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Heterometallic Complexes of Macrocyclic Oxamide with Polycarboxylates: Syntheses, Crystal Structures, and Magnetic Properties[1]

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Abstract—Three complexes with the formula $[Co(Ip)(CuL)(H_2O)_2] \cdot H_2O$ (**I**), $[Co(Ip)(NiL)(H_2O)_2] \cdot H_2O$ (**II**), $[Co(CuL)_2(Hbtc)(H_2O)]$ (**III**), (H_2Ip = *m*-isophthalic acid; H_2L = 2,3-dioxo-5,6,14,15-dibenzo-1,4,8,12-tetraazacyclo-pentadeca-7,13-dien; H_3Btc = 1,3,5-benzenetricarboxylic acid) were synthesized and structurally characterized by elemental analysis, IR and UV spectroscopy. Single-crystal X-ray analyses reveal that the complexes **I** and **II** contain neutral heterometallic binuclear CoM (for **I** and **II**, M = Cu, Ni, respectively) moieties, and complex **III** contains discrete neutral trinuclear $CoCu_2$ moieties. The structures of **I**–**III** consist of two-dimensional supramolecular architecture formed by strong O–H···O intermolecular hydrogen bonds. Furthermore, the magnetic properties of complex **I** were investigated and discussed in detail.

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INSTRODUCTION

Substantial interest has been devoted to the development of synthesis, design and characterization of supramolecular complexes over the past decade [1–3]. Many self-assembly supramolecular networks exhibit novel structural topologies and interesting electrical, magnetic, optical, catalytic, or biological properties [4–6]. Especially, the synthesis of heterometallic (3*d*–3*d* and 3*d*–4*f*) supramolecular complexes is one of current focus, because the combination of two dissimilar metal centers can lead to fascinating structures and new topological features with the promise for interesting magnetic, magneto-optical and optoelectronic properties [7–13]. Up to date, there are two main synthetic approaches to obtain the heterometallic supramolecular complexes. One is one-pot synthetic approach, adopting this synthetic approach, the ligand design strategy is very important in the construction of unusual heterometallic coordination frameworks [14–16]. However, the design and synthesis of heterometallic complexes are still a challenge to chemists, especially in the cases of 3*d*–3*d* heterometallic systems, because one-pot synthetic approach can lead to a statistical mixture of homo- and heterometallic architectures [17]. The other synthetic approach is given by the concept of 'complex ligand', i.e., utilizing a metal complex as ligand to coordinate an appropriate additional metal ion [18]. In recent years, this field has been extended by using the macrocyclic analogues of the oxamides [19, 20]. Noncyclic oxamides may adopt a *cis* or *trans* conformation on coordination, and this flexibility restricts the control over the type of the complex formed [11]. The macrocyclic oxamides allow the synthesis of heterometallic systems in a more controlled fashion, and it has been found that the oxamide group serves as a pathway through which electron spin interaction takes place [21].

On the other hand, aromatic multicarboxylic acid not only possesses versatile coordination modes and easily links metal ion cores to form polymeric structures, but also has the ability to construct a novel metal-organic supramolecular network through hydrogen bonds as well as π–π stacking [22, 23]. However, systematic studies on these kinds of ligands in the coordination chemistry are still an active field of research. In our continuing efforts to investigate the synthesis and properties of heterometallic polynuclear complexes, in this paper, we report that the macrocyclic oxamido complex was used as ligand with co-ligand H_2Ip, H_3Btc to synthesize two binuclear $Co^{II}M^{II}$ (M = Cu, Ni) and one trinuclear $Co^{II}Cu^{II}_2$ supramolecular complexes $[Co(Ip)(CuL)(H_2O)_2] \cdot H_2O$ (**I**), $[Co(Ip)(NiL)(H_2O)_2] \cdot H_2O$ (**II**), $[Co(CuL)_2(Hbtc)(H_2O)]$ (**III**) (H_2Ip = *m*-isophthalic acid; H_2L = 2,3-dioxo-5,6,14,15-dibenzo-1,4,8,12-tetraazacyclo-pentadeca-7,13-dien; H_3Btc = 1,3,5-benzenetricarboxylic acid). Furthermore, the magnetic

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properties of complex **I** were investigated and discussed in detail.

EXPERIMENTAL

All the starting reagents were of A.R. grade and were used as purchased. The complex ligand ML was prepared as described elsewhere [24]. Analyses of C, H, and N were determined on a PerkinElmer 240 Elemental analyzer. IR spectrum was recorded as KBr discs on a Shimadzu IR-408 infrared spectrophotometer in the 4000–600 cm^{-1} range. Electronic spectra for solid samples were recorded on a Shimadzu UV-2101 PC scanning spectrophotometer. Variable-temperature magnetic susceptibilities of single crystals were measured on an MPMS-7 SQUID magnetometer. Diamagnetic corrections were made with Pascal's constants for all the constituent atoms [25].

Synthesis of complex I. A mixture of $Co(Ac)_2 \cdot 6H_2O$ (0.05 mmol, 12.5 mg), H_2Ip (0.05 mmol, 8.3 mg), CuL (0.025 mmol, 10.2 mg), H_2O (10 mL), and CH_3OH (2 mL) was stired for 20 min at room temperature, and the pH value of the solution was adjusted to about 7–8 with triethylamine. Then, the mixture was transferred to a 18 mL Teflon-lined reactor, which was heated to 140°C for 60 h. Last the reaction system was gradually cooled to room temperature for 36 h, and brown block crystals of **I** were obtained.

For $C_{27}H_{26}N_4O_9CoCu$			
anal. calcd, %:	C, 48.14;	H, 3.86;	N, 8.32.
Found, %:	C, 48.16;	H, 3.83;	N, 8.35.

IR bands (ν, cm^{-1}): 1641 $\nu_s(COO^-)$, 1610 ν(C=O), 1564 ν(C=N).

Synthesis of complex II. The synthetic procedure was similar to that described for the preparation of **I** except using NiL (0.03 mmol, 11.8 mg) instead of CuL. The red block crystals of **II** were obtained.

For $C_{27}H_{26}N_4O_9CoNi$			
anal. calcd, %:	C, 48.49;	H, 3.89;	N, 8.38.
Found, %:	C, 48.36;	H, 3.86;	N, 8.35.

IR bands (ν, cm^{-1}): 1640 $\nu_s(COO^-)$, 1612 ν(C=O), 1565 ν(C=N).

Synthesis of complex III. A mixture of $Co(Ac)_2 \cdot 6H_2O$ (0.05 mmol, 12.5 mg), H_3Btc (0.05 mmol, 10.5 mg), CuL (0.025 mmol, 10.2 mg), H_2O (10 mL), and CH_3OH (4 mL) was stired for 20 min at room temperature, and the pH value of the solution was adjusted to about 6–7 with triethylamine. Then, the mixture was transferred to a 18 mL Teflon-lined reactor, which was heated to 140°C for 60 h. Last the reaction system was gradually cooled to room temperature for 36 h, and brown block crystals of **III** were obtained.

For $C_{47}H_{38}N_8O_{11}CoCu_2$			
anal. calcd, %:	C, 52.36;	H, 3.52;	N, 10.38.
Found, %:	C, 52.37;	H, 3.56;	N, 10.40.

IR bands (ν, cm^{-1}): 1672 ν_{as}(COOH), 1625 $\nu_s(COO^-)$, 1609 ν(C=O), 1556 ν(C=N).

X-ray crystallography. The data were collected on a Bruker Smart-1000-CCD area detector, all using graphite-monchromated MoK_α radiation (λ = 0.71073 Å). The structures were solved by direct method and subsequent Fourier difference techniques and refined using full-matrix least-squares procedure on F^2 with anisotropic thermal parameters for all non-hydrogen atoms (SHELXS-97 and SHELXL-97). Hydrogen atoms were added geometrically and refined with riding model position parameters and fixed isotropic thermal parameters. Crystal data collection and refinement parameters are given in Table 1, and selected bond lengths and angles for **I–III** are listed in Table 2. Crystallographic data (excluding structure factors) for structures **I–III** have been deposited with the Cambridge Crystallographic Data Centre (nos. 895937–895939; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

By using *m*-isophthalic acid, 1,3,5-benzenetricarboxylic acid and macrocyclic oxamido mixed ligands as the metal linker, three new complexes have been synthesized under hydrothermal conditions. During the course of the reacations, a series of experiments were performed by varying the pH value of the reaction system in the range of 4–9. The results show that compound **I** and **II** were obtained at relatively lower pH (6–7), whereas compound **III** was obtained at relatively higher pH (7–8). In order to explore the effect of the other reaction parameters in the preparing complexes **I–III**, a large number of experiments were also carried out via varying the reaction temperature (100–180°C) and time (3 to 10 days). And the results show that the single-crystal products suitable for X-ray analysis can be readily cbtained at 140°C for 2.5 days.

The IR spectra of the three complexes clearly show the existence of the *m*-isophthalic acid, 1,3,5-benzenetricarboxylic acid and macrocyclic oxamido moieties in the molecules, respectively. The IR spectra of **I–III** exhibit broad absorption bands in the range 3260–3450 cm^{-1}, demonstrating the existence of water, and the spectra exhibit strong absorption bands in the region 1612–1609 and 1565–1556 cm^{-1} due to the ν(C=O) and the ν(C=N) vibrations of oxamide group, respectively. The IR spectrum of the **III** shows one band around 1672 cm^{-1} which is characteristic of

Table 1. Crystal data and structure refinement for complexes **I**–**III**

Parameter	Value		
	I	**II**	**III**
Fw	672.99	668.16	1076.86
Crystal size, mm	0.38 × 0.32 × 0.30	0.32 × 0.28 × 0.22	0.22 × 0.16 × 0.15
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/n$
a, Å	12.9063(6)	12.8429(6)	11.2985(9)
b, Å	11.6766(6)	11.6726(6)	23.0322(18)
c, Å	17.8857(9)	17.8902(9)	17.0688(13)
b, deg	92.4040(10)	92.1740(10)	100.8210
V, Å^3	2693.0(2)	2680.0(2)	4362.8(6)
Z	4	4	4
ρ_{caled}, g/cm^3	1.660	1.656	1.639
μ, mm^{-1}	1.469	1.385	1.416
F(000)	1376	1372	2196
R_{int}	0.0152	0.0171	0.0499
Goodness-F^2	1.040	1.032	1.034
R_1* ($I > 2s(I)$)	0.0244	0.0241	0.0358
wR_2* (all data)	0.0701	0.0650	0.0841

* $R_1 = B||F_o| - |F_c||/B|F_o|$; $wR_2 = \{B[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o)^2]\}^{1/2}$.

the protonation of the carboxyl groups. While the IR spectra of those compounds show one band around 1640 cm^{-1} in **I** and **II** and around 1625 cm^{-1} in **III**, which are characteristic of the unprotonation of the carboxyl groups [26].

The electronic absorption spectra of complexes **I**–**III** were measured in DMF solution. For **I** and **III**, a broad band centered at 613 nm can be attributed to the *d*–*d* transitions of copper ions with four coordination [27]. For **II**, a broad band centered at 450 nm can be attributed to the *d*–*d* transitions of nickel ions with four coordination [27]. A broad band centered at 368 nm can be attributed to charge-transfer transitions in the [ML] chromophores. All complexes exhibit intense bands below 360 nm, assignable to intraligand π–π* and/or *n*–π* interaction [27].

Compounds **I** and **II** are isostructural, hence only the structure of **I** will be discussed in detail as a representative. The complex **I** is a neutral binuclear molecule and its asymmetric unit contains one Cu^{2+} ion, one Co^{2+} ion, one macrocyclic oxamide group, one *m*-isophthalic acid, and three water molecules. As shown in Fig. 1a, the Cu^{2+} ion is coordinated by four nitrogen atoms from the macrocylic organic ligand with the [CuN_4] geometry exhibiting a distorted square planarity. The Co^{2+} ion is six-coordinated by two oxygen atoms from one oxamide ligand (Co(1)–O(1) 2.1115(14) and Co(1)–O(2) 2.1036(13) Å), two carbaoxylate oxygen atoms from one *m*-isophthalate, and two oxygen atoms from two different water molecules. The [CoO_6] geometry exhibits a distort octahedron. Copper and cobalt ions are interlinked by the macrocyclic oxamide ligand to form heterobinuclear CoCu unit. As shown in Fig. 2a, the [Co(Ip)(CuL)$(H_2O)_2$] · H_2O units are linked together with O–H···O hydrogen bond to create a 2D network. The hydrogen bonding system in **I** consists of the uncoordinated oxygen atoms on COO^- group from Ip^{2-} with the hydrogen atoms on the one free water and coordinated water from three neighboring molecule, respectively, and the coordinated oxygen atom on COO^- group from Ip^{2-} with the hydrogen atom on the free water, and the oxygen atom on free water with the hydrogen atom on the coordinated water. The O···O distances are in the range of 2.654–2.813 Å (Table 3). In addition, there are π–π interactions between benzene rings of Ip^{2-} of different [Co(Ip)(CuL)$(H_2O)_2$] in the cell, which are antiparallel to each other and the distance between benzene rings is about 3.576 Å. It is no doubt that these strong hydrogen bonding and π–π interactions contribute significantly to the alignment of the molecules of **I** in the crystalline state.

A perspective view of the structure **III** unit of trinuclear [$Co(CuL)_2$(HBtc)(H_2O)] is depicted in Fig. 1b. In the [$Co(CuL)_2$(HBtc)(H_2O)] unit, the central cobalt(II) ion is linked to two external copper(II)

Table 2. Selected bond distances (Å) and angles (deg) for **I–III**

Bond	*d*, Å	Bond	*d*, Å
I			
Co(1)–O(7)	2.0499(14)	Co(1)–O(8)	2.0601(15)
Co(1)–O(3)	2.1012(13)	Co(1)–O(2)	2.1036(13)
Co(1)–O(1)	2.1115(14)	Co(1)–O(4)	2.1881(15)
Cu(1)–N(1)	1.9381(17)	Cu(1)–N(3)	1.9355(18)
Cu(1)–N(4)	1.964(2)	Cu(1)–N(2)	1.9588(16)
II			
Co(1)–O(8)	2.0489(13)	Co(1)–O(7)	2.0514(14)
Co(1)–O(4)	2.0963(12)	Co(1)–O(1)	2.1107(13)
Co(1)–O(2)	2.1176(13)	Co(1)–O(3)	2.1756(13)
Ni(1)–N(3)	1.8807(18)	Ni(1)–N(4)	1.8745(17)
Ni(1)–N(1)	1.9065(16)	Ni(1)–N(2)	1.8873(16)
III			
Co(1)–O(11)	2.0018(19)	Co(1)–O(5)	2.003(2)
Co(1)–O(1)	2.116(2)	Co(1)–O(2)	2.1596(18)
Co(1)–O(4)	2.2181(19)	Co(1)–O(3)	2.221(2)
Cu(1)–N(3)	1.927(2)	Cu(1)–N(1)	1.929(2)
Cu(1)–N(4)	1.953(2)	Cu(1)–N(2)	1.960(2)
Angle	ω, deg	Angle	ω, deg
I			
O(3)Co(1)O(2)	159.27(6)	O(8)Co(1)O(2)	97.34(6)
O(8)Co(1)O(1)	96.32(6)	O(7)Co(1)O(1)	163.75(6)
O(2)Co(1)O(1)	76.70(5)	O(3)Co(1)O(1)	88.97(5)
O(8)Co(1)O(4)	160.10(6)	O(7)Co(1)O(4)	87.67(6)
O(2)Co(1)O(4)	102.38(5)	O(3)Co(1)O(4)	61.12(5)
N(1)Cu(1)N(2)	86.53(7)	N(3)Cu(1)N(2)	94.41(8)
N(1)Cu(1)N(4)	92.54(8)	N(3)Cu(1)N(4)	91.81(9)
II			
O(4)Co(1)O(1)	159.54(5)	O(7)Co(1)O(1)	97.57(6)
O(7)Co(1)O(2)	96.47(6)	O(8)Co(1)O(2)	163.40(5)
O(1)Co(1)O(2)	76.77(5)	O(4)Co(1)O(2)	89.11(5)
O(7)Co(1)O(3)	160.07(5)	O(8)Co(1)O(3)	87.77(5)
O(1)Co(1)O(3)	102.21(5)	O(4)Co(1)O(3)	61.48(5)
N(4)Ni(1)N(3)	90.68(8)	N(4)Ni(1)N(2)	164.60(7)
N(3)Ni(1)N(2)	92.31(8)	N(4)Ni(1)N(1)	94.52(7)
N(3)Ni(1)N(1)	163.28(7)	N(2)Ni(1)N(1)	86.88(7)
III			
O(11)Co(1)O(5)	95.11(8)	O(11)Co(1)O(1)	172.03(7)
O(5)Co(1)O(2)	119.89(8)	O(1)Co(1)O(2)	76.54(7)
O(2)Co(1)O(4)	149.47(7)	O(2)Co(1)O(3)	77.33(7)
O(4)Co(1)O(3)	72.79(7)	O(1)Co(1)O(3)	83.79(8)
O(2)Co(1)O(3)	77.33(7)	O(11)Co(1)O(2)	95.75(7)
N(3)Cu(1)N(1)	164.71(10)	N(1)Cu(1)N(4)	86.82(9)
N(4)Cu(1)N(2)	157.93(10)	N(8)Cu(2)N(6)	160.97(10)
N(8)Cu(2)N(7)	94.36(10)	N(6)Cu(2)N(7)	92.22(10)

ions via the exo-*cis* oxygen donors of the macrocyclic oxamide ligand, one $HBtc^{2-}$ and a water molecular in a *cis* configuration. The cobalt(II) ion has a distorted octahedral geometry with four oxygen atoms from two oxamido bridges, one oxygen atom from $HBtc^{2-}$ ligands and one oxygen atom from water. The Co–O distances vary from 2.0018(19) to 2.221(2) Å. The external Cu(1) ion is coordinated by four nitrogen atoms from the macrocyclic organic ligand with the $[CuN_4]$ chromophore exhibiting distort planarity. The deviations of N(1), N(2), N(3), N(4) atoms from their mean plane are 0.3126, –0.3189, 0.2887, and –0.3271 Å, respectively, and copper ion is 0.0448 Å out of the plane. The three metal ions $CoCu_2$ form a V-type arrangement through the oxamide bridges with the Co···Cu separations of 5.3008 and 5.4938 Å. The $[Co(CuL)_2(HBtc)(H_2O)]$ units are alternately linked by O–H···O hydrogen bond to form a two-dimensional network (Fig. 2b). The hydrogen bonding system in **III** consists of the uncoordinated oxygen atoms on COO^- group from $HBtc^{2-}$ with the hydrogen atoms on COOH and coordinated water from two neighboring molecule, respectively. The corresponding O···O distances are 2.521–2.757 Å (Table 3).

The magnetization measurement for the complex **I** has been carried out under 1 kOe. The value $\chi_M T = 2.72\ cm^3\ mol^{-1}\ K$ at 300 K for powder sample **I** is larger than the spin-only value of 2.25 $cm^3\ mol^{-1}\ K$ expected for the uncoupled $Cu^{II}Co^{II}$ binuclear system (Fig. 3). This indicates an important contribution from the orbital momentum typical for the high-spin octahedral Co(II) with $^4T_{1g}$ ground state. On lowering the temperature, $\chi_M T$ decreases continuously and reaches 0.30 $cm^3\ mol^{-1}\ K$ at 2 K. The shape of the $\chi_M T$ vs. T curve suggests an overall antiferromagnetic behavior. On the basis of the crystal structure of **I**, the coupling topology deduced from the crystal structure has to be considered as the CuCo binuclear unit. First, the magnetic susceptibility expression (1) for the binuclear unit CuCo can be derived from the spin Hamiltonian:

$$\hat{H} = -2J\hat{S}_{Co}\hat{S}_{Cu} + g_{Co}\beta\hat{H}_Z\hat{S}_{CoZ} + g_{Cu}\beta\hat{H}_Z\hat{S}_{CuZ},$$

$$\chi_{CuCo} = \frac{N\beta^2}{kT}\left[\frac{10g^2 + 2g_1\exp\left(\frac{-4J}{kT}\right)}{5 + 3\exp\left(\frac{-4J}{kT}\right)}\right], \quad (1)$$

$$g_1 = -\frac{1}{4}g_{Cu} + \frac{5}{4}g_{Co}, \quad g_2 = \frac{1}{4}g_{Cu} + \frac{3}{4}g_{Co}.$$

Then, part of the orbital angular momentum of Co^{2+} ion is reflected in the temperature dependence of the g_{Co} factor (Eq. (2)) [28].

$$g_{Co} = \sqrt{\frac{3kT\chi_{Co}}{N\beta^2 S(S+1)}}, \quad (2)$$

$$\chi_{Co} = \frac{N\beta^2}{3kT}\frac{F_1}{F_2},$$

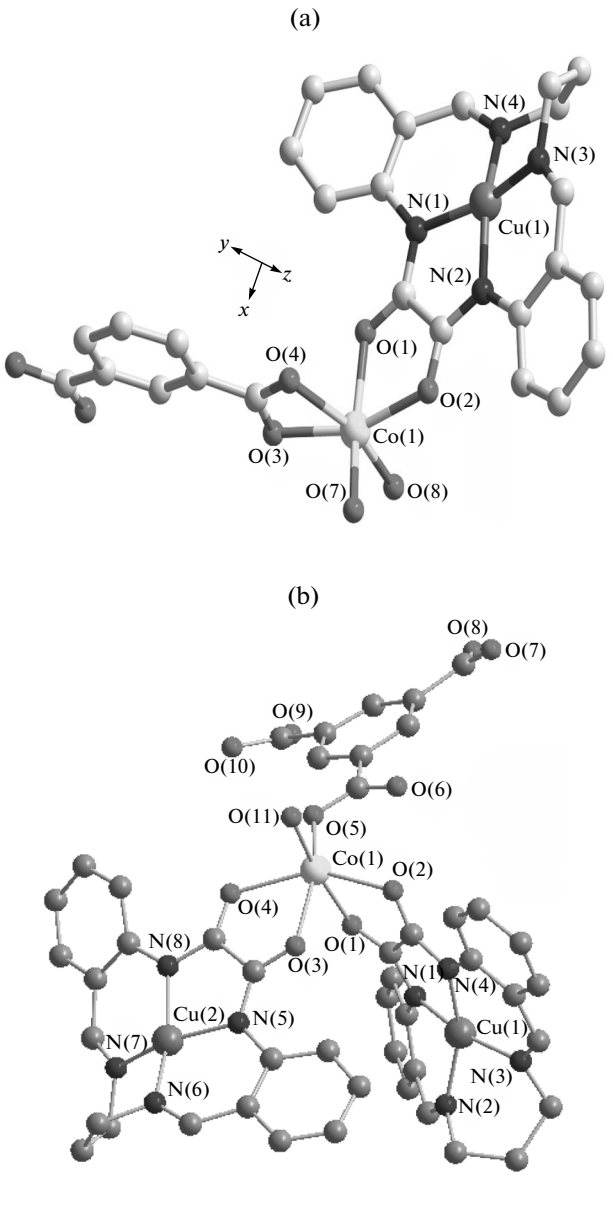

Fig. 1. Perspective view of the trinuclear complexes of **I** (a) and **III** (b).

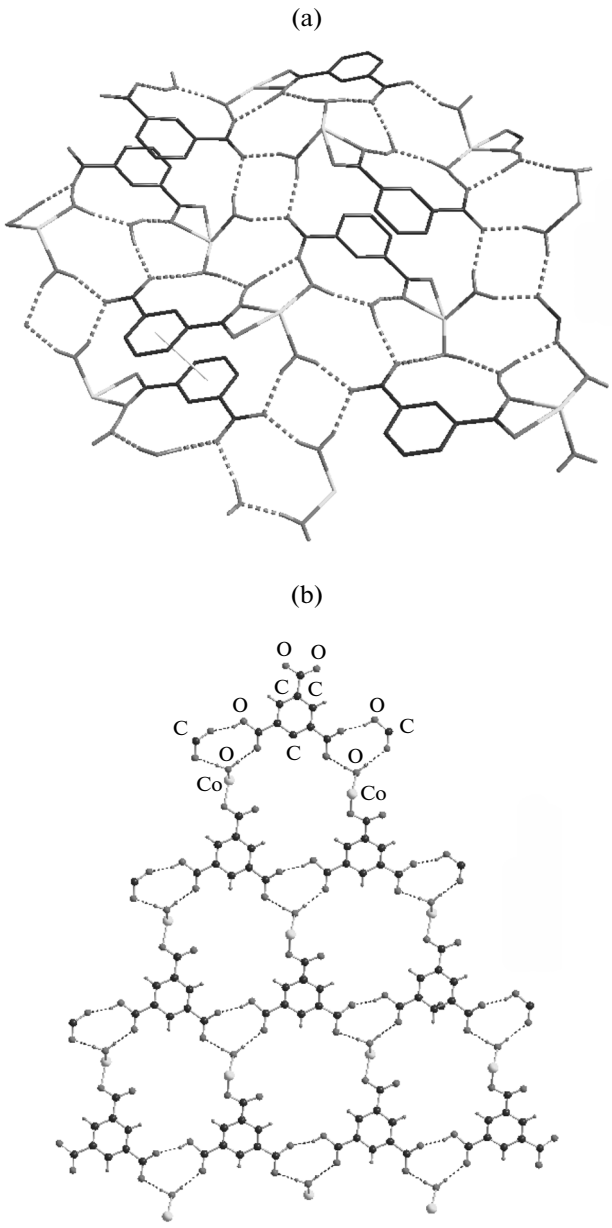

Fig. 2. View of the self-assembly 2D superamolecular architecture through O–H···O hydrogen bond interactions in **I** (a) and **III** (b).

$$F_1 = \frac{7\lambda(3-A)^2}{5kT} + \frac{12(2+A)^2}{25A} + \left[\frac{2\lambda(11-2A)^2}{45kT} + \frac{176(A+2)^2}{675A}\right]\exp\left(\frac{-5A\lambda}{2kT}\right) + \left[\frac{\lambda(A+5)^2}{9kT} - \frac{20(A+2)^2}{27A}\right]\exp\left(\frac{-4A\lambda}{kT}\right),$$

$$F_2 = \frac{\lambda}{3kT}\left[3 + 2\exp\left(\frac{-5A\lambda}{2kT}\right) + \exp\left(\frac{-4A\lambda}{kT}\right)\right].$$

In Eqs. (1)–(2), J is the exchange integral between Cu^{2+} and Co^{2+} ions through the oxamido-bridge, and A is ligand field parameter ($A = 1$, strong field limit; $A = 1.5$, weak field limit), and λ is spin–orbit coupling parameter ($\lambda = -170$ cm^{-1} for free cobalt(II)).

The least-squares fit to the experimental data was found with $J = -16.98$ cm^{-1}, $g_{Cu} = 2.00$ (fixed), $A = 1.33$ and $\lambda = -163$ cm^{-1}, the agreement factor defined as $R = \Sigma[(\chi_M)^{Cal} - (\chi_M)^{obsd}]^2/\Sigma[(\chi_M)^{obsd}]^2$ is 4.69×10^{-6}. The point below 16 K can not be reproduced with this model, possibly due to the intermolecular magnetic interactions. The fitted results show that the oxamido-bridge promotes an antiferromagnetic interaction between Cu^{2+} and Co^{2+} ions. In addition,

Table 3. Geometric parameters of hydrogen bonds for **I*** and **III****

D–H···A	Distance, Å			Angle DHA
	D–H	H···A	D···A	
		I		
O(7)–H(7)'···O(5)[a]	0.850	1.96	2.771	159
O(7)–H(7)"···O(5)[b]	0.850	1.88	2.6979	161
O(8)–H(11)'···O(9)	0.850	1.81	2.654	171
O(8)–H(11)"···O(6)[c]	0.850	1.98	2.811	165
O(9)–H(11)'···O(3)[c]	0.850	1.99	2.813	163
O(9)–H(11)"···O(6)[a]	0.850	1.85	2.679	165
* Symmetry codes: [a] $x, -1+y, z$; [b] $2-x, 2-y, -z$; [c] $2-x, -0.5+y, 0.5-z$.				
		II		
O(10–H(10)···O(7)[a]	0.820	1.728	2.521	161.82
O(11)–H(11)'···O(8)[b]	0.850	1.785	2.634	176.45
O(11)–H(11)"···O(9)[c]	0.850	1.916	2.757	169.88
** Symmetry codes: [a] $x-1/2, -y+3/2, z-1/2$; [b] $x+1/2, -y+3/2, z-1/2$; [c] $x+1, y, z$.				

spin–orbit coupling of Co^{2+} ion plays an important role in the magnetic behaviors. The antiferromagnetic interaction through oxamido group arises from the nonzero overlap between the magnetic orbital around Cu^{2+} and Co^{2+} [29], comparing with some cobalt(II)–copper(II) species incorporating noncyclic oxamide or macrocyclic oxamide ligands reported previously, the exchange integral in **I** is in the range of those reported [30, 31]. The difference in the magnetic exchange of cobalt(II)–copper(II) complexes may be explained on the basis of structural distortions, distances and the molecular topology. In these regards, one of the relevant factors is the value of the dihedral angle (γ) between the mean equatorial plane of the metal ion and the oxamido plane [32, 33]: the greater the value of γ the smaller antiferromagnetic coupling. The longer distance of Cu···Co the weaker antiferromagnetic coupling. In addition, the molecular topology has an important influence on the magnetic property.

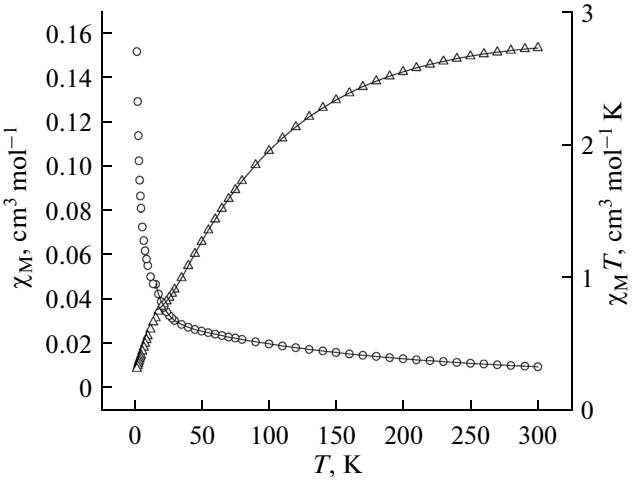

Fig. 3. χ_M (○) and $\chi_M T$ (Δ) vs. T plots for the complex **I**.

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