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Syntheses, Structure and Magnetism of Heterobinuclear μ-Oxamido Cu(II)–Ni(II) Complexes Containing tacn as a Terminal Ligand

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Two new heterobinuclear complexes, namely Ni(tacn)Cu(oxpn)$(ClO_4)_2 \cdot 2H_2O$ (**1**) and Ni(tacn)Cu(pmoxd)$(ClO_4)_2 \cdot CH_3OH$ (**2**), have been prepared from the planar fragments Cu(oxpn) and Cu(pmoxd) (tacn denotes 1,4,7-triazacyclononane, oxpn and pmoxd stand for the dianions of *N,N′*-bis(3-aminopropyl)oxamide and *N,N′*-bis(2-pyridylmethyl)oxamide, respectively). Compound **1** crystallizes in the triclinic system, space group $P\bar{1}$, with $a = 8.573(2)$, $b = 12.808(3)$, $c = 13.122(3)$ Å, $\alpha = 99.63(3)$, $\beta = 104.72(3)$ and $\gamma = 96.45(3)°$ at 299 K, $Z = 2$. The Cu(II) ions are in square-pyramidal surroundings and the Ni(II) ions in octahedral surroundings. The temperature dependence of the magnetic susceptibilities of **1** has been studied in the 5–300 K range, giving the exchange integral $J = -92.7\ cm^{-1}$. This value, while close to those reported for other Cu(II)–Ni(II) complexes involving Cu(oxpn), represents the minimum exchange constant of such heterobinuclear system.

Key words: heterobinuclear compounds, Cu(II)–Ni(II) complexes, oxamide, 1,4,7-triazacyclononane, X-ray structure, magnetism

Heterobinuclear complexes play an important role in molecular magnetism [1]. This situation can be attributed to the fact that the types of magnetic interaction between different magnetic centers are much more diverse than that between identical ones. One of the best strategies to design and synthesize heterobinuclear complexes is the 'complex as ligand' approach, *i.e.* using mononuclear complexes that contain potential donor groups for attachment to another metal ion. A good candidate for this is represented by the use of the Cu(II) complexes of *N,N′*-disubstituted oxamides as ligands. It is known that the oxamido group has a remarkable efficiency to propagate magnetic interaction between two neighboring metal ions, the type and magnitude of the interaction depending on the kind of metal ions and their environment. Using the above Cu(II) precursors, a large number of oxamido-bridged heterobinuclear complexes have been synthesized and studied in recent years and the Cu(II)–Ni(II) system has received much attention [2–13]. However, in most cases reported, the terminal ligands coordinating to the Ni(II) ion were either monodentate small molecules [2,3] or

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bidentate chelating agents [3–12], and in a few cases relatively flexible macrocyclic groups [11–13] were employed as terminal ligands.

In this work, two new Cu(II)–Ni(II) complexes, in which the terminal Ni(II) ion is blocked with the more rigid macrocycle tacn (tacn = 1,4,7-triazacyclononane), have been synthesized and characterized. These complexes can be denoted as Ni(tacn)Cu(oxpn)$(ClO_4)_2 \cdot 2H_2O$ (**1**) and Ni(tacn)Cu(pmoxd)$(ClO_4)_2 \cdot CH_3OH$ (**2**), where oxpn, pmoxd stand for the dianions of *N,N′*-bis(3-aminopropyl)oxamide and *N,N′*-bis(2-pyridylmethyl)oxamide, respectively. The crystal structure of **1** has been determined and its magnetic properties investigated as well.

EXPERIMENTAL

Materials. All the reagents used in the synthesis were analytical grade. The planar fragment Cu(oxpn) was synthesized as previously described [14] and Cu(pmoxd)$\cdot H_2O$ prepared by a similar procedure from 2-aminomethyl-pyridine, diethyl oxalate and copper hydroxide.

Synthesis of the Cu(II)–Ni(II) complexes. Preparation of Ni(tacn)Cu(oxpn)$(ClO_4)_2 \cdot 2H_2O$ (**1**). To 0.3 mmol (79 mg) of Cu(oxpn) stirred in 5 ml of methanol were successively added a solution of 0.3 mmol (110 mg) nickel(II) perchlorate in 5 ml of methanol and a solution of 0.3 mmol tacn in 3 ml of methanol. The resulting violet-red solution was allowed to evaporate slowly at room temperature. Two weeks later, violet-red crystals suitable for X-ray investigations were obtained.

Anal. Calcd. for $C_{14}H_{35}N_7O_{12}Cl_2CuNi$: C, 24.47; H, 5.10; N, 14.28. Found: C, 24.32; H, 4.70; N, 14.46.

Preparation of Ni(tacn)Cu(pmoxd)$(ClO_4)_2 \cdot CH_3OH$ (2). To 0.3 mmol (105 mg) of Cu((pmoxd)$\cdot H_2O$ stirred in 5 ml of methanol were successively added a solution of 0.3 mmol (110 mg) nickel(II) perchlorate in 5 ml of methanol and a solution of 0.3 mmol tacn in 3 ml of methanol. After stirred for 1 h at room temperature, the mixture was filtered. The precipitate thus obtained then recrystallized in 1:1(v/v) acetonitrile-methanol mixture giving purple microcrystals.

Anal. Calcd. for $C_{21}H_{31}N_7O_{11}Cl_2CuNi$: C, 33.58; H, 4.13; N, 13.06. Found: C, 33.11; H, 3.97; N, 12.76.

Physical measurements. Elemental analyses (C, H, N) were performed on a Perkin-Elmer 240 analyser. IR spectra were recorded on a Shimadzu IR-408 spectrometer using KBr pellets. The electronic spectra were measured on a Shimadzu UV-2101 PC UV-VIS scanning spectrophotometer. Variable-temperature magnetic susceptibilities (4.2–300 K) were performed at the Institute of Physics, Chinese Academy of Science, using a SQUID MPMS-7 magnetometer. Diamagnetic corrections were evaluated from Pascal's constants for all the constituent atoms.

Crystal data collection and refinement. A summary of the crystallographic data and structure refinement parameters are given in Table 1. The crystal structure was solved by direct methods and refined by full-matrix least-squares on F. The function minimized was $\Sigma w(|F_0| - |F_c|)^2$, where $w = 1/(\sigma^2(F) + 0.0001F^2)$. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were not located. The final R factor was 0.068 (R_w = 0.070) for all the observed reflections.

Table 1. Crystallographic data for Ni(tacn)Cu(oxpn)$(ClO_4)_2 \cdot 2H_2O$ (**1**).

Formula	$C_{14}H_{35}N_7O_{12}Cl_2CuNi$
Formula weight	686.63
Crystal size, mm	0.25×0.30×0.35
Color	violet-red
Temperature, K	299 (1)
Instrument	CAD-4
Radiation	monochromated MoKα (λ = 0.71073 Å)
Crystal system	triclinic

Table 1 (continuation)

Space group	$P\bar{1}$
Unit cell	
a, Å	8.573 (2)
b, Å	12.808 (3)
c, Å	13.122(3)
α, deg	99.63(3)°
β, deg	104.72(3)°
γ, deg	96.45(3)°
V, Å^3	1356
Z	2
μ(Mo Kα), mm^{-1}	1.7477
Density (calculated)	1.682×10^3 Kg/m^3
Scan mode	$\omega/2\theta$
$2\theta_{\max}$, deg	50
Reflections collected	4993
Independent reflections	4284
Observed reflections ($I \geq 3\sigma(I)$)	3089
Absorption correction	empirical
Parameters	334
R	0.068
R$_w$	0.070
Goodness-of-fit on F	1.17
Largest difference peak and hole (e Å^{-3})	0.84 and –0.59

RESULTS AND DISCUSSION

General characterization. Elemental analyses and spectral data for the products indicate that the reaction of Cu(oxpn) or Cu(pmoxd)·H_2O with Ni$(ClO_4)_2\cdot6H_2O$ and tacn yielded heterobinuclear complexes. In the infrared spectra, the complexes both exhibit a strong, wide band centered at 1100 cm^{-1} attributable to the ClO_4^- anions, a weak band at 2900 cm^{-1} attributable to the C–H bonds as well as a broad band in the range 3100–3600 cm^{-1} due to the presence of co-crystallized water or methanol molecules and hydrogen bonds. The N–H stretching vibrations for tacn or Cu(oxpn) fragment, expected at around 3150 cm^{-1}, are hidden by the broad bands. The strong, wide bands centered at 1610 cm^{-1} for **1** and 1645 cm^{-1} for **2** are assigned to the bridging oxamido ligands. It is noted that both these bands shift towards higher frequencies in comparison to the corresponding Cu(II) precursors (Cu(oxpn), 1590 cm^{-1}; Cu(pmoxd), 1610 cm^{-1}), which indicate coordination of the oxamido carbonyl groups to the Ni(II) atom [15]. In the electronic absorption spectra of the complexes in acetonitrile, the weak bands at 541 nm for **1** and 550 nm for **2** are attributed to the superposition of the *d*-*d* transitions of Cu(II) and Ni(II) chromophores; these data agree well with those reported before [13]. The strong, wide band centered at 228 nm for **1** may be attributed to charge-transfer absorption and the strong, broad band in the range 220–270 nm for **2** may be interpreted as the envelop of charge-transfer and intra-ligand absorptions.

Description of the structure: Ni(tacn)Cu(oxpn)$(ClO_4)_2 \cdot 2H_2O$ (1). A perspective view of the cation [Ni(tacn)(H_2O)Cu(oxpn)$(ClO_4)]^+$ with the atom-labeling scheme is showed in Figure 1. Selected bond lengths and angles are listed in Table 2.

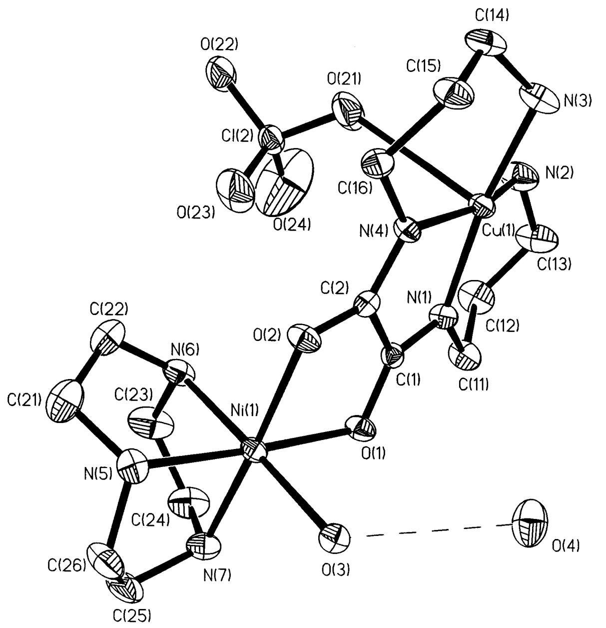

Figure 1. Perspective view of the cation [Ni(tacn)(H_2O)Cu(oxpn)$(ClO_4)]^+$ with the atom-labeling scheme.

Table 2. Selected interatomic distances (Å) and bond angles (°).

Bond lengths			
Ni(1)–O(1)	2.057 (5)	Cu(1)–N(3)	2.029 (9)
Ni(1)–O(2)	2.066 (6)	Cu(1)–N(4)	1.953 (6)
Ni(1)–O(3)	2.103 (6)	O(1)–C(1)	1.266 (9)
Ni(1)–N(5)	2.072 (7)	O(2)–C(2)	1.280 (8)
Ni(1)–N(6)	2.108 (7)	C(1)–C(2)	1.550 (1)
Ni(1)–N(7)	2.101 (9)	C(1)–N(1)	1.295 (8)
Cu(1)–N(1)	1.961 (7)	C(2)–N(4)	1.260 (10)
Cu(1)–N(2)	2.020 (8)		
Bond angles			
O(1)–Ni(1)–O(2)	81.5(2)	N(6)–Ni(1)–N(7)	82.6(3)
O(1)–Ni(1)–O(3)	86.9(2)	N(1)–Cu(1)–N(2)	93.1(3)
O(2)–Ni(1)–O(3)	90.3(2)	N(1)–Cu(1)–N(3)	168.3(3)
O(1)–Ni(1)–N(5)	176.1(3)	N(2)–Cu(1)–N(3)	92.2(3)
O(2)–Ni(1)–N(5)	98.0(3)	N(1)–Cu(1)–N(4)	84.1(3)

Table 2 (continuation)

O(3)–Ni(1)–N(5)	97.0(2)	N(2)–Cu(1)–N(4)	163.6(4)
O(1)–Ni(1)–N(6)	92.8(3)	N(3)–Cu(1)–N(4)	93.7(3)
O(2)–Ni(1)–N(6)	91.7(3)	O(1)–C(1)–C(2)	117.6(6)
O(3)–Ni(1)–N(6)	177.9(3)	O(1)–C(1)–N(1)	128.0(8)
N(5)–Ni(1)–N(6)	83.4(3)	C(2)–C(1)–N(1)	114.4(7)
O(1)–Ni(1)–N(7)	95.7(3)	O(2)–C(2)–C(1)	115.7(7)
O(2)–Ni(1)–N(7)	173.6(2)	O(2)–C(2)–N(4)	128.8(8)
O(3)–Ni(1)–N(7)	95.3(3)	C(1)–C(2)–N(4)	115.4(6)
N(5)–Ni(1)–N(7)	84.4(3)		

In the binuclear cation, Cu(II) and Ni(II) ions are linked by a *cis*-configuration μ-oxamido ligand and the Cu···Ni distance is 5.273 Å. The Ni(II) ion is in a distorted octahedral coordination environment, being surrounded by two oxamido oxygen atoms (O(1), O(2)), three nitrogen atoms (N(5), N(6), N(7)) of the tacn ligand, and an aqua oxygen atom (O(3)). N(6) and O(3) occupy the apical positions and the N(6)–Ni–O(3) angle is 177.9°. The nickel atom is displaced by 0.088 Å from the O(1)O(2)N(5)N(7) least-squares basal plane (denoted as P1) toward O(3). As a result of the rigidity of the tacn ligand, the three angles formed by Ni(II) and N(5), N(6), N(7) are all acute, being 82.6, 83.4 and 84.3°, respectively. The Cu(II) ion is in a square pyramidal surrounding with the four nitrogen atoms (N(1), N(2), N(3), N(4)) of the oxpn ligand placed in the basal positions and one oxygen atom (O21) of the ClO_4^- anion in the apical position. The four Cu–N distances are very close to 2.0 Å while the Cu–O distance is 2.799 Å. The copper atom lies only 0.04 Å beneath the least-squares basal plane through N(1), N(2), N(3) and N(4) atoms (denoted as P2).

The bridging atoms O(1), O(2), C(1), C(2), N(1), N(2) are roughly coplanar with the mean atom-to-plane distance equal to 0.044 Å. The least-squares plane through them is denoted as P3. The Cu(II), Ni(II) ions both lie on the same side of P3 with deviations of 0.019 Å for the Cu(II) ion and 0.381 Å for the Ni(II) ion. The dihedral angles between P3 and P1, P2 are 17.3, 13.6°, respectively. Hence, P1 and P2 are somewhat tilted with respect to each other and the dihedral angle between them reaches 24.7°.

The packing of the molecules in the crystal lattice is showed in Figure 2. Owing to the linkage of hydrogen bonds between the coordinated water molecule and one oxygen atom of the oxamido bridge of the neighboring binuclear cation (O(3)···O(2a), 2.714 Å), two binuclear cations related by an inversion center form a bis binuclear entity. The structure is made up of such entities and noncoordinated perchlorate anions and water molecules. Hydrogen bonds also occur between coordinated and noncoordinated water molecules (O(3)···O(4), 2.851 Å).

Magnetic properties. Variable temperature susceptibility data (5–300 K) were recorded for complex **1**. Applying the Hamiltonian $\boldsymbol{H} = -\boldsymbol{J}\boldsymbol{S}_{\mathrm{Cu}}\boldsymbol{S}_{\mathrm{Ni}}$, the theoretical expression for the susceptibility for such a compound is [16]

$$\chi_{\mathrm{M}} = (N\beta^2/4kT)[10g_{3/2}^2 + g_{1/2}^2\exp(-3J/2kT)]/[2 + \exp(-3J/2kT)]$$

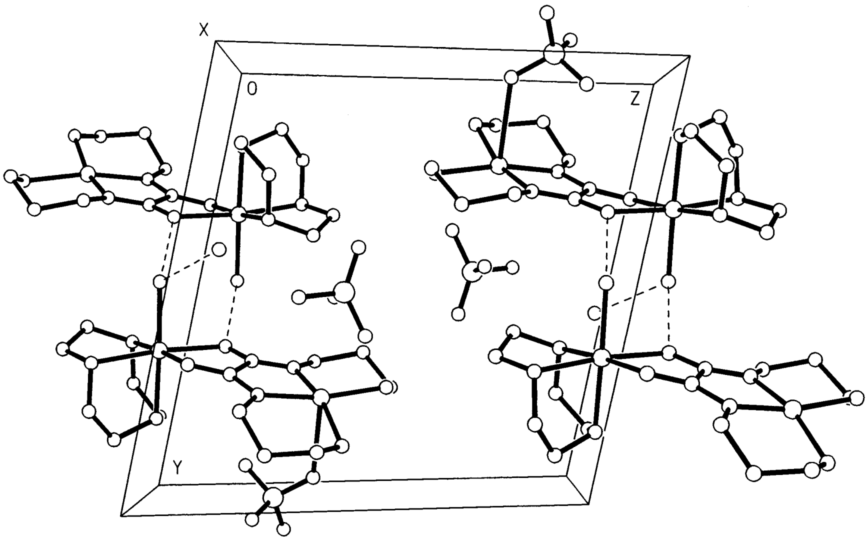

Figure 2. Unit cell for complex **1**.

where χ_M denotes the susceptibility per binuclear complex and $g_{1/2}$ and $g_{3/2}$ are g factors associated with the doublet and quartet states, respectively. They are related to the local g factors g_{Cu} and g_{Ni}, assumed to be isotropic through $g_{1/2} = (4g_{Ni} - g_{Cu})/3$, $g_{3/2} = (2g_{Ni} + g_{Cu})/3$. The remaining symbols have their usual meanings. As shown in Figure 3, good fits to the experimental data were attained with $J = -92.7\ \text{cm}^{-1}$, $g_{Ni} = 2.10$ and $g_{Cu} = 2.01$. The agreement factor R defined here as $R = \Sigma[(\chi_M)_{calcd} - (\chi_M)_{obsd}]^2/(\chi_M)_{obsd}{}^2$ was then equal to 2.2×10^{-4}.

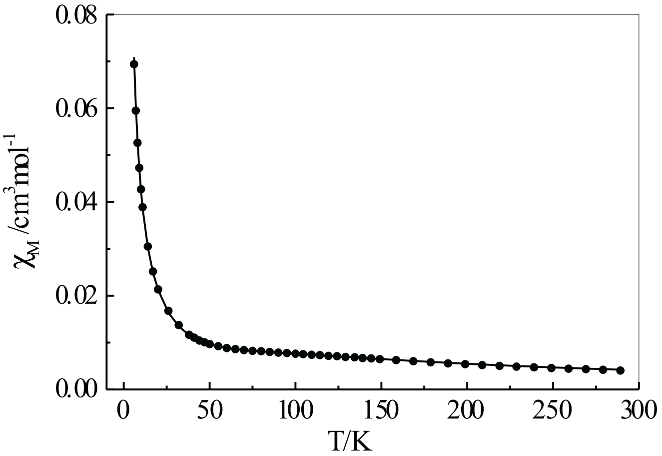

Figure 3. Temperature dependence of magnetic susceptibility (•) for complex **1**. The solid line results from a fit of the data to the theoretical equation given in the text.

It is known that in a binuclear complex the coplanarity between mononuclear fragments thus the magnitude of magnetic interaction between two metals may be modified by applying different terminal ligands. Starting from Cu(oxpn), a number of Cu(II)–Ni(II) binuclear complexes have been prepared [3–7,12,13]. The terminal ligands involved were monodentate small molecules, bidentate chelating agents or relatively flexible macrocyclic groups. While the exchange constant for the complex $[\mathrm{Ni(cth)Cu(oxpn)}](\mathrm{ClO_4})_2$ (cth = *d*,*l*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) [13] was equal to $-96.3\ \mathrm{cm^{-1}}$, for most cases the exchange constants were around $-110\ \mathrm{cm^{-1}}$ (-103 – $-113\ \mathrm{cm^{-1}}$). Since neither Cu(II), Ni(II) polyhedron in **1** bears significant deformation in comparison to those in other Cu(II)–Ni(II) complexes with the oxpn bridge, the slightly weaker magnetic interaction for **1** should be attributed to the fact that its $\mathrm{Cu(N_2C_2O_2)Ni}$ bridging network is considerably distorted from planar owing to the rigidity of tacn ligand, which diminishes the overlap between the magnetic orbitals.

Supplementary material. Crystallographic data for complex 1 have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 190146. Copies of this information are available from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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