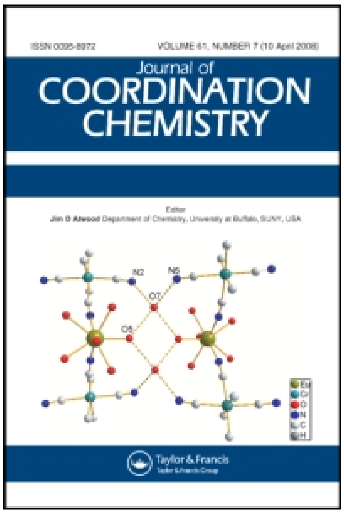

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A heterobinuclear Cu(II)-Ni(II) complex of a macrocyclic oxamide: synthesis, crystal structure, spectroscopic and magnetic properties

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A heterobinuclear Cu(II)–Ni(II) complex of a macrocyclic oxamide: synthesis, crystal structure, spectroscopic and magnetic properties

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A novel oxamido-bridged heterobinuclear copper(II)–nickel(II) complex $[(CuL)Ni(tmd)_2](ClO_4)_2$ (L = the dianion of 2,3-diono-5,6,14,15-dibenzo-7,13-bis(ethoxycarbonyl)-1,4,8,12-tetraazacyclotetradecane-7,12-diene, tmd = 1,3-diaminopropane) has been synthesized and characterized structurally and magnetically. Single-crystal X-ray analysis reveals that the four-coordinate copper(II) center displays slightly distorted planar geometry and is linked to nickel(II) through the *exo-cis* oxygen atoms of the oxamido macrocyclic ligand; the six-coordinate nickel(II) center assumes a distorted octahedral environment. Spectroscopic and magnetic properties are discussed.

Keywords: Oxamido-bridge; Copper(II); Nickel(II) complex; Crystal structure; Magnetic properties; Spectroscopic properties

1. Introduction

Study of the spin exchange interaction between metal centers through extended bridges has been an active subject in the field of coordination chemistry. Binuclear metal complexes with extended bridged structures are of great interest because of spin-exchange and charge transfer between metal ions and in metalloenzymes and homogeneous catalysis [1]. Molecules that contain two kinds of metal ions play an important part in molecular magnetism [2–5]. A large diversity of situations can be encountered concerning the interaction between two different spin carriers within a molecular unit. With several kinds of magnetic centers it is possible to design lattices showing unusual spin topologies. Compared with the rich variety of polymetallic systems of noncyclic oxamides, those containing macrocyclic oxamides are more limited.

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The use of mononuclear complexes that contain potential donor groups for another metal ion is one of the best strategies when designing and synthesizing heteronuclear species [6, 7]. Copper(II) complexes of ligands derived from oxalates are known to act as paramagnetic ligands towards other metal ions [1, 8]. In continuation of our interest in polynuclear complexes, we report the synthesis, structure, spectroscopic and magnetic properties of a new oxamido-bridged heterobinuclear copper(II)–nickel(II) macrocyclic complex, $[(CuL)Ni(tmd)_2](ClO_4)_2$ (L = the dianion of 2,3-diono-5,6,14,15-dibenzo-7,13-bis(ethoxycarbonyl)-1,4,8,12-tetraazacyclotetradecane-7,12-diene, tmd = 1,3-diamino-propane).

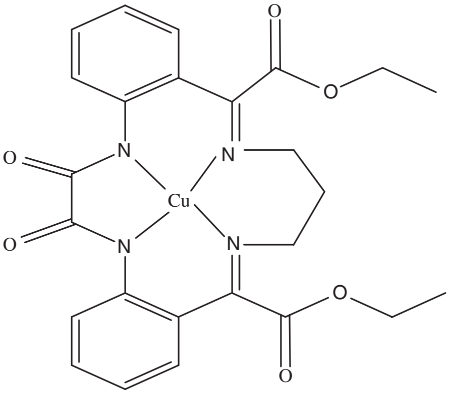
2. Experimental

All reagents used in the syntheses were of analytical grade, purchased from the Aldrich Company, and used without further purification. **Caution! Perchlorate salts of metal complexes are potentially explosive. Only a small amount of material should be prepared, and this should be handled with care.**

IR spectra were obtained using a Shimadzu IR-408 spectrophotometer in the 4000–600 cm^{-1} region. Elemental analyses (C, H, N) were performed on a Perkin-Elmer 240C instrument. Electronic spectra were measured on a Shimadzu UV-2101 PC spectrophotometer and X-band ESR spectra on a Bruker ER 200D-SRC ESR spectrometer. Variable-temperature magnetic susceptibilities were measured using a LDJ 9600 vibrating sample magnetometer with a field of 5000 G. Diamagnetic corrections were made with Pascal's constants for all constituent atoms.

2.1. *$[(CuL)Ni(tmd)_2](ClO_4)_2$*

The copper (II) precursor, [CuL] (scheme 1), was synthesized as described previously [9]. $[(CuL)Ni(tmd)_2](ClO_4)_2$ was synthesized by addition of 10 cm^3 of an ethanol solution of $Ni(ClO_4)_2 \cdot 6H_2O$ (0.368 g, 1 mmol) to 15 cm^3 of an ethanol solution of CuL (0.54 g, 1 mmol). The mixture was stirred and refluxed for 4 h, and then



Scheme 1. A heterobinuclear Cu(II)-Ni(II) complex of a macrocyclic oxamide: synthesis, crystal structure, spectroscopic and magnetic properties.

Table 1. Summary of crystallographic data for the complex.

Empirical formula	$C_{31}H_{44}N_8O_{14}Cl_2CuNi$
Formula weight	945.89
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, *Pbcn*
Unit cell dimensions	$a = 13.951(5)$ Å $b = 15.059(6)$ Å $c = 18.218(7)$ Å
Volume	3827(3) $Å^3$
Z	4
Absorption coefficient	1.265 mm^{-1}
$F(000)$	1956
Crystal size	0.22 × 0.20 × 0.16 mm
θ range for data collection	1.99 to 26.43°
Limiting indices	$-17 \leq h \leq 17$, $-14 \leq k \leq 18$, $-19 \leq l \leq 22$
Reflections collected/unique	20 943/3941 [R(int) = 0.0422]
Completeness to $\theta = 26.43$	99.7%
Absorption correction	Semiempirical from equivalents
Max. and min. transmission	1.000 and 0.848
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3941/118/303
Goodness-of-fit on F^2	1.047
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0489$, $wR2 = 0.1252$
R indices (all data)	$R1 = 0.0805$, $wR2 = 0.1452$
Largest diff. peak and hole	0.654 and −0.648 e A^{-3}

1,3-diaminopropane (0.18 g, 2.5 mmol) was added. The resulting mixture was stirred for 2 h, then cooled and filtered. Dark green crystals suitable for X-ray determination were obtained by slow evaporation of the filtrate during 1 month (yield: 48%). Anal. Calcd for $C_{31}H_{44}N_8O_{14}Cl_2CuNi$(%): C, 39.33; H, 4.69; N, 11.84. Found: C, 39.62, H, 4.70, N, 11.93.

2.2. *Structure determination*

X-ray diffraction data were collected at 293 K on a Bruker Smart 1000 diffractometer equipped with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). A summary of crystallographic data is given in table 1. The structure was solved by direct methods using the SHELXS-97 program [10]. H atoms were assigned common isotropic displacement factors and included in the final refinement by use of geometrical restraints. A full-matrix least-squares refinement on F^2 was carried out using the SHELXL-97 package [11]. Selected bond lengths and angles are given in table 2.

3. Results and discussion

3.1. *Crystal structure*

The complex consists of asymmetric, heterodinuclear complex $[(CuL)Ni(tmd)_2]^{2+}$ cations and perchlorate anions. A perspective view of the dinuclear cation is depicted in figure 1. In the binuclear unit, the copper atom (Cu1) of CuL is connected to the nickel atom (Ni1) through the *exo-cis* oxygen atoms of the oxamido group. Cu1–N1 and Cu1–N2 are 1.926(4) and 1.953(4) Å, respectively. Deviations of the four donor

Table 2. Bond lengths [Å] and angles [°] for the complex.

Ni(1)–N(4)	2.084(4)
Ni(1)–N(3)	2.102(4)
Ni(1)–O(1)	2.109(3)
Cu(1)–N(1)	1.926(4)
Cu(1)–N(2)	1.953(4)
O(1)–C(1)	1.241(5)
O(2)–C(11)	1.188(6)
O(3)–C(11)	1.296(6)
O(3)–C(12′)	1.449(11)
O(3)–C(12)	1.460(7)
N(1)–C(1)	1.319(5)
N(1)–C(2)	1.413(5)
N(3)–C(14)	1.467(6)
N(4)–C(16)	1.487(6)
N(4)–Ni(1)–N(4A)	95.4(2)
N(4)–Ni(1)–N(3)	88.07(16)
N(4A) –Ni(1)–N(3)	93.26(16)
N(3)–Ni(1)–N(3A)	178.0(2)
N(4)–Ni(1)–O(1)	170.77(13)
N(4A) –Ni(1)–O(1)	93.65(14)
N(3)–Ni(1)–O(1)	89.50(13)
N(3A)–Ni(1)–O(1)	88.95(14)
O(1)–Ni(1)–O(1A)	77.40(16)
N(1)–Cu(1)–N(1A)	87.1(2)
N(1)–Cu(1)–N(2)	93.71(15)
N(1)–Cu(1)–N(2A)	160.01(15)
N(2)–Cu(1)–N(2A)	92.3(2)

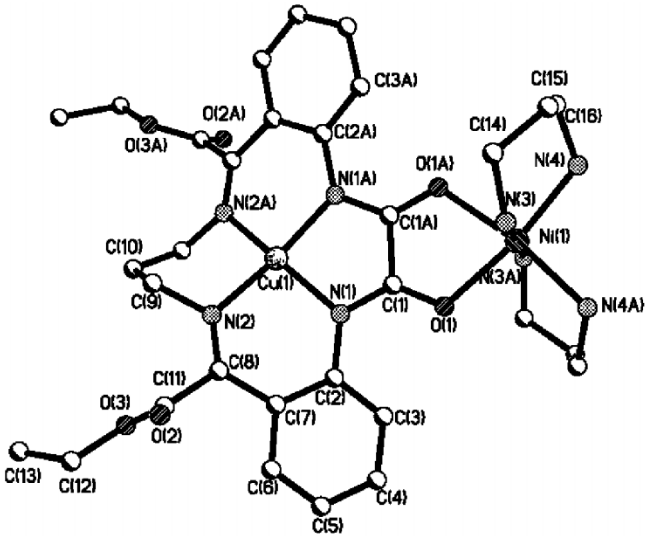


Figure 1. An ORTEP drawing of the complex with 30% probability thermal ellipsoids showing the atom labeling scheme. Hydrogen atoms are omitted for clarity.

atoms N1, N1A, N2 and N2A from their mean plane are −0.3445, +0.3445, 0.3220, −0.3220 Å, respectively.

The Ni(1) atom assumes an asymmetrical distorted octahedral environment (as shown in figure 1), with two carbonyl O atoms (O1 and O1A) of the macrocyclic oxamido ligand and two N atoms (N4 and N4A) from two tmd ligands in equatorial positions, and the other two N atoms (N3 and N3A) of two tmd ligands in axial positions. Distances between Ni and O (O1 and O1A) are 2.109(3) Å, while Ni1–N4 and Ni1–N3 distances are 2.084(4) and 2.102(4) Å, respectively. The Cu–Ni distance through the oxamido bridge is 5.350 Å and the dihedral angle between the equatorial NiN_2O_2 and the CuN_4 mean planes is 14.95(3)°. The shortest metal-to-metal separation between dinuclear entities is 7.308 Å (Cu1···Ni1A). The average C–O and C–N bond lengths in the oxamido group of the complex are 1.241 and 1.314 Å, respectively, while the corresponding distances for the mononuclear [CuL] precursor are 1.211 and 1.355 Å, respectively [12]. The observed increase in C–O and decrease in C–N distances in the binuclear complex reflect delocalization of electron density from the N atoms towards the O atoms upon coordination of the latter to Ni. In the lattice the noncoordinated perchlorate ions lie between the dinuclear entities.

3.2. *Infrared spectra*

There are distinct differences between IR spectra of [CuL] and $[(CuL)Ni(tmd)_2](ClO_4)_2$. Bands at ca 1730 and 1600 cm^{-1} show no significant shift relative to corresponding bands of the mononuclear precursor [CuL] and are attributed to ν(C=O) (ester) and ν(C=N), respectively [13]. The strong ν(C=O) (oxamido) band at 1670 cm^{-1} in the spectrum of the mononuclear precursor is replaced by a strong and sharp band at 1620 cm^{-1} in the spectrum of the heteronuclear complex. The very sharp, medium-intensity band at 3225–3250 m^{-1} and the broad strong band at approximately 1080 cm^{-1} are characteristic absorptions of the NH group in tmd and the perchlorate ion [14], respectively.

3.3. *Electronic spectra*

Electronic spectra of the binuclear complex were measured in acetonitrile solution. Spectra below 500 nm are dominated by intense bands due to intraligand and charge-transfer transitions in the Cu(II) chromophore [12]. In the 500–1000 nm region, the complex exhibits two broad bands. A weak near-IR absorption ($\varepsilon = 47\,\mathrm{M^{-1}\,cm^{-1}}$) centered at 935 nm is assignable to the $^3A_{2g} \rightarrow {}^3T_{2g}$ (Ni) transition, assuming O_h site symmetry for Ni((II) [15]. A more intense band centered at 635 nm ($\varepsilon = 247\,\mathrm{M^{-1}\,cm^{-1}}$) can be attributed to the envelope of two spin-allowed transitions, $^2B_{1g} \rightarrow {}^2E_g$ (Cu) in an environment that is nearly square planar and $^3A_{2g} \rightarrow {}^3T_{1g}$ (Ni) [16].

3.4. *ESR spectra*

Polycrystalline X-band ESR spectra were measured at room temperature. The complex exhibits a broad intense band centered at $g \approx 2.18$. The antiferromagnetic interaction in Cu(II)–Ni(II) pairs gives rise to an $S = 1/2$ ground state and $S = 3/2$ excited state. The allowed $|1/2, -1/2\rangle \rightarrow |1/2, 1/2\rangle$ transition in the doublet state will exhibit a resonance at a field corresponding approximately to $g = 2$.

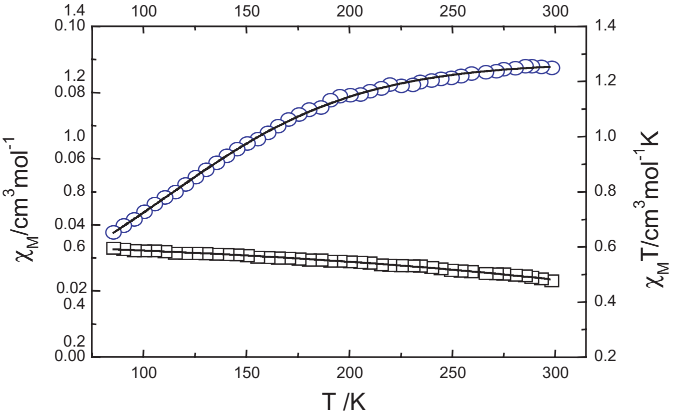


Figure 2. Plots of χ_M (○) and $\chi_M T$ (□) *vs* T for [(CuL)Ni(tmd)$_2$](ClO$_4$)$_2$. The solid line is the line of best fit.

3.5. *Magnetic properties*

Magnetic susceptibilities were measured in the range 77–300 K. Plots of $\chi_M T$ and χ_M *versus* T for the complex are shown in figure 2. The $\chi_M T$ value per molecule is equal to 1.24 cm^3 mol^{-1} K at room temperature; the value is lower than the spin-only value (1.38 cm^3 mol^{-1} K) expected for the uncoupled Cu(II)–Ni(II) unit. Upon cooling, $\chi_M T$ decreases steadily to 0.64 cm^3 mol^{-1} K at 77 K, indicating the existence of an antiferromagnetic spin exchange interaction between Cu1 and the Ni1. According to the crystal structure and magnetic behavior of the complex, the magnetic susceptibility data were analyzed by the isotropic spin Hamiltonian $\hat{H} = -2J\hat{S}_{\mathrm{Cu}}\hat{S}_{\mathrm{Ni}}$, where J is the interaction parameter between two paramagnetic centers. The magnetic susceptibility of the complex can be expressed as

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

where 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 $g_{3/2} = (2g_{\mathrm{Ni}} + g_{\mathrm{Cu}})/3$, $N\alpha$ is the temperature-independent paramagnetism (200×10^{-6} cm^3 mol^{-1}), and the other symbols have their usual meanings. The best fit parameters are $g_{\mathrm{Ni}} = 2.21$, $g_{\mathrm{Cu}} = 2.10$, $J = -64.78$ cm^{-1} with $R = 3.8 \times 10^{-4}$, where R is defined as follows:

$$R = \sum[(\chi_M)_{\mathrm{obs}} - (\chi_M)_{\mathrm{calc}}]^2 \Big/ \sum(\chi_M)_{\mathrm{obs}}^2$$

The antiferromagnetic interaction between copper(II) and nickel(II) in this complex is consistent with those reported for related systems. Table 3 summarizes magnetic coupling constant data for similar complexes. The antiferromagnetic interaction arises from the nonzero overlap between the $d_{x^2-y^2}$ magnetic orbitals centered on the two metal ions and delocalized towards the ligand. Differences in magnetic exchange may be explained on the basis of structural distortions.

Table 3. Magnetic coupling constants (J) for oxamido-bridged heterobinuclear copper(II)–nickel(II) macrocyclic complexes.

Complex	J ($\mathrm{cm^{-1}}$)	g_{Cu}	g_{Ni}	R	Reference
$[\mathrm{Cu(L^a)Ni(en)_2](ClO_4)_2 \cdot 0.5C_2H_5OH \cdot H_2O}$	−52.8	2.00	2.20	2.1×10^{-4}	[15]
$[\mathrm{Cu(L^a)Ni(tmd)_2](ClO_4)_2 \cdot 4H_2O}$	−45.7	2.01	2.20	8.9×10^{-4}	[15]
$[\mathrm{Cu(L^a)Ni(}\mathit{rac}\mathrm{\text{-}cth)_2](ClO_4)_2 \cdot CH_3OH}$	−56.9	2.01	2.16	1.3×10^{-4}	[15]
$[\mathrm{Cu(L^1)Ni(}\mathit{rac}\mathrm{\text{-}cth)_2](ClO_4)_2 \cdot H_2O}$	−63.9	2.11	2.23	2.72×10^{-4}	[12]
$[\mathrm{Cu(L^2)Ni(}\mathit{rac}\mathrm{\text{-}cth)_2](ClO_4)_2 \cdot 0.5C_2H_5OH}$	−67.4	2.10	2.19	2.6×10^{-4}	[12]
$[\mathrm{Cu(L^1)Ni(tmd)_2](ClO_4)_2}$	−64.78	2.10	2.21	3.8×10^{-4}	This work

$\mathrm{L^a}$ = 1,4,8,11-tetraazacyclotetradecane-2,3-dione, $\mathrm{L^1}$ = 2,3-diono-5,6,14,15-dibenzo-7,13-bis(ethoxycarbonyl)-1,4,8,12-tetraazacyclotetradecane-7,12-diene, $\mathrm{L^2}$ = 2,3-diono-5,6,13,14-dibenzo-7,12-bis(ethoxycarbonyl)-1,4,8,11-tetraazacyclotetradecane-7,11-diene, *rac*-cth = *rac*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, en = 1,2-diaminoethane, tmd = 1,3-diaminopropane.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 232057. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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