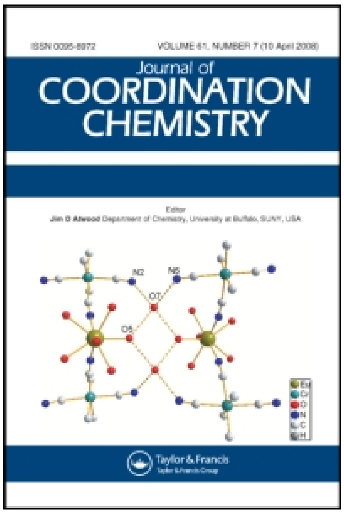

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Synthesis, crystal structure and magnetic properties of a new binuclear copper(II)-copper(II) complex of a macrocyclic oxamide

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Synthesis, crystal structure and magnetic properties of a new binuclear copper(II)-copper(II) complex of a macrocyclic oxamide

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The binuclear metal complex $[Cu(\mu\text{-}exoO_2)cyclamCu(bpy)](ClO_4)_2 \cdot H_2O$ (bpy = 2,2′-bipyridine and ($exoO_2$)cyclam = 1,4,8,11-tetraazacyclotradecanne-2,3-dione) has been synthesized and characterized by single-crystal X-ray analysis and spectroscopic and magnetic measurements. The structure consists of homobinuclear $[Cu(\mu\text{-}exoO_2)cyclamCu(bpy)]^{2+}$ cations, a weakly coordinated water molecule and perchlorate ions. In each binuclear unit, Cu1, coordinated by four nitrogen atoms of the macrocyclic organic ligand is connected to Cu2 via the *exo-cis* oxygen atoms of the macrocyclic ligand with Cu···Cu separations of 5.151 Å; Cu2 assumes square-pyramidal geometry. Magnetic properties measured at 2–300 K show antiferromagnetic exchange between adjacent copper(II) ions.

Keywords: Copper(II); Crystal structure; Oxamido bridge; Macrocyclic ligand; Magnetic properties

1. Introduction

In recent years, the design synthesis and magnetic characterization of heterospin metal complexes derived from paramagnetic metal ions and open-shell organic molecules have gained much attention [1–3]. Complexes with extended ligand bridges have found many applications as catalysts, mimics for metallobiomolecules and in investigations concerning the mutual influence of two or more metal centres on electronic, magnetic and electrochemical properties [4–6].

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In view of the effective bridging function of the oxamido group, many efforts have been devoted to the synthesis of μ-oxamido complexes containing transition metal ions. Non-cyclic oxamides may adopt a *cis* or *trans* conformation on coordination, and this flexibility restricts the control over the type of complex formed [7]. Macrocyclic oxamides, in which the *exo*-*cis* conformation of the oxygen donors is enforced, permit the synthesis of bimetallic systems and model magnetic systems in a more controlled fashion [8]. Complexes of this kind with various terminal ligands and metal ions have been synthesized and magnetic properties and crystal structures studied [9–15]. As an extension of these investigations, this paper deals with the synthesis, crystal structure, electronic spectra and magnetic properties of the binuclear metal complex $[Cu(\mu\text{-}exoO_2)cyclamCu(bpy)](ClO_4)_2 \cdot H_2O$ (bpy = 2,2′-bipyridine and $(exoO_2)$ cyclam = 1,4,8,11-tetraazacyclotradecanne-2,3-dione).

2. Experimental

2.1. *Materials and synthesis*

All starting materials were of analytical grade and used as purchased without further purification. The $[Cu^{II}L]$ precursor was prepared according to literature methods [16]. An aqueous solution ($5\,cm^3$) of $Cu(ClO_4)_2 \cdot 6H_2O$ (1 mmol, 371 mg) was added to a suspension of $Cu^{II}L$ (1 mmol, 289 mg) in $10\,cm^3$ of water. To the resulting solution was added dropwise an aqueous solution ($20\,cm^3$) of bpy (1 mmol, 156 mg) with constant stirring. Dark brown crystals were obtained by slow evaporation of the resulting solution at room temperature. Anal. Calcd for $C_{20}H_{26}Cl_2N_6O_{11}Cu_2$ (%): C, 33.16; H, 3.62; N, 11.6. Found: C, 33.08; H, 3.60; N, 11.51.

2.2. *Physical measurements*

IR spectra were recorded (KBr discs) on a Shimadzu IR-408 spectrophotometer in the 4000–600 cm^{-1} region. Electronic spectra were measured on a Shimadzu UV-2101 PC spectrophotometer. Elemental analyses (C, H, N) were carried out on a Perkin–Elmer 240 instrument. Variable-temperature magnetic susceptibilities were measured on a Quantum Design MPMS 5S SQUID magnetometer in the temperature range 2–300 K.

2.3. *X-ray crystallography*

A single crystal of the complex of dimensions $0.36\,mm \times 0.28\,mm \times 0.12\,mm$ was mounted on a BRUKER SMART 1000-CCD area detector using graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å) and data were collected with the ω scan technique at 293(2) K in the range $2.35 \leq \theta \leq 24.80$. Semi-empirical absorption corrections were performed using the SADABS program. The structure was solved using direct methods and successive difference Fourier syntheses (SHELXS-97) and refined using full-matrix least-squares methods on F^2 with anisotropic thermal parameters for all non-hydrogen atoms (SHELXL-97) [17]. Hydrogen atoms were added theoretically and refined with the riding model and fixed isotropic thermal parameters. Further details of the structure analysis are given in table 1. Positional parameters and selected bond lengths and angles are listed in tables 2 and 3, respectively.

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

Empirical formula	$C_{20}H_{26}C_{12}Cu_2N_6O_{11}$
Formula weight	724.45
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	9.053(5)
b (Å)	24.535(14)
c (Å)	12.340(7)
α (°)	90
β (°)	96.222(10)
γ (°)	90
V (Å^3)	2725(3)
Z	4
D_{calc}/(g cm^{-3})	1.766
Absorption coefficient (mm^{-1})	1.826
F(000)	1472
Crystal size (mm^3)	$0.36 \times 0.28 \times 0.12$
θ Range (°)	1.66–26.53
Reflections collected	15705
Independent reflections	5622 [R(int) = 0.0553]
Absorption correction	Semi-empirical from equivalents
Max./min. transmission	1.000000/0.630020
Goodness-of-fit on F^2	1.027
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0575$; $wR_2 = 0.1508$
Largest diff. peak and hole	0.783 and -0.705 e Å^{-3}

3. Results and discussion

3.1. *Description of the structure*

The structure consists of homobinuclear [Cu(μ-*exo*O_2)cyclamCu(bpy)]$^{2+}$ cations, weakly coordinated water molecules and perchlorate ions. A perspective view of the binuclear cation is depicted in figure 1 and selected bond lengths and angles are listed in table 2. Cu1 is coordinated by four nitrogen atoms of the macrocyclic ligand with the atoms deviating from the mean plane by 0.2063 (N1), −0.2103 (N2), 0.2025 (N3) and −0.1984 Å (N4). Cu1 is connected to Cu2 via the *exo-cis* oxygen atoms of the macrocyclic ligand with a Cu···Cu separation of 5.151 Å; Cu2 assumes a square-pyramidal coordination environment, with the two carbonyl O-atoms O(1) and O(2) of the oxamido ligand and two nitrogen atoms from bpy in equatorial positions, and one weakly coordinated oxygen atom belonging to a water molecule in the axial position. Cu1 is displaced from the least-squares basal plane away from the water molecule by 0.0134 Å. Cu1 and Cu2 are displaced towards the same side of the bridge plane between them, which is planar, by −0.0558 and −0.1888 Å, respectively. As depicted in figure 2, adjacent binuclear cations are parallel to each other with a separation distance of 3.498 Å.

3.2. *Spectroscopic properties*

The IR spectrum of the complex shows two strong bands at *ca.* 1620 and 1450 cm^{-1}, attributed to ν(N–C–O) stretching, characteristic of the bridging oxamido group [18]. The appearance of a strong, broad band at *ca.* 1100 cm^{-1} indicates the presence of perchlorate ions [19]. The electronic spectrum of the complex in dimethylsulphoxide

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for $[\mathrm{Cu}(\mu\text{-}exo\mathrm{O_2})\mathrm{cyclamCu(bpy)}](\mathrm{ClO_4})_2 \cdot \mathrm{H_2O}$.

Atom	x/a	y/b	z/c	U(eq)
Cu(1)	6888(1)	1478(1)	1266(1)	41(1)
Cu(2)	3956(1)	184(1)	3530(1)	41(1)
O(1)	4570(4)	948(2)	3620(3)	41(1)
O(2)	5212(4)	119(2)	2378(3)	47(1)
O(3)	1894(5)	483(2)	2288(3)	61(1)
N(1)	5695(5)	1531(2)	2499(4)	41(1)
N(2)	6599(5)	699(2)	1413(4)	42(1)
N(3)	8487(6)	1410(2)	266(5)	62(2)
N(4)	6865(6)	2267(2)	882(4)	55(1)
N(5)	3661(5)	−609(2)	3637(4)	43(1)
N(6)	2820(5)	180(2)	4807(4)	44(1)
C(1)	5297(5)	1062(2)	2820(4)	35(1)
C(2)	5744(6)	586(2)	2139(5)	38(1)
C(3)	7015(7)	268(3)	681(6)	56(2)
C(4)	8420(8)	400(3)	213(6)	68(2)
C(5)	8459(8)	917(3)	−431(5)	64(2)
C(6)	8562(9)	1919(3)	−342(6)	70(2)
C(7)	8225(8)	2387(3)	410(6)	68(2)
C(8)	6495(9)	2659(3)	1726(6)	66(2)
C(9)	5106(9)	2499(3)	2219(6)	67(2)
C(10)	5272(8)	2040(2)	3019(5)	53(2)
C(11)	4246(7)	−988(3)	3015(5)	53(2)
C(12)	4011(9)	−1537(3)	3042(6)	66(2)
C(13)	3134(9)	−1700(3)	3939(7)	73(2)
C(14)	2530(8)	−1311(3)	4574(7)	69(2)
C(15)	2829(6)	769(3)	4404(5)	47(2)
C(16)	2315(6)	−315(3)	5079(5)	47(2)
C(17)	1448(7)	−379(3)	5908(5)	59(2)
C(18)	1091(7)	74(3)	6507(5)	62(2)
C(19)	1638(7)	579(3)	6249(5)	59(2)
C(20)	2485(6)	617(3)	5387(5)	50(2)
Cl(1)	9571(2)	8164(1)	6748(1)	51(1)
Cl(2)	6981(2)	8584(1)	390(1)	57(1)
O(4)	9268(17)	7588(3)	6784(12)	115(6)
O(5)	9224(14)	8355(5)	5666(7)	83(4)
O(6)	8794(19)	8442(8)	7524(12)	219(12)
O(7)	11156(9)	8233(6)	7052(10)	85(4)
O(4′)	8708(12)	7814(5)	7369(9)	116(5)
O(5′)	8551(13)	8499(4)	6058(10)	119(5)
O(6′)	10 469(12)	8522(4)	7425(8)	90(4)
O(7′)	10 434(15)	7838(6)	6093(11)	181(8)
O(8′)	7180(30)	8015(4)	197(17)	77(7)
O(9)	5438(12)	8707(12)	382(18)	75(7)
O(10)	7730(30)	8715(10)	1462(11)	170(20)
O(11)	7650(30)	8905(10)	−398(11)	92(8)
O(8′)	7619(17)	8109(5)	−42(12)	116(5)
O(9′)	5419(7)	8490(7)	469(9)	83(4)
O(10′)	7717(11)	8713(4)	1426(6)	91(6)
O(11′)	7085(19)	9033(4)	−358(8)	91(4)

(DMSO) solution was measured at room temperature in the range 200–800 nm. Below 400 nm it is dominated by intense bands due to intraligand and charge-transfer transitions in the Cu(II) chromophore [20]. The band at 261 nm ($\varepsilon = 2.07 \times 10^4\,\mathrm{M^{-1}\,cm^{-1}}$) and a shoulder at 302 nm ($\varepsilon = 1.60 \times 10^4\,\mathrm{M^{-1}\,cm^{-1}}$) can be ascribed to π–π^* transitions in the macrocyclic ligand. The band at 424 nm ($\varepsilon = 1.38 \times 10^3\,\mathrm{M^{-1}\,cm^{-1}}$) can be ascribed to an intraligand and/or charge-transfer transition in [$\mathrm{Cu^{II}L}$] moieties.

Table 3. Selected bond lengths (Å) and angles (°) for the complex.

Cu(1)–N(2)	1.941(5)	N(2)–Cu(1)–N(1)	84.37(19)
Cu(1)–N(1)	1.963(5)	N(2)–Cu(1)–N(4)	87.3(4)
Cu(1)–N(4)	1.993(5)	N(1)–Cu(1)–N(4)	97.3(2)
Cu(1)–N(3)	2.008(5)	N(2)–Cu(1)–N(3)	95.1(2)
Cu(2)–O(2)	1.921(4)	N(1)–Cu(1)–N(3)	167.3(2)
Cu(2)–O(1)	1.955(4)	N(4)–Cu(1)–N(3)	85.6(2)
Cu(2)–N(5)	1.972(5)	O(2)–Cu(2)–O(1)	86.22(15)
Cu(2)–N(6)	1.973(5)	O(2)–Cu(2)–N(5)	93.59(19)
Cu(2)–O(3)	2.398(4)	O(1)–Cu(2)–N(5)	169.40(17)
N(1)–C(1)	1.282(7)	O(2)–Cu(2)–N(6)	172.92(19)
N(1)–C(10)	1.474(7)	O(1)–Cu(2)–N(6)	97.45(18)
N(2)–C(2)	1.276(7)	N(5)–Cu(2)–N(6)	81.7(2)
N(2)–C(3)	1.465(7)	O(2)–Cu(2)–O(3)	91.96(18)
N(3)–C(6)	1.463(9)	O(1)–Cu(2)–O(3)	86.57(17)
N(3)–C(5)	1.484(9)	N(5)–Cu(2)–O(3)	104.02(17)
N(4)–C(7)	1.448(8)	N(6)–Cu(2)–O(3)	94.29(18)
N(4)–C(8)	1.482(9)	Cu(2)–O(3)–H(3C)	120.0
N(5)–C(15)	1.332(8)	Cu(2)–O(3)–H(3D)	119.9

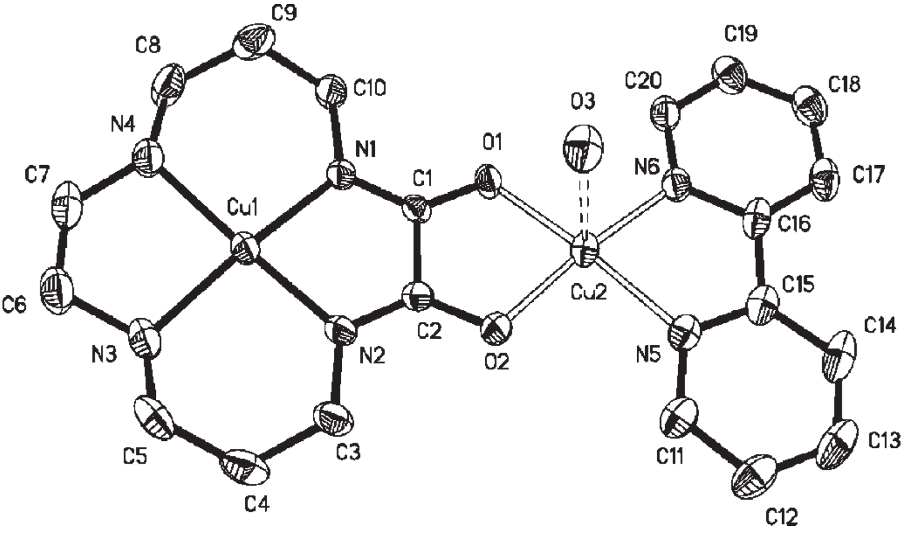

Figure 1. ORTEP view of the complex with H atoms and ClO_4^- ions omitted for clarity.

3.3. *Magnetic properties*

Magnetic suscepbilities (χ_M) were measured at 2–300 K and the temperature dependence of the molar magnetic susceptibility ($\chi_M T$) is shown in figure 3. The $\chi_M T$ value of the complex at room temperature is $2.35\,cm^3\,mol^{-1}\,K$, lower than the spin-only value of $2.49\,cm^3\,mol^{-1}\,K$ for the Cu(II) ion. Upon cooling, $\chi_M T$ decreases sharply to $0.348\,cm^3\,mol^{-1}\,K$ at 28 K, indicating intramolecular antiferromgnetic coupling between copper(II) ions. To quantitatively interpret the magnetic behaviour of the complex, magnetic data were analysed by the theoretical expression (the Hamiltonian being $\hat{H} = -2J\hat{S}_t \cdot \hat{S}_{t+1}$ for a binuclear complex with a local spin, $S = (1/2)$) $\chi_M = [N\beta^2 g^2/(kT)][3 + \exp(-2J/kT)] + N\alpha$, where J is the exchange coupling parameter describing the magnetic interaction between the copper(II) ions, $N\alpha$ is the

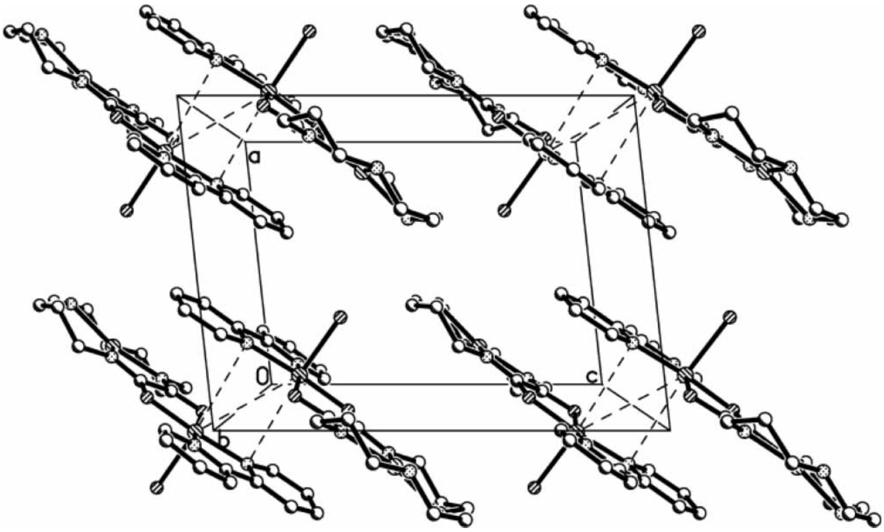

Figure 2. A perspective view of the molecular packing of the complex along the *c* axis.

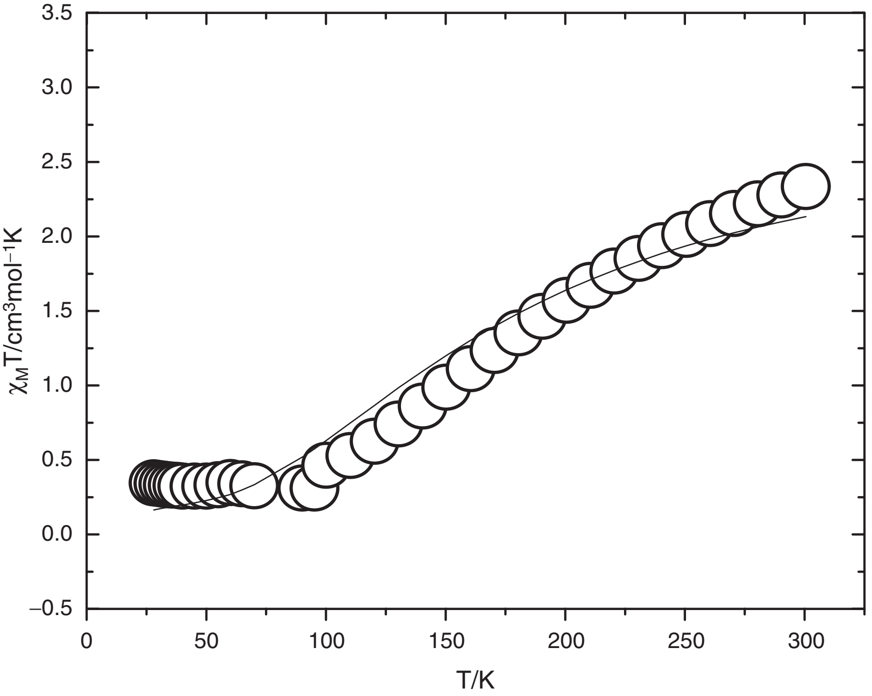

Figure 3. A $\chi_M T$ (◯) versus T plot for the complex.

tempetature-independent paramagnetism (120×10^{-6}) and other symbols have their usual meanings. The parameters obtained by simulation of the experimental data using the above expression are $J=-158.6$, $g=2.18$. The agreement factor F defined here as $\sum_I (X_i^{obs})^{-1}(X_i^{obs}-X_i^{calc})^2$ is equal to 7.79×10^{-5}. These results (negative, large J value) indicate that the complex has a strong antiferromagnetic Cu(II)-Cu(II) spin-exchange interaction. According to Kahn [21], the antiferromagnetic interaction arises from the non-zero overlap between the $d_{x^2-y^2}$ magnetic orbitals centred on the two copper(II) ions and delocalized towards ligands.

Supplementary material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication number CCDC 256456. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223/336-033; Email: deposit@ccdc.cam.ac.uk).

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