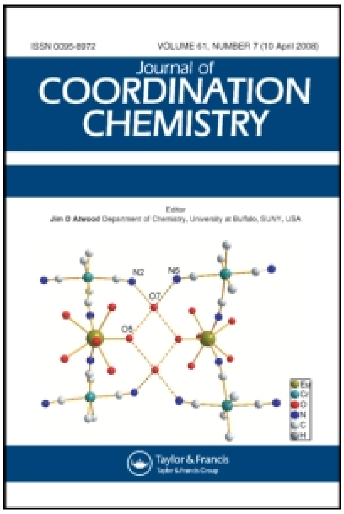

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Synthesis, crystal structure and magnetic properties of a new macrocyclic trinuclear Cu^{II}-Cu^{II}-Cu^{II} complex

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Synthesis, crystal structure and magnetic properties of a new macrocyclic trinuclear Cu^{II}-Cu^{II}-Cu^{II} complex

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A new oxamido-bridged trinuclear copper(II) complex $[(CuL)_2Cu](ClO_4)_2 \cdot 0.5H_2O$ (L = the dianion of 2,3-dioxo-5,6,14,15-dibenzo-7,13-bis(ethoxycarbonyl)-1,4,8,12-tetraazacyclotetradeca-7,12-diene) has been synthesized by self-assembly and characterized. X-ray diffraction analysis reveals that the title complex is monoclinic, space group $P2_1$, with $a = 16.213(5)$, $b = 9.811(3)$, $c = 18.802(6)$ Å, $\beta = 96.790(5)^{\circ}$. The central copper(II) ion lies in a distorted octahedral environment. Terminal coppers have square pyramidal coordination geometry. Magnetic measurements show there is strong antiferromagnetic interaction between the central and the terminal Cu(II) ions.

Keywords: Macrocyclic ligand; Oxamido-bridge; Trinuclear complex; Crystal structure; Antiferromagnetic interaction

1. Introduction

Recently, research has focused on the ability to control construction and the rational design of functional materials [1]. The pathways used to obtain these species are mainly based on the following synthetic schemes: (a) the self-assembled method; (b) the use of polynucleating ligands; (c) the use of complexes as ligands [2]. One of the best strategies to design and synthesize polynuclear species is the "complex as ligand" approach [3, 4]. The design and molecular magnetism of polynuclear complexes are of considerable interest for designing new magnetic materials [5–10]. The oxamido group has proven to be an interesting multiatomic bridge to link metals in polynuclear complexes [11, 12]. The study of the exchange interaction between metal centers through extended bridges has been one of the most active research fields in magnetism [13, 14]. With these facts in mind, we report the synthesis, crystal structure and magnetic properties of a trinuclear copper(II) complex $[(CuL)_2Cu](ClO_4)_2 \cdot 0.5H_2O$, where

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L stands for the dianions of 2,3-dioxo-5,6,14,15-dibenzo-7,13-bis(ethoxycarbonyl)-1,4,8,12-tetraazacyclotetradeca-7,12-diene.

2. Experimental

2.1. *Starting materials*

All starting materials were of analytical grade purchased from the Aldrich Company and used without further purification.

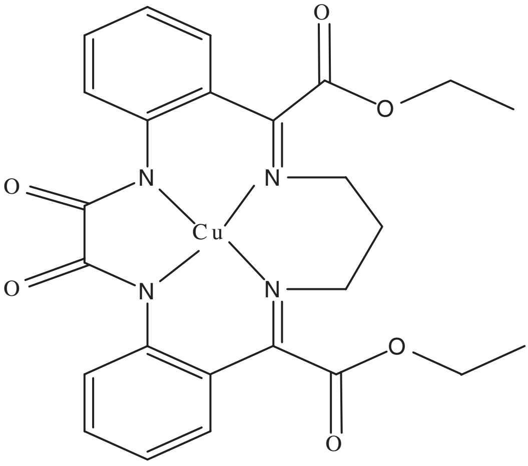
Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only a small amount of material should be prepared, and this should be handled with caution.

2.2. *Physical measurements*

Elemental analyses for carbon, hydrogen and nitrogen were carried out on a Perkin-Elmer 240 instrument. The infrared spectrum was recorded on a Shimadzu IR-408 spectrophotometer in the 4000 to 600 cm^{-1} region, using KBr pellets. Magnetic susceptibility measurements of a crystalline sample were carried out in the temperature range 77–300 K, on a LDJ9600VSM magnetometer at a field strength of 5000 G. Diamagnetic corrections were made with Pascal's constants for all constituent atoms, and the magnetic moments were calculated using the equation $\mu_{\text{eff}} = 2.828(\chi_M T)^{1/2}$.

2.3. *Preparation of $[(CuL)_2Cu](ClO_4)_2 \cdot 0.5H_2O$*

The copper(II) precursor, [CuL] (scheme 1), was prepared as described elsewhere [15]. The complex $[(CuL)_2Cu](ClO_4)_2 \cdot 0.5H_2O$ was synthesized by the addition of a 10 cm^3



Scheme 1. $[Cu^{II}L]$.

ethanol solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.371 g, 1 mmol) to 15 cm^3 of an ethanol solution of CuL (0.108 g, 2 mmol). The mixture was stirred and refluxed for 4 h, and then filtered. The dark-green solution was left to evaporate slowly at room temperature. Dark-green crystals suitable for X-ray determination were collected after nearly 3 months. Yield: 58%. Anal. Calcd. for $C_{25}H_{24.5}N_4O_{10.25}ClCu_{1.5}$(%): C, 44.39; H, 3.65; N, 8.28. Found: C, 44.45, H, 3.69, N, 8.36.

2.4. *Crystal structure determination*

A dark-green, single crystal of the title complex with approximate dimensions $0.25 \times 0.20 \times 0.15$ mm was selected and mounted on a Bruker Smart 1000 diffractometer equipped with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Data were collected at room temperature by the $\omega - 2\phi$ scan technique in the range $2.39^\circ \leq \theta \leq 25.03^\circ$ with index ranges $-19 \leq h \leq 17$, $-8 \leq k \leq 11$, $-22 \leq l \leq 19$. A total of 10 558 reflections was collected, including 5069 independent ($R_{\text{int}} = 0.0631$). A summary of crystallographic data is given in table 1. The structure was solved with direct methods using SHELXS-97 [16]. 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 SHELXL-97 [17]. The final agreement factor values were $R_1 = 0.0597$, $wR_2 = 0.1225$ $(I > 2\sigma(I))$, $R_1 = \sum(||F_0| - |F_c||)/\sum|F_0|$, $wR_2 = (\sum(|F_0|^2 - |F_c|^2)^2/\sum w|F_0|^2)^2$, $w = 1/[\sigma^2(F_0^2) + (0.0682P)^2 + 0.0000P]$, where $P = (F_0^2 + F_c^2)/3$.

Table 1. Crystal data and structure refinement detail for the complex.

Empirical formula	$C_{25}H_{24.50}N_4O_{10.25}ClCu_{1.50}$
Formula weight	675.75
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2(1)/c$
Unit-cell dimensions	$a = 16.213(5)$ Å $b = 9.811(3)$ Å, $\beta = 96.790(5)^\circ$ $c = 18.802(6)$ Å
Volume, Z	3235.1(11) Å^3, 4
Absorption coefficient	1.234 mm^{-1}
$F(000)$	1380
Crystal size	$0.25 \times 0.20 \times 0.15$ mm
θ range for data collection	2.39–25.03°
Limiting indices	$-19 \leq h \leq 17$ $-8 \leq k \leq 11$ $-22 \leq l \leq 19$
Reflections collected	10 558
Independent reflections	5069 (R_{int}) = 0.0631
Completeness to $\theta = 25.03$	96.4%
Absorption correction	Semiempirical from equivalents
Max. and min. transmission	1.000 and 0.822
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5069/36/393
Goodness-of-fit on F^2	1.027
Final R indices $[I > 2\sigma(I)]$	$R1 = 0.0597$, $wR2 = 0.1225$
R indices (all data)	$R1 = 0.1110$, $wR2 = 0.1424$
Largest diff. peak and hole	0.578 and -0.350 e^{-3}

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\mathrm{Å}^2 \times 10^3$) for $[(CuL)_2Cu](ClO_4)_20 \cdot 5H_2O$.

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*(eq)
Cu(1)	2962(1)	3138(1)	2934(1)	28(1)
Cu(2)	5000	5000	5000	37(1)
N(1)	3152(2)	4874(4)	3422(2)	27(1)
N(2)	3991(2)	2525(4)	3468(2)	27(1)
N(3)	3061(3)	1838(4)	2163(2)	31(1)
N(4)	1839(2)	3629(4)	2538(2)	29(1)
O(1)	4059(2)	5635(3)	4385(2)	34(1)
O(2)	4801(2)	3306(3)	4486(2)	34(1)
C(1)	3770(3)	4761(5)	3923(3)	27(1)
C(2)	4229(3)	3402(5)	3976(3)	27(1)
C(3)	4344(3)	1224(5)	3424(3)	31(1)
C(4)	4879(3)	651(6)	3976(3)	45(2)
C(5)	5230(4)	−606(6)	3910(4)	54(2)
C(6)	5052(4)	−1349(7)	3298(4)	58(2)
C(7)	4532(4)	−821(6)	2750(3)	46(2)
C(8)	4155(3)	460(5)	2788(3)	31(1)

Table 3. Selected bond lengths (Å) and angles (°) for $[(CuL)_2Cu](ClO_4)_2 \cdot 0.5H_2O$.

Cu(1)–N(2)	1.938(4)	N(2)–Cu(1)–N(1)	87.06(17)
Cu(1)–N(1)	1.942(4)	N(2)–Cu(1)–N(4)	169.99(18)
Cu(1)–N(4)	1.945(4)	N(1)–Cu(1)–N(4)	93.01(17)
Cu(1)–N(3)	1.951(4)	N(2)–Cu(1)–N(3)	92.34(17)
Cu(2)–O(1)	1.907(3)	N(1)–Cu(1)–N(3)	154.41(18)
Cu(2)–O(2)	1.931(3)	N(4)–Cu(1)–N(3)	91.90(18)
O(1)–C(1)	1.269(6)	O(1A)–Cu(2)–O(2)	95.58(14)
O(2)–C(2)	1.255(6)	O(1)–Cu(2)–O(2)	84.42(14)
O(3)–C(20)	1.187(6)		
O(4)–C(20)	1.311(6)		
O(4)–C(21)	1.460(7)		
O(5)–C(23)	1.188(7)		
O(6)–C(23)	1.306(7)		
N(1)–C(1)	1.297(6)		
N(2)–C(2)	1.309(6)		

Positional parameters and selected bond distances and angles are given in tables 2 and 3, respectively.

3. Results and discussion

3.1. *Description of the crystal structure of* $[(CuL)_2Cu](ClO_4)_2 \cdot 0.5H_2O$

The title compound consists of a centrosymmetric trinuclear complex cation $[(CuL)_2Cu]^{2+}$, two perchlorate anions and water molecules. A perspective view of the trinuclear cation is depicted in figure 1. In the cations, two terminal copper atoms (Cu1 and Cu1A) from the precursor CuL are connected to the central copper (Cu2) via the *exo*-*cis* oxygen atoms of the oxamido macrocyclic precursor. The terminal Cu

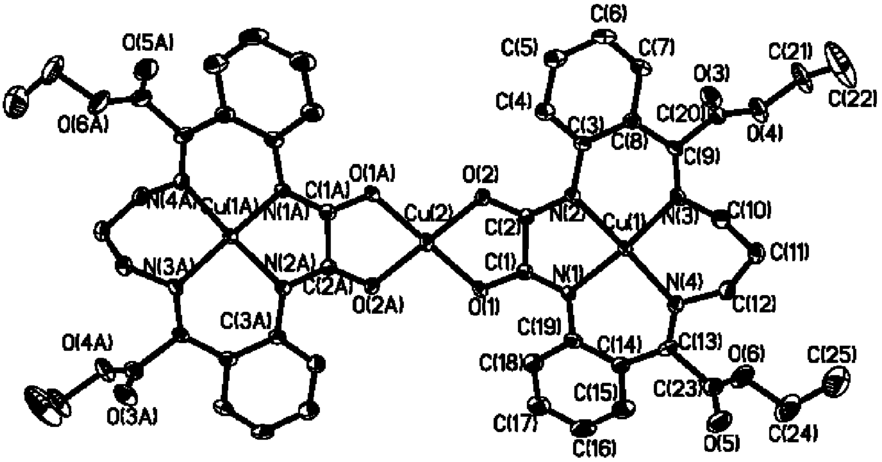


Figure 1. ORTEP diagram of the cation $[(CuL)_2Cu]^{2+}$. Hydrogen atoms and two perchlorate anions are omitted for clarity.

atoms have four nitrogen atoms in the basal plane. Nitrogen atoms surrounding Cu(I) include two amidate nitrogen atoms (N1 and N2) and two imino nitrogen atoms (N3 and N4). Cu–N bond lengths are 1.938, 1.942, 1.945 and 1.951 Å, respectively. Deviations of the four donor atoms (N1, N2, N3 and N4) from their mean plane are −0.3038(3), + 0.3051(4), −0.2898(2) and +0.2885(6) Å, respectively, and Cu(1) lies 0.2288(1) Å out of the plane. One oxygen atom from ClO_4^- occupies the fifth position.

The central Cu2 atom is in a 4 + 2 environment (as shown in figure 2), with an equatorial plane formed by four O atoms of two oxamido groups; axial positions are filled by oxygen atoms from the ester carbonyl of two neighboring entities. The distances Cu2–O are 1.907(3) Å (Cu2–O1) and 1.931(3) Å (Cu2–O2), respectively. The distance Cu2–O3# (O3# from the ester) is 2.635 Å, to give an elongated octahedral environment. In the complex the dihedral angle between the C1C2O1O2 moiety and the C1C2N1N2 group is 3.2(3)°. Three metal atoms form an exactly linear arrangement. The distance between Cu2 and each terminal Cu atom is 5.129(2) Å. The shortest Cu–Cu separation between trinuclear entities is 7.425 Å.

3.2. *Spectroscopic studies*

IR spectra of both [CuL] and the title complex display a sharp band at 1730 cm^{-1}, the characteristic absorption of the ester C=O [18]. 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 1600 cm^{-1} in the spectrum of the title complex. The significant shift to lower wavenumber is due to the coordination of the related O atoms to the central Cu2 atom, as confirmed by the X-ray crystallographic analysis. The band at 1580 cm^{-1}, which shows no significant shift relative to the corresponding band of the mononuclear precursor [CuL], is attributed to ν(C=N) [19]. There is a strong absorption of ClO_4^- at 1100 cm^{-1} in the spectrum of the complex.

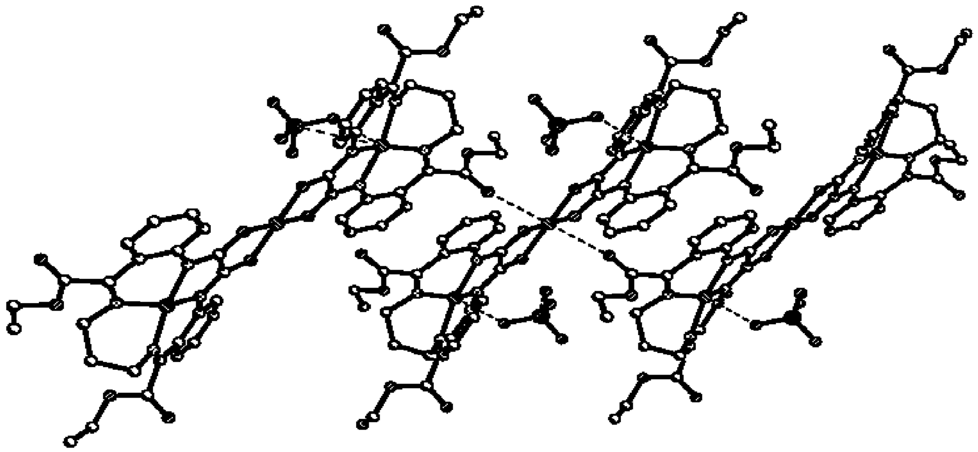


Figure 2. ORTEP view of the trimer unit of $[(CuL)_2Cu](ClO_4)_2$. Ellipsoids are drawn at the 30% probability level.

3.3. *Magnetic properties*

The temperature dependence of the magnetic susceptibility for the complex was investigated in the temperature range 77–300 K, with an applied field of 5000 G. Plots of $\chi_M T$ (χ_M = molar magnetic susceptibility) and χ_M *vs.* T for the title complex are shown in figure 3. The $\chi_M T$ value is equal to $0.70\,\mathrm{cm^3\,mol^{-1}\,K}$ at room temperature; the value is lower than the spin-only value ($1.12\,\mathrm{cm^3\,mol^{-1}\,K}$) expected for the uncoupled Cu(II)–Cu(II)–Cu(II) unit. When the temperature is lowered, $\chi_M T$ decreases gradually, implying antiferromagnetic spin exchange between the central Cu2 and the terminal Cu (from CuL).

The spin hamiltonian appropriate for describing the magnetic properties of isolated trimers is given in equation (1), where J corresponds to the interaction coupling parameter between the central and the terminal copper(II) ions through the oxamido-bridge:

$$\hat{H} = -2J\left(\hat{S}_{\mathrm{Cu1}}\hat{S}_{\mathrm{Cu2}} + \hat{S}_{\mathrm{Cu1a}}\hat{S}_{\mathrm{Cu2}}\right) \tag{1}$$

The magnetic susceptibility deduced from the hamiltonian is given in equation (2).

$$\chi_{\mathrm{M}} = \frac{Ng^2\beta^2}{4KT}\left[\frac{5+\exp(-3J/KT)}{1+\exp(-3J/KT)}\right] + N_a, \quad N_a = 120\times10^{-6} \tag{2}$$

The best-fit parameters were $g = 2.09$, $J = -119.02\,\mathrm{cm^{-1}}$ with $R = 2.8723\times10^{-4}$, where R is defined as in equation (3).

$$R = \sum\left[(\chi_{\mathrm{M}})_{\mathrm{obs}} - (\chi_{\mathrm{M}})_{\mathrm{calc}}\right]^2 \Big/ \sum(\chi_{\mathrm{M}})^2_{\mathrm{obs}} \tag{3}$$

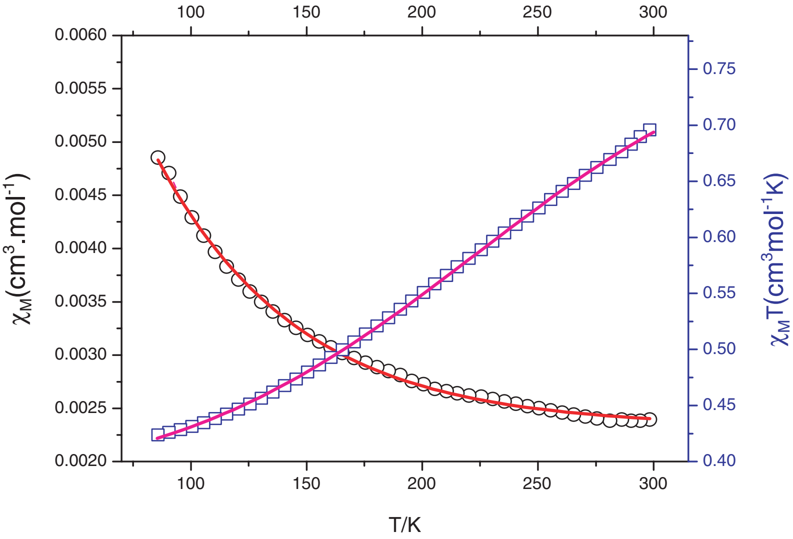


Figure 3. Plots of (χ_M) (○) and (χ_MT) (□) *vs.* T for $[(CuL)_2Cu](ClO_4)_2 \cdot 0.5H_2O$.

The result ($J = -119.02\,cm^{-1}$) indicates that a strong antiferromagnetic interaction exists between the central and the terminal Cu(II) ions, consistent with other results [20].

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 25884. 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; email: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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