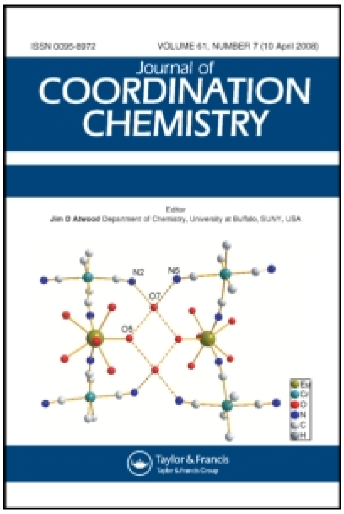

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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Hui Liu[a]; Jin-Lei Tian[a]; Wen Gu[a]; Ying-Ying Kou[a]; Li Feng[ab]; Xiao-Fang Ma[a]; Dong-Dong Li[a]; Shi-Ping Yan[a]; Dai-Zheng Liao[a]
[a] Department of Chemistry, Nankai University, Tianjin 300071, P. R. China [b] Tianjin University of Traditional Chinese Medicine, Tianjin 300193, P. R. China

To cite this Article Liu, Hui , Tian, Jin-Lei , Gu, Wen , Kou, Ying-Ying , Feng, Li , Ma, Xiao-Fang , Li, Dong-Dong , Yan, Shi-Ping and Liao, Dai-Zheng(2008) 'Synthesis, crystal structure and magnetic properties of an oxamato-bridged heterobinuclear $Ni^{II}Cu^{II}$ complex $[Ni(cyclam)Cu(opba)]_2\cdot 3DMSO$', Journal of Coordination Chemistry, 61: 11, 1804 — 1810

To link to this Article: DOI: 10.1080/00958970701624294

URL: http://dx.doi.org/10.1080/00958970701624294

Journal of Coordination Chemistry
Vol. 61, No. 11, 10 June 2008, 1804–1810

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Synthesis, crystal structure and magnetic properties of an oxamato-bridged heterobinuclear $Ni^{II}Cu^{II}$ complex $[Ni(cyclam)Cu(opba)]_2 \cdot 3DMSO$

HUI LIU†, JIN-LEI TIAN†, WEN GU†, YING-YING KOU†, LI FENG†‡,
XIAO-FANG MA†, DONG-DONG LI†, SHI-PING YAN*† and
DAI-ZHENG LIAO†

†Department of Chemistry, Nankai University, Tianjin 300071, P. R. China
‡Tianjin University of Traditional Chinese Medicine, Tianjin 300193, P. R. China

(*Received 1 June 2007; in final form 9 July 2007*)

An oxamato-bridged heterobinuclear $Ni^{II}Cu^{II}$ complex $[Ni(cyclam)Cu(opba)]_2 \cdot 3DMSO$ (**1**) has been synthesized, characterized by elemental analysis, infrared spectra and magnetic susceptibility, where cyclam is 1, 4, 8, 11-tetraazacyclotetradecane and opba is o-phenylenebis(oxamato). The complex crystallizes in the triclinic system, space group $P\bar{1}$ with $a = 12.006(\mathbf{3})$ Å, $b = 12.783(\mathbf{3})$ Å, $c = 20.977(\mathbf{5})$ Å, $\alpha = 76.634(\mathbf{4})^\circ$, $\beta = 75.172(\mathbf{4})^\circ$, $\gamma = 80.818(\mathbf{4})^\circ$ and $Z = 2$. According to X-ray crystallographic studies, the four-coordinate copper(II) atom is a slightly distorted planar geometry and is linked to nickel(II) through the *exo-cis* oxygen atoms of $[Cu(opba)]^{2-}$; the six-coordinate nickel(II) center lies in a highly distorted octahedral environment. Magnetic susceptibility measurements of the complex in the temperature range 2–300 K indicate that the heterobinuclear $Ni^{II}Cu^{II}$ units are coupled antiferromagnetically with $J = -57.38\,\mathrm{cm}^{-1}$, $g_{Ni} = 2.25$ and $g_{Cu} = 2.02$.

Keywords: Macrocyclic complex; Heterobinuclear; Crystal structure; Magnetism

1. Introduction

The design of polynuclear complexes through extended bridges is of current interest in coordination chemistry owing to spin-exchange and charge transfer between metals [1–5]. To design and synthesize polynuclear species, one of the best strategies is the 'complex as ligand' approach, using mononuclear complexes that contain potential donor groups for another metal ion as ligand [6–16]. The *N,N′*-substituted bis(oxamato)copper(II) complexes are good examples of 'complex ligands', particularly suitable for designing heteronuclear complexes [6–16]. We tried to synthesize an oxamato-bridged heterometallic complex from reaction of $[Ni(cyclam)(ClO_4)_2]$ and $Na_2[Cu(opba)] \cdot 3H_2O$ (cyclam = 1, 4, 8, 11-tetraazacyclo tetradecane, opba = o-phenylenebis(oxamato). As a result, a heterobinuclear $Ni^{II}Cu^{II}$ complex $[Ni(cyclam)Cu(opba)]_2 \cdot 3DMSO$ (**1**) was obtained, in which

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*Corresponding author. Email: yansp@nankai.edu.cn

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2008 Taylor & Francis
DOI: 10.1080/00958970701624294

$[Cu(opba)]^{2-}$ acts as a bridging bis-bidentate ligand and the macrocycle adopts a folded conformation.

2. Experimental

All the starting reagents were of analytical grade and used without further purification. IR spectra on KBr pellets were recorded on a Bruker Tensor 27 spectrophotometer in 4000–400 cm^{-1} regions. Elemental analyses (C, H, N) were performed on a Perkin-Elmer 240 analyzer. Variable-temperature magnetic susceptibility measurements were performed on a MPMS XL-7 SQUID over the temperature range 2–300 K with an applied field of 2000 Oe. Diamagnetic correction was made with *Pascal's* constant for all the constituent atoms.

2.1. *$[Ni(cyclam)Cu(opba)]_2 \cdot 3DMSO$ (1)*

The mononuclear precursors, $Na_2[Cu(opba)] \cdot 3H_2O$ [12] and $[Ni(cyclam)(ClO_4)_2]$ [17] were prepared as described elsewhere. Complex **1** was prepared by dropwise adding $[Ni(cyclam)(ClO_4)_2]$ (0.2 mmol) dissolved in 10 mL methanol solution to a continuously stirred aqueous solution (10 mL) of $Na_2[Cu(opba)] \cdot 3H_2O$ (0.2 mmol); the mixture was stirred at reflux for 2 h. Then the solution was cooled to room temperature and a blue microcrystalline powder formed which was filtered off, washed with methanol, and dried in air. Recrystallization from DMSO gave X-ray quality crystals. Anal. Calcd for (%) $C_{46}H_{74}Cu_2N_{12}Ni_2O_{15}S_3$: C, 40.16; H, 5.42; N, 12.22. Found: C, 40.08; H, 5.45; N, 12.12. IR (KBr, cm^{-1}): 3422 m, 3245 m, 2958 m, 2924 m, 2859 m, 1675s,1628vs, 1573s, 1470s,1401w, 1354s, 1279s, 1200w, 1180w, 976, 865 m, 779 m, 764 m.

2.2. *Structure determination*

Determination of the unit cell and data collection was performed on a **BRUKER SMART** 1000 diffractometer using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 293(2) K with crystal size $0.20 \times 0.12 \times 0.10$ mm. A total of 4194 [$R_{int} = 0.0336$] independent reflections were collected by the ω-2θ scan technique in the range $1.02 \leq \theta \leq 25.01^\circ$ with index ranges $-12 \leq h \leq 14$, $-12 \leq k \leq 15$, $-24 \leq l \leq 23$. Semiempirical absorption corrections were applied using the **SADABS** program. The structure was solved by direct methods and successive Fourier difference syntheses (SHELX-97) and refined by full-matrix least-squares procedure on F^2 with anisotropic thermal parameters for all non-hydrogen atoms (SHELXL-97). [18] The final agreement factor values are $R_1 = 0.0779$, $wR_2 = 0.2212$ ($I > 2\sigma$), $R_1 = \Sigma(||F_0| - |F_c||)/\Sigma|F_0|$, $wR_2 = (\Sigma(|F_0|^2 - |F_c|^2)^2/\Sigma wF_0|^2)^2$. The weight, $w = 1/[\sigma^2(F_0^2) + (0.0461P)^2 + 1.24P]$, where $P = (F_0^2 + 2F_c^2)/3$. Further details of the structure analysis are given in table 1. Selected bond lengths and angles are presented in tables 2 and 3.

Table 1. Data collection and processing parameters for **1**.

Empirical formula	$C_{46}H_{74}Cu_2N_{12}Ni_2O_{15}S_3$
Formula weight	1375.85
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
space group	$P\bar{1}$
Unit cell dimensions (Å, °)	
a	12.006(3)
b	12.783(3)
c	20.977(5)
α	76.634(4)
β	75.172(4)
γ	80.818(4)
Volume ($Å^3$)	3010.5(13)
Z, Calcd density ($g\,cm^{-3}$)	2, 1.518
Absorption coefficient (mm^{-1})	1.488
$F(000)$	1432
θ Range for data collection (°)	1.02–25.01
Limiting indices	$-12 \le h \le 14$, $-12 \le k \le 15$, $-24 \le l \le 23$
Reflections collected/unique	14962/10413 [$R_{(int)} = 0.0336$]
Completeness to $\theta = 25.01$	98.0%
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	10413/42/749
Goodness-of-fit on F^2	1.055
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0779$, $wR_2 = 0.2212$
R indices (all data)	$R_1 = 0.1165$, $wR_2 = 0.2535$
Largest diff. peak and hole ($e\,Å^{-3}$)	1.689 and −0.698

Table 2. Selected bond lengths (Å) for **1**.

Cu(1)–N(6)	1.893(6)	Cu(2)–N(12)	1.896(7)
Cu(1)–N(5)	1.910(7)	Cu(2)–N(11)	1.906(7)
Cu(1)–O(10)	1.938(6)	Cu(2)–O(12)	1.930(6)
Cu(1)–O(9)	1.979(6)	Cu(2)–O(11)	1.974(6)
Ni(1)–N(4)	2.092(7)	Ni(2)–N(9)	2.076(8)
Ni(1)–N(3)	2.095(7)	Ni(2)–N(7)	2.086(8)
Ni(1)–N(2)	2.097(8)	Ni(2)–N(10)	2.088(7)
Ni(1)–N(1)	2.099(8)	Ni(2)–N(8)	2.099(8)
Ni(1)–O(2)	2.104(6)	Ni(2)–O(6)	2.111(6)
Ni(1)–O(1)	2.125(6)	Ni(2)–O(5)	2.133(6)
O(1)–C(11)	1.247(10)	O(5)–C(31)	1.235(10)
O(2)–C(12)	1.252(10)	O(6)–C(32)	1.260(10)
O(3)–C(19)	1.237(10)	O(7)–C(39)	1.239(10)
O(4)–C(20)	1.201(12)	O(8)–C(40)	1.207(11)
O(9)–C(11)	1.260(11)	O(11)–C(31)	1.274(10)
O(10)–C(20)	1.310(11)	O(12)–C(40)	1.288(11)

3. Results and discussion

3.1. *Crystal structure*

The structure consists of two heterobinuclear neutral [Ni(cyclam)Cu(opba)] units and three DMSO molecules. A perspective view of the neutral [Ni(cyclam)Cu(opba)] units with atom-numbering scheme is depicted in figure 1. Two neutral [Ni(cyclam)Cu(opba)]

Table 3. Selected bond angles (°) for **1**.

N(6)–Cu(1)–N(5)	83.5(3)	N(12)–Cu(2)–N(11)	83.8(3)
N(6)–Cu(1)–O(10)	85.8(3)	N(12)–Cu(2)–O(12)	85.6(3)
N(5)–Cu(1)–O(10)	169.3(3)	N(11)–Cu(2)–O(12)	169.3(3)
N(6)–Cu(1)–O(9)	167.5(3)	N(12)–Cu(2)–O(11)	167.8(3)
N(5)–Cu(1)–O(9)	84.7(3)	N(11)–Cu(2)–O(11)	85.0(3)
O(10)–Cu(1)–O(9)	105.9(2)	O(12)–Cu(2)–O(11)	105.4(3)
N(4)–Ni(1)–N(3)	91.7(3)	N(9)–Ni(2)–N(10)	91.8(3)
N(4)–Ni(1)–N(2)	101.3(3)	N(10)–Ni(2)–N(8)	101.7(3)
N(3)–Ni(1)–N(2)	83.7(3)	N(9)–Ni(2)–N(8)	83.8(3)
N(4)–Ni(1)–N(1)	84.9(3)	N(7)–Ni(2)–N(10)	84.3(3)
N(3)–Ni(1)–N(1)	173.2(3)	N(9)–Ni(2)–N(7)	173.1(3)
N(2)–Ni(1)–N(1)	91.2(3)	N(7)–Ni(2)–N(8)	91.4(3)
N(4)–Ni(1)–O(2)	166.1(3)	N(10)–Ni(2)–O(6)	166.9(3)
N(3)–Ni(1)–O(2)	94.0(3)	N(9)–Ni(2)–O(6)	92.3(3)
N(2)–Ni(1)–O(2)	92.0(3)	N(8)–Ni(2)–O(6)	91.1(3)
N(1)–Ni(1)–O(2)	90.6(3)	N(7)–Ni(2)–O(6)	92.8(3)
N(4)–Ni(1)–O(1)	87.6(3)	N(10)–Ni(2)–O(5)	87.8(3)
N(3)–Ni(1)–O(1)	93.5(3)	N(9)–Ni(2)–O(5)	93.5(3)
N(2)–Ni(1)–O(1)	170.7(3)	N(8)–Ni(2)–O(5)	170.2(3)
N(1)–Ni(1)–O(1)	92.3(3)	N(7)–Ni(2)–O(5)	92.1(3)
O(2)–Ni(1)–O(1)	79.4(2)	O(6)–Ni(2)–O(5)	79.6(2)

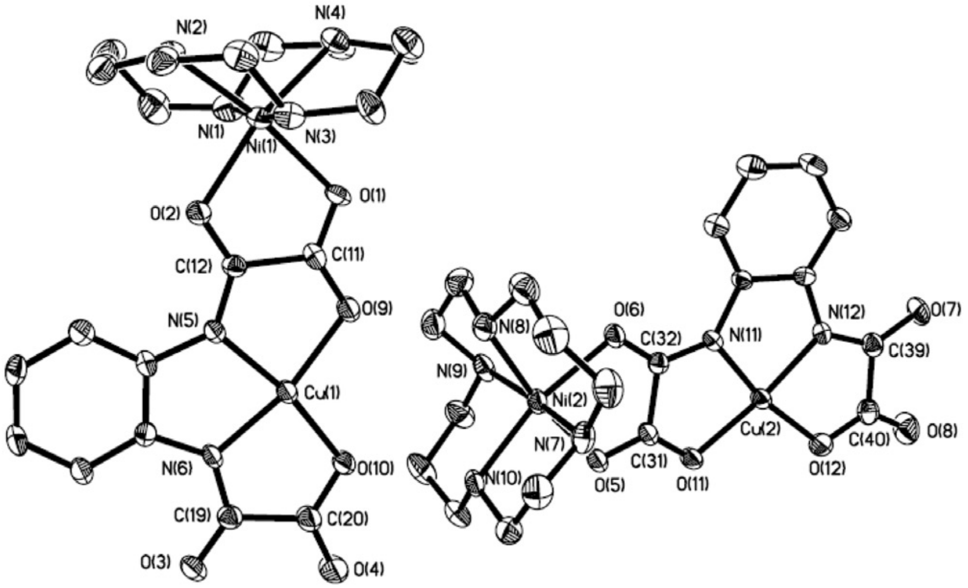

Figure 1. ORTEP view of the binuclear $Ni^{II}Cu^{II}$ units. The thermal ellipsoids are drawn at the 30% probability level.

units (unit A and B) are crystallographically independent but chemically similar. According to tables 2 and 3, the corresponding bond distances and angles of the two units are similar, so we only use unit A for describing the structure.

In the hererbinuclear unit A, the copper (Cu1) is connected to the nickel (Ni1) through the *exo*-*cis* oxygen atoms of $[Cu(opba)]^{2-}$. The Cu1 is four coordinate with two O and two N atoms supplied from the oxamato groups in slightly distorted square-planar coordination geometry. The deviations of the donor atoms N5, N6, O9, O10 from the N2O2 mean plane are 0.0190, −0.0351, −0.0313, 0.0122 Å, respectively, and the copper atom is 0.0351 Å out of the plane. The Cu–N distances are 1.893(6) and 1.910(7) Å, while the Cu–O distances are 1.938(6) and 1.979(6) Å. The C11–O1 and Cu1–O9 distances, 1.247(10) and 1.979(6), are significantly longer than C20–O4 and Cu1–O10, 1.201(13) and 1.938(6), respectively, while the C11–O9 distance (1.260(11)) is appreciably shorter than C20–O10 (1.310(11)). These differences are consistent with the bridging and nonbridging coordination modes of the two CO_2^- carboxylato groups.

The geometry at the nickel (II) centers (Ni1) is distorted octahedral, with ligation provided by the four nitrogen atoms of the cyclam ligand and two oxygen atoms of the bridging oxamido group. The axial coordination sites are occupied by N1 and N3 from cyclam, while the equatorial plane is formed by N1, N4 supplied by cyclam and O1, O2 supplied by oxamido (maximum deviation from the least-squares plane is 0.0693 Å). The nickel is shifted by 0.0135 Å from the equatorial plane. The Ni–O distances are 2.099(8)–2.104(6) Å, while the Ni–N distance is 2.092(7)–2.099(8) Å. These values are very close to those reported for oxamido-bridged polynuclear nickel (II) complexes [15]. The dihedral angle between the equatorial NiN2O2 and CuN2O2 mean planes is 11°. The distance of Cu1 and Ni1 through the oxamato bridge is 5.340(2) Å and displaced toward the same side of the bridge plane by 0.0356 and 0.1552 Å.

3.2. *Magnetic properties*

Variable-temperature magnetic susceptibility measurements were performed on a powder sample in the temperature range 2–300 K under 2000 Oe. The effective magnetic moment (μ_{eff}) and the molar magnetic susceptibilities (χ_{M}) *versus* T are plotted in figure 2.

At room temperature, μ_{eff} is equal to 3.2 μ_{B}, continuously decreased upon cooling, finally reached a plateau below ca. 50 K with μ_{eff} between 2.02 and 2.04 μ_{B}. This behavior is typical of Cu(II)–Ni(II) pairs with antiferromagnetic intramolecular interaction [8, 9]. The plateau indicates that only the doublet ground state is thermally populated at low temperature.

On the basis of the isotropic spin Hamiltonian $\hat{H} = -J \hat{S}_{Cu} \cdot \hat{S}_{Ni}$, the expression of the magnetic susceptibility for a CuNi pair is

$$\chi_M = \frac{N\beta^2}{4kT}\left[\frac{g_{1/2}^2 + 10g_{3/2}^2 \exp(3J/2kT)}{1 + 2\exp(3J/2kT)}\right]$$

where the g_s ($S = 1/2$, $3/2$) factors are related to local g factors by $g_{1/2} = (4g_{\mathrm{Ni}} - g_{\mathrm{Cu}})/3$, and $g_{3/2} = (2g_{\mathrm{Ni}} + g_{\mathrm{Cu}})/3$, and the other symbols have their usual meanings. The parameters obtained by the simulation of the experimental data using the above expression are $J = -57.38\,\mathrm{cm}^{-1}$, $g_{\mathrm{Cu}} = 2.02$, $g_{\mathrm{Ni}} = 2.25$, $R = \sum(\chi_{\mathrm{obsd}} - \chi_{\mathrm{cacld}})^2 / \sum \chi_{\mathrm{obsd}}^2 = 4.26 \times 10^{-4}$.

The above J values suggests an antiferromagnetic exchange between Cu(II) and Ni(II) ions. The antiferromagnetic interaction between Cu(II) and Ni(II) ions is due to the non-zero overlap between the $d_{x^2-y^2}$ magnetic orbitals around the two ions and

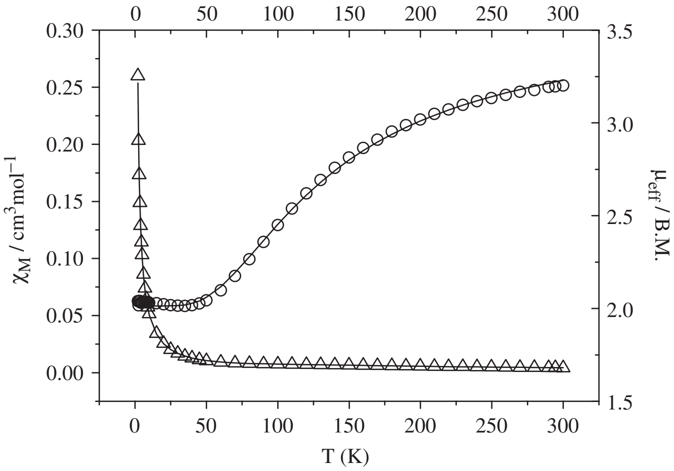

Figure 2. χ_M (Δ) *vs*. T and μ_{eff} ($\circ$) *vs*. T plots for **1**.

delocalized towards ligand. A main factor influencing the magnitude of the interaction is the overlap between the molecular orbitals of the bridging groups and the singly-occupied d metal orbitals. The magnetic interaction is somewhat different from similar complexes, [15] maybe resulting from the structural distortions.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centra, CCDC reference number is 609329. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223-336-033; or email: deposit@ccdc.cam.ac.uk.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (No. 20331020).

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