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Crystal Structure and Magnetic Properties of Heterometallic Trinuclear Cu_2Ni Complex Containing Macrocyclic Ligands[1]

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Abstract—One novel heterometallic trinuclear complex of macrocyclic oxamide $[Ni(CuL)_2(HBTC)H_2O]$ (**I**) (H_2L = 2,3-dioxo-5,6,14,15-dibenzo-1,4,8,12-tetraazacyclopentadeca-7,13-dien; H_3BTC = 1,3,5-benzenetricarboxylic acid) has been solvothermally synthesized and structurally characterized by elemental analysis, IR spectroscopy, XRD, and single-crystal X-ray diffraction. The crystals crystallize in the monoclinic system, space group $P2_1/c$, $a = 11.435(3)$, $b = 20.646(5)$, $c = 18.430(5)$ Å, $\beta = 94.131(4)°$. The structure of **I** has oxamido-bridged trinuclear $[Cu^{II}_2Ni^{II}]$ units and consists of two-dimensional supramolecular architecture formed by strong intermolecular hydrogen bonds. Furthermore, the magnetic properties of complex **I** was investigated and discussed in detail.

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INTRODUCTION

The synthesis of heterometallic (3*d*–3*d* and 3*d*–4*f*) complexes is of current focus, which is justified not only by the fascinating structural diversity of such complexes but also by their potential applications as functional materials in magnetism, molecular adsorption, light conversion devices, and bimetallic catalysis [1–4]. The study of the exchange interaction between different metal centers through extended bridges has been one of the most active research fields in magnetism [5]. One of the most thoroughly investigated families of bridging ligands is N,N-bis(coordinating group substituted) oxamides. Noncyclic oxamides may adopt a *cis* or *trans* conformation on coordination, and this flexibility restricts the control over the type of the complex formed [6, 7]. The macrocyclic oxamides allow the synthesis of heterometallic systems in more controlled fashion, and it has been found that the oxamide group serves as a pathway through which electron spin interaction takes place [8–10]. Recently, in order to design and construct the diverse oxamido-bridged heteropolynuclear network, we have chosen the organic acid as co-ligand, such as 5-sulfosalicylic acid, 1,3,5-benzenetricarboxylic acid. A series of heterometallic complexes exhibiting interesting magnetic and luminescent properties have been prepared [11–13]. However, rational control in the construction of heterometallic complexes with macrocylic oxamide and organic acid as co-ligand still remains a great challenge in crystal engineering.

In our continuing efforts to investigate the synthesis and properties of heterometallic polynuclear complexes, in this paper, we report that the macrocyclic oxamide copper(II) complex was used as ligand with co-ligand 1,3,5-benzenetricarboxylic acid to synthesize the new complex $[Ni(CuL)_2(HBTC)H_2O]$ (**I**). Furthermore, the magnetic properties of complex **I** were investigated.

EXPERIMENTAL

All the starting reagents were of A.R. grade and were used as purchased. The complex ligand CuL was prepared as described elsewhere [14]. 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 in DMF were recorded on a Shimadzu UV-2101 PC scanning spectrophotometer. X-ray powder diffraction (XRPD) spectra for the powder were recorded on a Model D/MAX-2550V diffractometer (Rigaku, Japan). Variable-temperature magnetic susceptibilities were measured on an MPMS-7 SQUID magnetometer. Diamagnetic corrections were made with Pascal's constants for all the constituent atoms [15].

Synthesis of $[Ni(CuL)_2(HBTC)H_2O]$ (I). A mixture of $Ni(ClO_4)_2 \cdot 6H_2O$ (0.05 mmol), H_3BTC (0.05 mmol), CuL (0.025 mmol), H_2O (10 mL), and CH_3OH (3 mL) was stired for 40 min at room temperature, and the pH value of the solution was adjusted to about 6–7 with triethylamine. After stirring, the mix-

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Table 1. Crystal data and structure refinement for the complex **I**

Parameter	Value
M	1076.64
T, K	296(2)
System	Monoclinic
Space group	$P2_1/c$
a, Å	11.435(3)
b Å	20.646(5)
c, Å	18.430(5)
β, deg	94.131(4)
V, Å^3	4340.0(19)
Z	4
ρ_{calcd}, g/cm^3	1.648
$\mu(MoK_\alpha)$, mm^{-1}	1.475
F(000)	2200
Crystal size, mm	0.22 × 0.15 × 0.14
Scan type	φ and ω
θ Range, deg	1.48–25.01
Limiting indices h, k, l	$-13 \le h \le 13$, $-20 \le k \le 24$, $-21 \le l \le 18$
Reflection collected	21626
Independent reflections (R_{int})	7627 (0.0302)
Reflections with $I > 2\sigma(I)$	6553
Parameters refined	623
GOOF	1.052
R_1 ($I > 2\sigma(I)$)	0.0312
wR_2 (all data)	0.0897
Largest diff. peak and hole, e Å^{-3}	0.587 and –0.452

ture was transferred to a 18 mL Teflon-lined reactor, and heated at 150°C for 72 h. Then the reaction system was cooled to room temperature during 36 h, and deep brown-green crystal of compound **I** was isolated (the yield was 50.6% based on Mn).

For $C_{47}H_{38}N_8O_{11}NiCu_2$

anal. calcd., %:	C, 52.38;	H, 3.52;	N, 10.40
Found, %:	C, 52.37;	H, 3.51;	N, 10.38

IR bands (ν, cm^{-1}): 1688 ν_{as}(COOH), 1631 ν_s(COO$^-$), 1592 ν(C=O), 1561 ν(C=N).

Caution! Perchlorate salts of metal complexes with organic ligand are potentially explosive and should be handed in small quantities with care.

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 the direct method, 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) [16]. 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. Supplementary material for structure **I** has been deposited with the Cambridge Crystallographic Data Centre (no. 871850; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

Complex **I** consists of a neutral trinuclear $[Ni(CuL)_2(HBTC)H_2O]$ unit. A perspective view of the structure is depicted in Fig. 1, and selected bond lengths and angles are listed in Table 2. In the $[Ni(CuL)_2(HBTC)H_2O]$ unit, the central Ni^{2+} ion is linked to two external Cu^{2+} ions through the *exo-cis* oxygen donors of the macrocyclic oxamido ligands. The three metal ions form a *V*-type arrangement through the bridges with the Cu···Ni separations of 5.30 Å (Cu(1)···Ni(1)) and 5.32 Å (Cu(2)···Ni(1)), respectively, and the Cu···Cu separation of 9.19 Å. The Ni^{2+} ion has a distorted octahedral arrangement with four oxygen atoms from two oxamido bridges, one oxygen atom from COO$^-$ group of HBTC^{2-} and one oxygen atom from the coordinated water. The Ni–O distances vary from 2.0262(18) to 2.0927 Å. The external Cu^{2+} in **I** is coordinated by four nitrogen atoms from the macrocyclic organic ligand with the $[CuN_4]$ chromophore exhibiting distort planarity. The Cu(1) ion is displaced from the least-square plane by 0.0035 Å, the deviations of the four donor atoms (N(1), N(2), N(3), and N(4)) from their mean plane are 0.3226, –0.3105, 0.2990, –0.3147 Å, respectively. The deviation of Cu(2) and four nitrogen atoms (N(5), N(6), N(7), and N(8)) are –0.0339, –0.3261, 0.3313, –0.3053 and 0.3340 Å, respectively.

In **I**, as shown in Fig. 2, the neutral trinuclear $[Ni(CuL)_2(HBTC)H_2O]$ units are bound together by O–H···O intermolecular hydrogen bonds to form a two-dimensional network. The hydrogen bonding system in **I** consists of the uncoordinated oxygen atoms on COO$^-$ group from HBTC^{2-} with the hydrogen atoms on the COOH group and coordinated water from two neighboring molecules, respectively, and the uncoordinated oxygen atom on COO$^-$ group from HBTC^{2-} with the hydrogen atom on the coordinated water forms a intramolecular hydrogen bond. The corresponding O···O distances are 2.487–2.673 Å.

The IR spectra of **I** showing three strong bands around 1631, 1592 and 1561 cm^{-1}, attributed to the ν(C=O) and the ν(C=N) vibrations, respectively [17]. The band around 1688 cm^{-1} is characteristic of the protonation of the carboxyl groups [18].

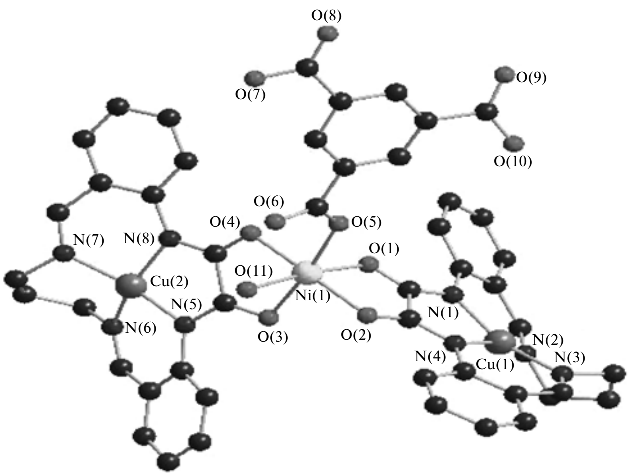

Fig. 1. Perspective view of the trinuclear complex of **I**.

The electronic absorption spectra of complex **I** were measured in DMF solution. The complex exhibits intense bands below 400 nm, assignable to charge-transfer transitions in the [CuL] chromophores and/or intraligand π–π* interaction [19]. In the 500–900 nm region, relatively stronger broad band centered at 531 nm is attributed to the envelop of two spin allowed *d–d* transitions: $^2B_{1g} \rightarrow {}^2E_g$(Cu) and $^3A_{2g} \rightarrow {}^3T_{1g}$(Ni). Because the *d–d* absorption of Ni^{2+} in an octahedral environment is usually weaker than that of Ni^{2+} in a tetragonal environment, this band may be dominated by former transition [19].

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

Bond	*d*, Å	Bond	*d*, Å
Cu(1)–N(1)	1.933(2)	Cu(1)–N(3)	1.938(2)
Cu(1)–N(4)	1.950(2)	Cu(1)–N(2)	1.950(2)
Cu(2)–N(5)	1.927(2)	Cu(2)–N(7)	1.928(2)
Cu(2)–N(8)	1.948(2)	Cu(2)–N(6)	1.952(2)
Ni(1)–O(5)	2.0262(18)	Ni(1)–O(11)	2.0355(18)
Ni(1)–O(1)	2.0416(18)	Ni(1)–O(2)	2.0753(18)
Ni(1)–O(4)	2.0808(18)	Ni(1)–O(3)	2.0927(18)
Angle	ω, deg	Angle	ω, deg
N(1)Cu(1)N(3)	161.72(9)	N(1)Cu(1)N(4)	86.56(9)
N(3)Cu(1)N(4)	95.89(9)	N(1)Cu(1)N(2)	92.60(9)
N(3)Cu(1)N(2)	90.87(9)	N(4)Cu(1)N(2)	160.92(9)
N(5)Cu(2)N(7)	163.18(9)	N(5)Cu(2)N(8)	87.46(9)
N(7)Cu(2)N(8)	95.53(9)	N(5)Cu(2)N(6)	92.49(9)
N(7)Cu(2)N(6)	90.84(9)	N(8)Cu(2)N(6)	158.06(10)
O(5)Ni(1)O(11)	95.71(7)	O(5)Ni(1)O(1)	90.71(7)
O(11)Ni(1)O(1)	172.47(7)	O(5)Ni(1)O(2)	91.53(7)
O(11)Ni(1)O(2)	96.12(7)	O(1)Ni(1)O(2)	79.73(7)
O(5)Ni(1)O(4)	93.64(7)	O(11)Ni(1)O(4)	89.37(7)
O(1)Ni(1)O(4)	94.16(7)	O(2)Ni(1)O(4)	172.05(7)

The crystalline phase purity of **I** was confirmed by the experimental XRPD patterns, which match well with the corresponding simulated ones obtained from the single-crystal data (Fig. 3).

The magnetization measurements for complex **I** have been carried out under 2 kOe. For complex **I**, the $\chi_M T$ value is equal to 1.60 $cm^3 mol^{-1}$ K at 300 K, which is slightly lower than the spin-only value (1.62 $cm^3 mol^{-1}$ K) expected for the uncoupled $Cu_2^{II}Ni^{II}$ trinuclear system (Fig. 4). Upon cooling, $\chi_M T$ decreases from 300 to 2 K and reaches 0.20 $cm^3 mol^{-1}$ K at 2 K. This feature is characteristic of a noticeable intramolecular antiferromagnetic interaction. On the basis of the crystal structure of **I**, the magnetic analysis was carried out by using the theoretical expression of the magnetic susceptibility deduced from the spin Hamiltonian $\hat{H} = -2J(\hat{S}_{Cu1}\hat{S}_{Ni} + \hat{S}_{Cu2}\hat{S}_{Ni})$. The magnetic susceptibility of the trinuclear complex can be calculated from the following equation:

$$\chi_{tri} = \frac{N\beta^2}{2kT}\frac{A}{B},$$

$$A = (g_{Ni} + g_{Cu})^2\left[5 + \exp\left(\frac{-4J}{kT}\right)\right] + 4g_{Ni}^2\exp\left(\frac{-2J}{kT}\right),$$

$$B = 5 + 3\exp\left(\frac{-4J}{kT}\right) + \exp\left(\frac{-6J}{kT}\right) + 3\exp\left(\frac{-2J}{kT}\right).$$

So far as magnetic interactions between the adjacent trinuclear Cu_2Ni units are concerned, the molecular field approximation was used $\chi_M = \chi_{tri}/[1 - \chi_{tri}(2zj'/Ng^2\beta^2)]$. Where *J* is the intramolecular exchange integral between copper(II) and nickel(II) ions, and *zj'* stands for the intermolecular exchange integral of $Cu_2^{II}Ni^{II}$ units. The best-fit parameters obtained were $J = -29.33$ cm^{-1}, g_{Cu}(fixed) = 2.0, $g_{Ni} = 2.08$, $zj' = -0.12$ cm^{-1}, and the agreement factor defined as $R = \Sigma[(\chi_M)^{Cal} - (\chi_M)^{obsd}]^2/\Sigma[(\chi_M)^{obsd}]^2$ is 1.46×10^{-5}.

According to Kahn, the antiferromagnetic interaction between Cu(II) and Ni(II) arises from the nonzero overlap between $d_{x^2-y^2}$ magnetic orbital centered on the two metal ions and delocalized towards ligand. And the *J* value for **I** is less than those reported in the literature for the Cu–Ni heteronuclear complexes with the oxamide bridge [20, 21]. The difference of the magnetic exchange may be explained on the basis of structural distortions. The larger distortion of the CuN_4 moiety disfavors the delocalization of the Cu(II) magnetic orbital and is expected to result in a

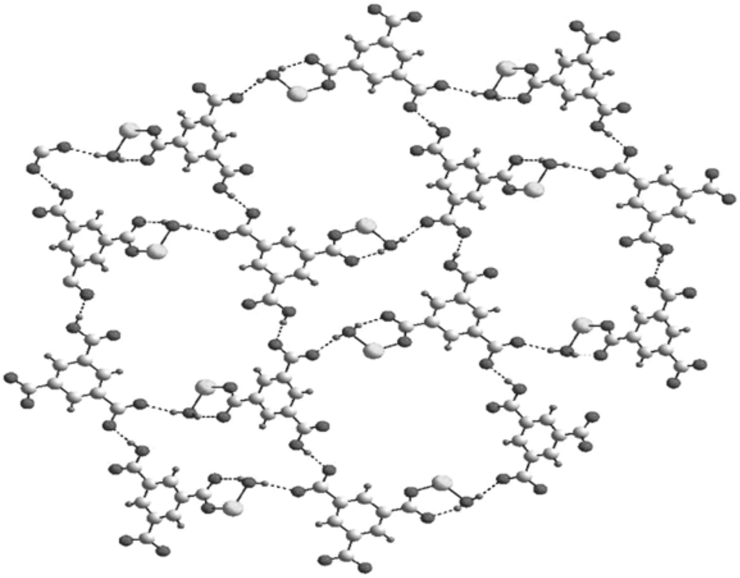

Fig. 2. View of the self-assembly 2D superamolecular architecture through O–H···O hydrogen bond interactions.

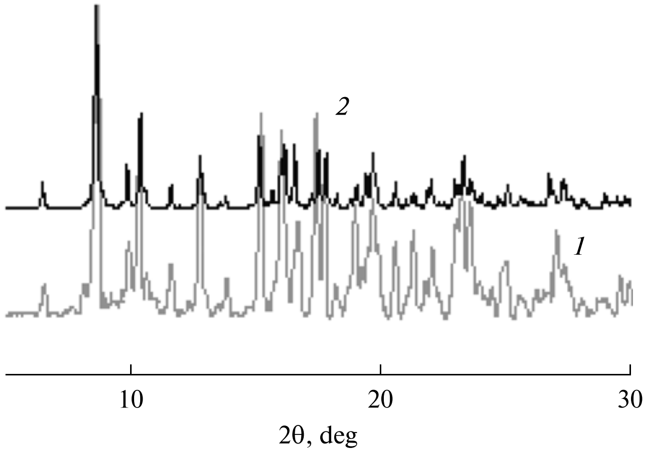

Fig. 3. Experimental (*1*) and simulated (*2*) XRPD spectra of the complex **I**.

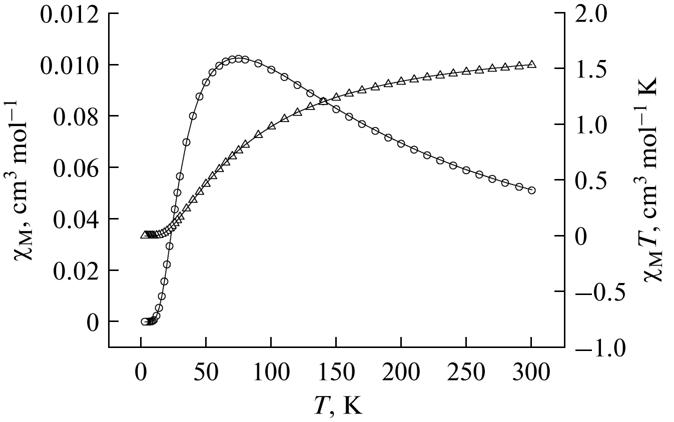

Fig. 4. χ_M (○) versus T and $\chi_M T$ (Δ) versus T plots for complex **I**.

weaker antiferromagnetic interaction than those reported in the literature.

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