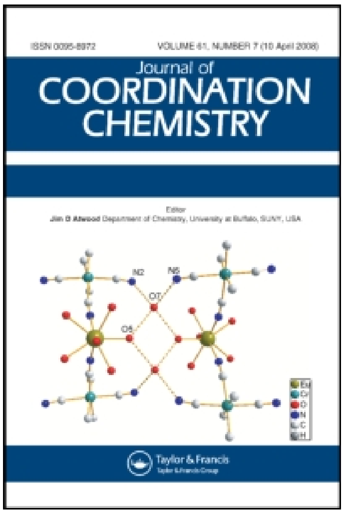

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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To cite this Article Hong, Zhou , Zheng-He, Peng , Zhi-Quan, Pan , Bo, Liu , Xue-Lei, Hu and Yong-Qiong, Liu(2005) 'Novel heterodinuclear transition metal macrocyclic complexes: syntheses, characterization and crystal structures', Journal of Coordination Chemistry, 58: 5, 443 — 451

To link to this Article: DOI: 10.1080/00958970412331336286
URL: http://dx.doi.org/10.1080/00958970412331336286

Journal of Coordination Chemistry
Vol. 58, No. 5, 20 March 2005, 443–451

Novel heterodinuclear transition metal macrocyclic complexes: Syntheses, characterization and crystal structures

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(Received in final form 7 September 2004)

Two unsymmetrical, macrocyclic, heterodinuclear complexes, $[Cu^{II}M^{II}(L)](ClO_4)_2 \cdot nH_2O$ ($n = 3$; M = Zn, Cd) have been obtained by cyclocondensation of *N*,*N*′-*bis*(3-formyl-5-*n*-butylsalicylidene)ethylenediimine and 1,3-diaminopropane in the presence of M^{2+}. The structures of both complexes were determined by X-ray diffraction techniques. In each complex, two metals are located in the tetraimine macrocyclic cavity, and a water molecule and a perchlorate group are separately coordinated to the metal ions on the same side of the ring. Coordination geometry around each metal is approximately square pyramidal. ESMS spectra were used to characterize the complexes and isotopic distributions were investigated.

Keywords: Heterodinuclear complex; Macrocycle; Synthesis; Crystal structure; ESMS; Isotopic distribution

1. Introduction

Dinuclear metal complexes of diphenolic Schiff base macrocyclic ligands have attracted much attention as they have contributed significantly to the understanding of the chemical behaviour of coupled systems [1–4]. Recently, considerable interest has been devoted to the design and synthesis of asymmetric, heterodinuclear, macrocyclic complexes [5–10]. Variation of substituent groups in asymmetric macrocyclic ligands with dissimilar coordination sites is of special importance because this modifies electronic, magnetic and redox properties. Many heterodinuclear Cu(II)–M(II) (M = Mn, Fe, Co, Ni, Cu) complexes have been synthesized by reaction of *N*,*N*′-*bis*(3-formyl-5-methylsalicylidene)ethylenediimine with polyamines [7,11], but complexes with

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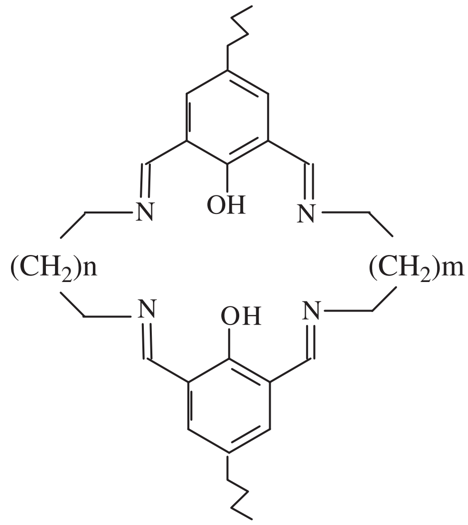
Journal of Coordination Chemistry
ISSN 0095-8972 print: ISSN 1029-0389 online © 2005 Taylor & Francis Group Ltd
DOI: 10.1080/00958970412331336286



H_2L n = 0, m = 1; H_2L' n = 0, m = 0, H_2L'' n = 1, m = 1

Scheme 1. Chemical structures of H_2L, H_2L', and H_2L''

metals coordinated on the same side of the macrocycle were not reported. To further understand the effects of substitutents on coordination, we have synthesized two new asymmetric macrocyclic complexes $[CuM(L)](ClO_4)_2 \cdot nH_2O$ ($n = 3$; M = Zn, Cd)] made by condensation of *N*,*N*′-*bis*(3-formyl-5-*n*-butylsalicylidene)ethylenediimine and 1,3-diaminopropane in the presence of Cu(II) and M(II), in which perchlorate and water coordinate to Cu(II) and M(II) on same side of macrocyclic plane. Here we report crystal structures and ESMS investigations. The structures of the macrocyclic ligands (H_2L, H_2L', and H_2L'') are shown in scheme 1.

2. Experimental

2.1. *Materials*

All solvents and chemicals were of analytical grade and used without further purification except for methanol, which was dehydrated by the Grignard method. 2,6-Diformyl-4-*n*-butylphenol was prepared using a literature method for the synthesis of 2,6-diformyl-4-methyl-phenol [12].

2.2. *Physical measurements*

IR spectra were measured using KBr discs on a Vector 22 FTIR spectrophotometer. Elemental analyses were made using a Perkin-Elmer 240 instrument. Metal contents were determined by titration with edta. Electrospray mass spectra (ESMS) were determined on a Finnigan LCQ ES-MS mass spectrometer using methanol as the mobile phase with a sample concentration of about 1.0 mmol dm^{-3}. The diluted solution was electrosprayed at a flow rate of 5×10^{-6} dm^3 min^{-1} with a needle voltage of +4.5 kV.

The temperature of the heated capillary in the interface was 200°C and a fused silica sprayer was used.

2.3. *Preparation of the complexes*

2.3.1. *N,N′-bis*(3-formyl-5-*n*-butylsalicylidene)ethylenediimine, L_1. The ligand was prepared by a slight modification of the method reported earlier [15]. 2,6-Diformyl- 4-*n*-butylphenol (1.236 g, 6 mmol) was dissolved in 30 cm^3 of warm absolute ethanol and 10 cm^3 of absolute ethanol solution containing ethylenediamine (0.18 g, 3 mmol) was added dropwise. After the resulting solution was stirred for 4 h, the orange solid that had formed was filtered off, washed with ethanol and ether and sucked dry. Yield: 0.85 g (65%), m.p.: 125–127°C. Anal. Calc. for $C_{26}H_{32}O_4N_2$ (%): C, 71.53; H, 7.39; N, 6.42. Found: C, 71.50; H, 7.36; N, 6.45. IR $\nu(cm^{-1})$: 3429 (O–H), 1680 (C=O) and 1637 (C=N).

2.3.2. Syntheses of macrocyclic complexes. *Caution* Although no problem was encountered in this work, transition metal perchlorates are potentially explosive and should be handled in small quantities. $[CuCd(L)](ClO_4)_2 \cdot 3H_2O$ (**1**): a suspension of $\mathbf{L_1}$ (0.218 g, 0.5 mmol) in 30 cm^3 of absolute methanol was added to a methanol solution of $Cu(OAc)_2 \cdot H_2O$ (0.001 g, 0.5 mmol) and the mixture stirred at room temperature for about 3 h. Triethylamine (5 cm^3) and a methanol solution (5 cm^3) of $Cd(ClO_4)_2 \cdot 6H_2O$ (0.2097 g, 0.5 mmol) were then added. The mixture was stirred for about 10 h and then a methanol solution (10 cm^3) of 1,3-diaminopropane (0.037 g, 0.5 mmol) was added dropwise over 40 min. The solution was refluxed for 1 h to give a red solution, then diethylether was added. A blue-black solid product was obtained in 32% yield (0.144 g). Blue-black needle-shaped crystals of $[Cu^{II}Cd^{II}(L)](ClO_4)_2 \cdot 3H_2O$ suitable for X-ray diffraction were obtained by slow diffusion of diethylether into the above filtrate over one week. Anal. Calc. for $C_{29}H_{42}N_4O_{13}Cl_2CuCd$ (%): C, 38.64; H, 4.70; N, 6.21; Cu, 7.05; Cd, 12.47. Found: C, 38.23; H, 4.52; N, 5.96; Cu, 7.13; Cd, 12.47. IR (KBr) $\nu(cm^{-1})$: 3447 (O–H), 1645 (C=N), 1088 and 621 (ClO_4^-).

Cubic red crystals of $[CuZn(L^1)](ClO_4)_2 \cdot 3H_2O$ (**2**) were prepared by a similar procedure as described above (0.149 g, yield 36%), except that cadmium perchlorate was used instead of zinc perchlorate. Anal. Calc. for $C_{29}H_{42}N_4O_{13}Cl_2CuZn$ (%): C, 40.76; H, 4.95; N, 6.56; Cu, 7.44; Zn, 7.65. Found: C, 40.37; H, 4.61; N, 6.72; Cu, 7.31; Zn, 7.42. IR (KBr) $\nu(cm^{-1})$: 3440 (O–H), 1644 (C=N), 1087 and 624 (ClO_4^-).

2.4. *Crystal structure determinations*

Diffraction intensity data for **1** and **2** were collected on a SMART-CCD area detector diffractometer at 293 K using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Data reduction and cell refinement were performed by the SMART and SAINT Programs [13]. The structures were solved by direct methods (Bruker SHELXTL) and refined on F^2 by full-matrix least-squares procedures (Bruker SHELXTL) using all unique data [14]. Non-H atoms in the structure were treated anisotropically. Hydrogen atoms were located geometrically and refined in riding mode.

3. Results and discussion

3.1. *Synthesis and characterization*

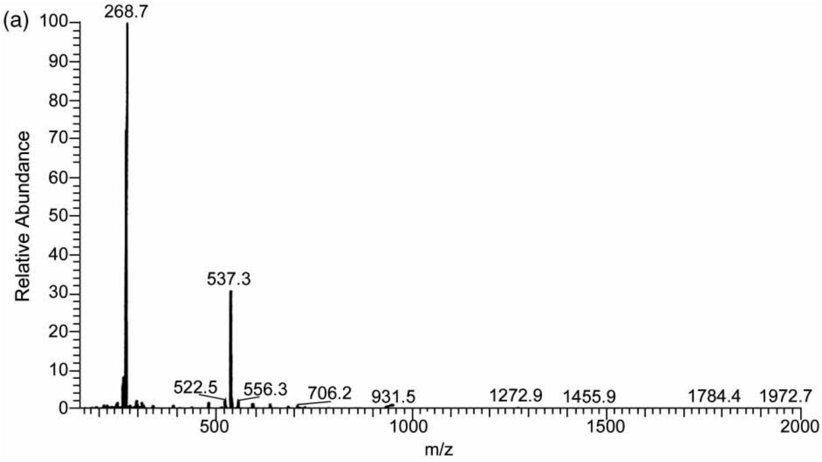
In the IR spectrum of $\mathbf{L_1}$, two fairly strong bands at 1680 and 1637 cm^{-1} are attributed to $\nu(C{=}O)$ and $\nu(C{=}N)$ vibration, respectively. In the complexes, the strong band at 1680 cm^{-1} disappears and sharp C=N stretching bands corresponding to imine groups of the macrocyclic framework are observed at 1645 cm^{-1} for **1** and 1643 cm^{-1} for **2**, indicating that the macrocyclic complexes formed. In addition, very strong bands at 1087, 621 cm^{-1} and 1086, 623 cm^{-1} can be ascribed to ClO_4^- groups in (**1**) and (**2**), respectively. The bands exhibit well-defined splitting band, implying that ClO_4^- groups are coordinated to the metal ions in the solid state.

3.2. *Electrospray mass spectra*

The ES-MS spectrum of **1** is shown in figure 1(a). A dominant peak at *m*/*z* 268.7 corresponding to $[CuLH_2]^{2+}$ is ascribed to the macrocyclic cation having lost Cd^{2+} and gained two protons; this explains the other peak at *m*/*z* 537.3, corresponding to $[CuLH]^+$. Assignment of the main peaks for **1** indicate that it is easier for Cd^{2+} to be lost from the macrocyclic ligand than Cu^{2+}. Theoretical and experimental isotope distribution of the two main peaks of **1** are shown in figures 1(b) and 1(c), revealing good agreement between observed and calculated data. The ESMS spectrum of **2** is shown in figure 2. The peak at *m*/*z* 300.6 corresponding to $[CuZnL]^{2+}$ is dominant and confirms the formation of the macrocyclic complex. The peak at *m*/*z* 701.1 is assigned to $[CuZnL(ClO_4)]^+$; both these main peaks indicate that the macrocyclic cation is stable in MeOH solution.

3.3. *Crystal structure of* $[Cu^{II}Cd^{II}(L)](ClO_4)_2 \cdot 3H_2O$

A perspective view of **1** is shown in figure 3(a), together with the atom numbering scheme. Crystallographic data and details concerning data collection are given in table 1. Selected bond lengths and angles are listed in table 2. Except for the *n*-butyl groups, which are disordered, the macrocyclic complex adopts an essentially flat structure and the coordination polyhedron around each of the metal ions is best described as square pyramidal, bridged by the two phenoxide oxygen atoms, with Cu–O–Cd angles 101.39(13) and 102.34(13)°. The copper and cadmium centres are separated by 3.104 Å, and in-plane copper-ligand distances fall in the range 1.939–1.957 Å. One oxygen atom of a perchlorate group occupies the apical position of the copper coordination sphere with Cu(1)–O(21) 2.739(3) Å and the copper center is displaced toward the perchlorate group by 0.0629 Å from the mean N_2O_2 basal plane. The distance between cadmium and coordinating atoms in the plane fall in the range 2.027(3)–2.090(3) Å and a water molecule occupies the apical position with Cd(1)–O(3) 2.183(3) Å; the cadmium center is displaced toward the water by 0.2519 Å from the mean N_2O_2 basal plane. The two N_2O_2 planes are approximately co-planar (dihedral angle 2.60°). The coordinating water molecule and perchlorate group are on the same side of the macrocyclic ring, a situation which is quite different from that found in similar macrocyclic complexes [16].



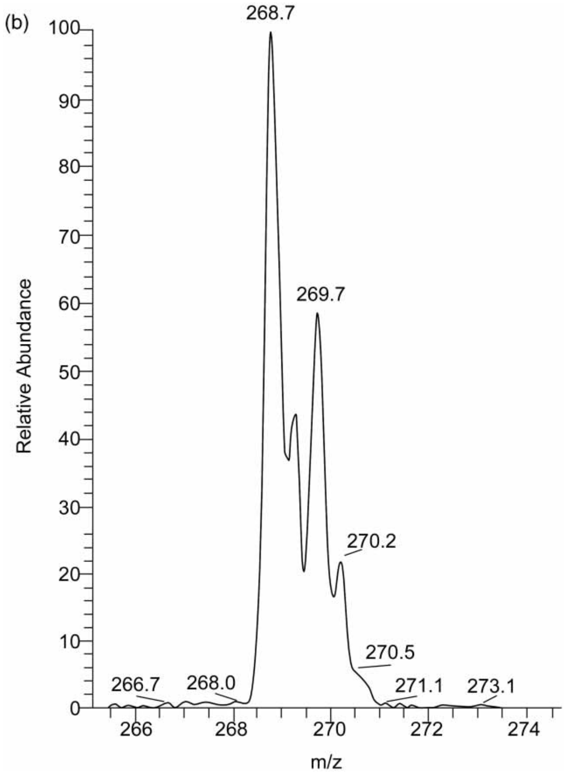


Figure 1. (a) ESMS spectrum of **1**; (b) isotopic distribution of the peak at $m/z = 268.7$ (left: experimental pattern; right: calculated). (c) Isotopic distribution of the peak at 537.3 (left: experimental pattern; right: calculated).

3.4. *Crystal structure of* $[Cu^{II}Zn^{II}(L)](ClO_4)_2 \cdot 3H_2O$

The structural features of **2** are essentially the same as those of **1**. A perspective view of **2** is shown in figure 3(b). Crystallographic data are listed in table 1 and selected bond distances and angles in table 2. Cell parameters differ slightly from that of **1**, possibly

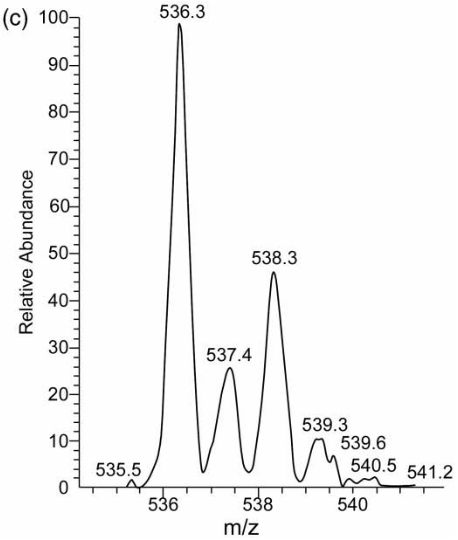


Figure 1. Continued.

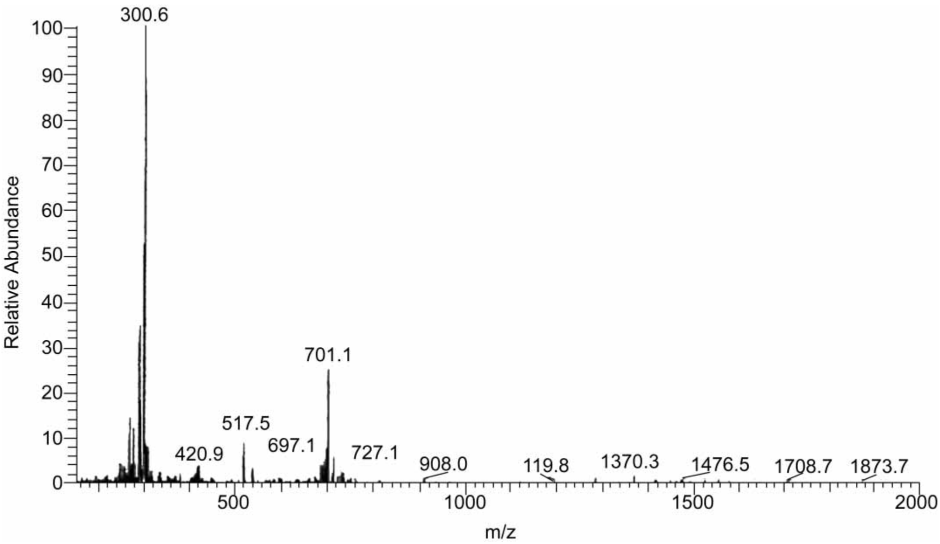


Figure 2. ESMS spectrum of complex **2**.

due to the fact that the radius of Cd^{2+} is greater than that of Zn^{2+}; consequently, bond lengths around Cd^{2+} are all greater than corresponding ones around Zn^{2+} **2**. The Cu–Zn separation is 3.036 Å, also shorter than that for Cu–Cd, and the two Cu–O–Zn angles, 100.88(11), 101.96(12)°, are somewhat smaller than counterparts in **1**. In the complexes, H-bonding (HO) interactions exist between both hydrogen atoms of the coordinated water molecule and an oxygen atom of the coordinated perchlorate ion. H-bond lengths are in the range 2.36–2.53 Å for **1** and 2.32–2.46 Å for **2**; these bonds may be one of the factors for water coordination to the metal on same side of the macrocycle as perchlorate.

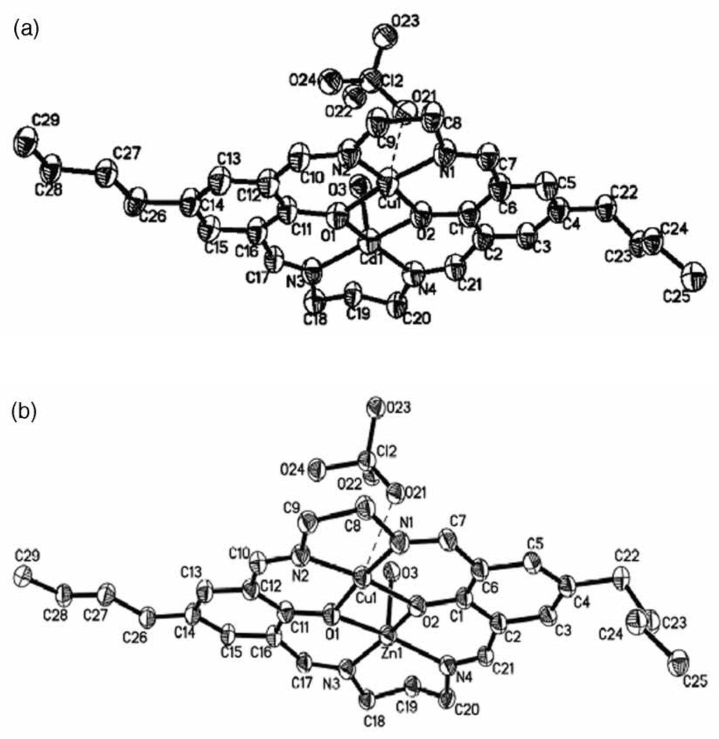


Figure 3. (a) The structure of **1** showing the atom numbering scheme; (b) the structure of **2** showing the atom numbering scheme. Hydrogen atoms have been omitted for clarity.

Table 1. Crystal data and details of structure determinations for **1** and **2**.

Formula	$C_{29}H_{42}N_4O_9Cl_2CuCd$	$C_{29}H_{42}N_4O_9Cl_2CuZn$
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	16.674(2)	16.077(3)
b (Å)	14.126(2)	13.905(2)
c (Å)	16.875(3)	16.495(3)
β (°)	91.761(3)	91.340(3)
V (Å^3)	3972.8(10)	3686.5(11)
Z	4	4
D(calc) (g cm^{-3})	1.507	1.540
μ(Mo Kα) (mm^{-1})	1.266	1.438
F(000)	1.836	1764
Crystal size (mm)	$0.15 \times 0.18 \times 0.28$	$0.22 \times 0.24 \times 0.33$
Data collection		
Temperature (K)	293	293
θ min, max (°)	2.2, 25.0	1.9, 26.0
Data set	−19:19; −16:16; −17:20	−19:19; −15:17; −13:20
Total, unique data, R(int)	23097, 6972, 0.010	19406, 7223, 0.027
Observed data $[I > 2.0\,\sigma(I)]$	5462	5600
Refinement		
Nref, Npar	6972, 453	7223, 453
R, $wR2$, S	0.0539, 0.1387, 1.03	0.0555, 0.1263, 1.01
Min, max res. dens. (e Å^{-3})	−0.52, 0.47	−0.77, 0.23

Table 2. Selected bond lengths (Å) and angles (°) for **1** and **2**. M(1) indicates Cd(1) for **1** and Zn(1) for **2**, respectively

	1	**2**		**1**	**2**
M(1)–O(1)	2.090(3)	2.004(3)	M(1)–O(3)	2.183(3)	2.156(3)
M(1)–O(2)	2.027(3)	2.031(2)	M(1)–N(3)	2.052(4)	2.006(3)
Cu(1)–O(1)	1.919(3)	1.903(2)	M(1)–N(4)	2.063(3)	1.995(3)
Cu(1)–O(2)	1.957(3)	1.906(3)	Cu(1)–N(1)	1.903(4)	1.886(3)
Cu(1)–O(21)	2.739(3)	2.660(3)	Cu(1)–N(2)	1.939(3)	1.912(3)
Bond angles			Bond angles		
O(1)–M(1)–O(3)	98.97(12)	98.31(10)	O(1)–M(1)–N(3)	90.22(13)	90.74(11)
O(1)–M(1)–N(4)	159.25(15)	159.22(11)	O(2)–M(1)–N(4)	90.81(15)	90.38(11)
O(2)–M(1)–N(3)	161.98(14)	162.92(11)	O(3)–M(1)–N(4)	97.47(16)	100.23(12)
O(3)–M(1)–N(3)	95.01(16)	93.75(11)	O(2)–Cu(1)–N(1)	94.30(13)	94.86(12)
N(3)–M(1)–N(4)	100.89(16)	100.23(12)	O(21)–Cu(1)–N(2)	104.30(16)	103.93(11)
O(1)–Cu(1)–N(2)	94.41(16)	93.22(11)	O(21)–Cu(1)–N(1)	75.89(16)	75.77(11)

We have tried to synthesize complexes **1** and **2** by Mohanta's method [1], but the symmetrical products $[Cu^{II}Cu^{II}(L')](ClO_4)_2$ and $[Cu^{II}Cu^{II}(L'')](ClO_4)_2$ (scheme 1) were obtained. In the presence of triethylamine, the two heteronuclear macrocyclic complexes $[Cu^{II}Cd^{II}(L)](ClO_4)_2 \cdot 3H_2O$ and $[Cu^{II}Zn^{II}(L)](ClO_4)_2 \cdot 3H_2O$ formed, one perchlorate ion and one water molecule coordinating to different metals on the same side of the plane of the macrocyclic ring; because of hydrogen bonding between water and perchlorate. Perchlorate generally coordinates weakly to metal ions and its bonding is often described as "semi-coordination" [17]. This is reflected in **1** and **2** by the rather long Cu–O bond lengths associated with the interaction.

Supplementary data

Full lists of crystallographic data have been deposited with the CCDC as file numbers CCDC 255803 for **1** and 255804 for **2**.

Acknowledgements

The project was supported by National Natural Science Foundation of China.

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