit. Moreover, the central Cu(II) (Cu1) atoms in complexes 1 and 2 are all tetra-coordinated in the N₂O₂ plane, but the coordination Fig. 3 The ORTEP view of the crystal structure with thermal ellipsoids was drawn at the 30% probability for complex 2, and hydrogen atoms have been omitted for clarity





modes of the N_2O_2 donor sites are especially different. These adopt the *cis*-conformation and come from the same ligand unit in complex **1**, whereas they adopt the *trans*conformation and come from two ligand units in complex **2**. These differences may be explained by the templating effect resulting from the different ligands. When the *O*alkyl chain length increases, the L2- moieties become more flexible and long enough to accommodate two Cu(II) atoms so as to resist the steric effect of the phenyl group at position 1 of the ligands. So the complex is a mononuclear structure when the *O*-alkyl chain length is short (two CH₂ groups), while a dinuclear structure is obtained when the *O*-alkyl chain is longer (three CH₂ groups).

In addition, in complex **2**, oxygen (O9) from one DMF ligand coordinates to one Cu(II) atom (Cu2) if one considers Cu2-O9 with distance of a 2.642 Å as a weak bond. The coordination numbers of the Cu(II) atoms are four and

five. But in complex 1, there is no solvent coordinating to the central Cu(II) atom, and the coordination number of the Cu(II) atoms is four. These differences may be attributed to the solvent effect.

Conclusion

Two new mono- and dinuclear Cu(II) complexes with bisoxime ligands derived from 4-acyl-pyrazolone and *O*alkyldiamines of varying *O*-alkyl backbone chain lengths have been synthesized and structurally characterized by Xray crystallography. Because of the different performance of the ligands and the introduction of solvent molecules, the complexes present different structural features. As the *O*-alkyl chain length increases in the resulting complexes, the L^{2-} moieties become more flexible and long enough to accommodate two Cu(II) atoms so as to resist the steric effect of the phenyl at position 1 of ligand. So the complex is mononuclear when the O-alkyl chain length is short, while a dinuclear structure is obtained when the O-alkyl chain is larger. In addition, the coordination environment around Cu(II) changes from square-planar in complex 1 to square-pyramidal in complex 2 with the introduction of a solvent ligand in complex 2.

Supplementary material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication, No. CCDC 757702 and 757711 for complexes **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 (Telephone: +44-01223-762910; Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk). These data can be also obtained free of charge at www.ccdc. cam.ac.uk/conts/retrieving.html.

Acknowledgments This work was supported by the Foundation of the Education Department of Gansu Province (No. 0904-11) and the 'JingLan' Talent Engineering Funds of Lanzhou Jiaotong University, which are gratefully acknowledged.

References

- 1. Akine S, Taniguchi T, Nabeshima T (2001) Chem Lett 30(7):682
- Akine S, Taniguchi T, Dong WK, Nabeshima T (2005) J Org Chem 70(5):1704
- Dong WK, Zhao CY, Sun YX, Tang XL, He XN (2009) Inorg Chem Commun 12:234

- Kalarani N, Sangeetha S, Kamalakannan P, Venkappayya D (2003) Russ J Coord Chem 29:845
- Dong WK, He XN, Yan HB, Lv ZW, Chen X, Zhao CY, Tang XL (2009) Polyhedron 28:1419
- 6. Akine S, Dong WK, Nabeshima T (2006) Inorg Chem 45(12): 4677
- Dong WK, Zhu CE, Wu HL, Ding YJ, Yu TZ (2007) Synth React Inorg Met-Org Nano-Met Chem 37:61
- 8. Akine S, Taniguchi T, Nabeshima T (2004) Inorg Chem 43:6142
- 9. Dong WK, Sun YX, Zhang YP, Li L, He XN, Tang XL (2009) Inorg Chim Acta 362:117
- Dong WK, Chen X, Sun YX, Yang YH, Zhao L, Xu L, Yu TZ (2009) Spectrochim Acta Part A 74:719
- Dong WK, Duan JG, Guan YH, Shi JY, Zhao CY (2009) Inorg Chim Acta 362(4):1129
- 12. Dixon DW, Weiss RH (1984) J Org Chem 49:4487
- 13. Dong WK, Duan JG, Liu GL (2007) Trans Met Chem 32:702
- 14. Sheldrick GM (1996) SADABS, siemens area detector absorption corrected software. University of Göttingen, Germany
- Sheldrick GM (1997) SHELXTL NT, version 5.1; program for solution and refinement of crystal structures. University of Göttingen, Germany
- Bovio B, Cingolani A, Marchetti F, Pettinari C (1993) J Organomet Chem 458:39
- Sen S, Talukder P, Dey SK, Mitra S, Rosair G, Hughes DL, Yap GPA, Pilet G, Gramlich V, Matsushita T (2006) Dalton Trans 1758
- Dong WK, Shi JY, Xu L, Zhong JK, Duan JG, Zhang YP (2008) Appl Organometal Chem 22(2):89
- Dong WK, Feng JH, Yang XQ (2007) Synth React Inorg Met-Org Nano-Met Chem 37(3):189
- Dong WK, Feng JH, Wang L, Xu L, Zhao L, Yang XQ (2007) Trans Met Chem 32(8):1101