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Synthesis, structure, and magnetic properties of a tetranuclear copper(fII) complex with a triazenido ligand

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Abstract The reaction of methyl anthranilate, sodium nitrite, and 2-aminopyridine produces a triazenide, namely, 1-[(2-carboxymethyl)benzene]-3-[2-pyridine]triazene (HL). In the presence of Et_3N, the reaction of HL and $CuCl_2{\cdot}2H_2O$ gives a μ_4-oxo-bridged tetranuclear copper(II) complex $[Cu_4OL_3Cl_3]{\cdot}1.5THF$ (**1**·1.5THF), which has been characterized by X-ray crystallography and magnetic susceptibility measurements.

Introduction

Polynuclear copper complexes have received increasing attention in recent years, owing to their applications in metallobiochemistry [1–3], materials science [4–7], and theoretical chemistry [8]. Particular interest has been directed toward the exchange phenomena in di- and polynuclear complexes of copper(II), which have led to valuable insights into their magnetostructural correlations [9, 10].

The use of different bridging and polydentate ligands has afforded an impressive array of coordination complexes with new architectures. Among them, the triazene ligands have attracted our attention, as these compounds have remarkable bridging ability to afford multinuclear complexes possessing potentially useful properties for the development of new magnetic materials and catalysts [11–13].

Although tetranuclear $\{Cu_4(\mu_4\text{–}O)\}$ cores have been known for some time and studied extensively [14–18], relatively few copper complexes with other polydentate ligands, such as triazenide ligands, have been developed. We have synthesized a new triazenide ligand, 1-[(2-carboxymethyl)benzene]-3-[2-pyridine]triazene (HL) by modification of a literature procedure [19]. The reaction of HL and $CuCl_2{\cdot}2H_2O$ gives a tetranuclear copper(II) complex **1**. In this paper, we describe the synthesis and characterization of HL**,** and its complex **1**, as well as the magnetic properties of **1**.

Experimental

^1H NMR spectra were measured on a Bruker AM 500 spectrometer in $CDCl_3$ solution. Magnetic susceptibility data for powder samples were collected in the temperature range 2–300 K with a Quantum Design SQUID Magnetometer MPMS XL-7. Effective magnetic moment was calculated by the equation $\mu_{eff} = g[\sum ZS(S + 1)]^{1/2}$, where χ_M is the molar magnetic susceptibility.

Synthesis of HL

A solution of methyl anthranilate (10 mmol) in water (5 mL) was mixed with 1 mol·L^{-1} HCl (30 mL, 30 mmol) at 0 °C. An aqueous solution (15%) of sodium nitrite (15 mmol) was added dropwise with stirring. Once the amine was dissolved, a 15% solution of 2-aminopyridine (10 mmol) in ethanol was added at 0 °C and the mixture was stirred for 6 h. The reaction mixture was neutralized with 15% aqueous $NaCH_3CO_2$ to give a yellow precipitate.

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The reaction mixture was filtered, and the solid was purified by crystallization at −4 °C from 9:1 ethyl acetate/hexanes to obtain yellow crystals, which were collected and dried in *vacuo* (1.8 g, 70%). Anal. Found (calcd) for $C_{13}H_{12}N_4O_2$: C 60.7 (60.9), H 4.8 (4.7), N 21.7 (21.9). ^1H NMR ($CDCl_3$): δ 8.58 (*d*, $J = 1$ Hz, 1H, py), 8.05 (*d*, $J = 2.6$ Hz, 1H, Py), 7.96 (*d*, $J = 2.8$ Hz, 1H, Py), 7.82 (*t*, $J = 2.7$ Hz, 1H, Py), 7.60 (*t*, $J = 2.7$ Hz, 2H, Ar), 7.25 (*t*, $J = 1.7$ Hz, 1H, Py), 7.16 (*t*, $J = 2.7$ Hz, 1 Hz, Py), 3.97 (*s*, 3H, $-OCH_3$).

Synthesis of complex 1

To a solution of the ligand (0.26 g, 1 mmol) and triethylamine (0.10 g, 1 mmol) in THF/methanol (15 mL, 1:1), $CuCl_2 \cdot 2H_2O$ (0.17 g, 1 mmol) was added and the mixture was stirred for 15 min. The solution was allowed to slowly evaporate to afford dark green crystals, which were collected and dried in *vacuo* (0.21 g, 56%). Anal. Found (calcd) for $C_{39}H_{33}Cl_3Cu_4N_{12}O_7$: C 39.9 (41.0), H 2.9 (2.9), N 14.3 (14.7).

X-ray crystallography

Data were collected with a Bruker SMART CCD area detector using graphite monochromated Mo-K radiation (0.71073 Å) at room temperature for HL, and at 150 K for complex **1**. Empirical absorption corrections were applied using the SADABS program [20]. Structures were solved using direct methods and the non-hydrogen atoms were refined anisotropically. All the hydrogen atoms of the ligands were placed in calculated positions with fixed isotropic thermal parameters and included in the structure factor calculations in the final stage of full-matrix least-squares refinement. All calculations were performed using the SHELXTL computer program [21]. Table 1 gives details of the crystal parameters, data collection and refinement for HL and **1**·1.5THF. The selected bond distances and angles for compounds HL, and **1**·1.5THF are listed in Tables 2 and 3.

Results and discussion

1-[(2-carboxymethyl)benzene]-3-[2-pyridine]triazene (HL) was synthesized by the reaction of methyl anthranilate, sodium nitrite, and 2-aminopyridine (Scheme 1 and Fig. s1 for ^1H NMR spectrum of HL). In the presence of Et_3N, complex **1** was obtained as deep green crystals in good yield by the reaction of HL and $CuCl_2 \cdot 2H_2O$ in THF/methanol.

Table 1 Crystallographic data for HL and **1**·1.5THF

Parameter	HL	**1**·1.5THF
Empirical formula	$C_{13}H_{12}N_4O_2$	$C_{44.5}H_{43}Cl_3Cu_4N_{12}O_{8.5}$
Formula weight	256.27	1,242.42
λ (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	*P*2(1)/c	*P*21/n
a/Å	15.064(3)	11.2188(5)
b/Å	6.197(1)	22.3976(9)
c/Å	27.545(6)	20.4830(4)
α/°	90	90
β/°	99.30(3)	98.8850(10)
γ/°	90	90
V/Å^3	2,537.3(9)	5,085.1(4)
Z	4	4
Dc/Mgm^{-3}	1.342	1.623
F(000)	1,072	2,516
θ range for data collection	3.09–27.48°	3.08–27.48°
Reflections collected/unique	21,893/5,713	30,079/8,700
Data/restraints/parameters	5,713/0/344	8,700/675/649
Goodness of fit on F^2	1.154	0.984
Final R indices [$I > 2\mathrm{sigma}(I)$]	$R_1 = 0.1123$	$R_1 = 0.0419$
	$wR_2 = 0.3209$	$wR_2 = 0.1075$
R indices (all data)	$R_1 = 0.1454$	$R_1 = 0.0555$
	$wR_2 = 0.3504$	$wR_2 = 0.1172$

Table 2 Selected bond lengths (Å) and angles (°) for HL

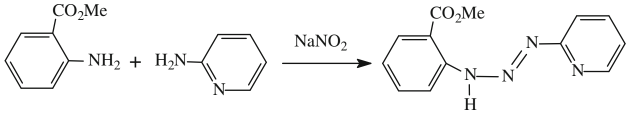
Bond distances			
N(1)–N(2)	1.333(4)	N(2)–N(3)	1.268(4)
N(1)–C(1)	1.376(5)		
Bond angles			
C(1)–N(1)–N(2)	119.7(3)	N(1)–N(2)–N(3)	111.8(3)
N(2)–N(3)–C(6)	113.0(3)	N(4)–C(1)–N(1)	114.5(3)

X-ray quality crystals of HL were obtained by hexane diffusion into an ethyl acetate solution of HL. An ORTEP view of HL is displayed in Fig. 1. HL contains a rigid N(2)=N(3) double bond and a potential NNNNO donor set. The N(1)–N(2) and N(2)–N(3) bond distances are 1.333(4) and 1.268(4) Å, respectively.

X-ray quality crystals of **1** were obtained by slow evaporation of a THF solution of **1**. The ORTEP view of **1,** excluding solvent molecules, is illustrated in Fig. 2. The structure of **1** is completed by four nitrogen atoms of the deprotonated ligand (L^-), a μ_4-bridging oxygen atom, and three μ-chloride atoms. The tetrahedron around the central oxygen O(1), with Cu–O(1) distances of 1.939(3), 1.941(2), 1.919(3) and 1.932(2) Å for Cu(1)–Cu(4) (Table 3) shows unusually high distortion. The observed bond angles vary from 103.89(11) and 112.01(13)° for Cu(1)–O(1)–Cu(3) and Cu(3)–O(1)–Cu(4) to 115.16(12)

Table 3 Selected bond distances (Å) and angles (°) for complex **1**·1.5THF

Bond distances			
Cu(1)–O(1)	1.939(3)	Cu(1)–N(9)	1.967(4)
Cu(1)–N(11)	2.014(3)	Cu(1)–Cl(1)	2.3319(11)
Cu(1)–Cl(2)	2.4228(11)	Cu(2)–O(1)	1.941(2)
Cu(2)–N(1)	1.964(3)	Cu(2)–N(3)	2.022(3)
Cu(2)–Cl(3)	2.2957(10)	Cu(2)–Cl(1)	2.5920(12)
Cu(3)–O(1)	1.919(3)	Cu(3)-N(5)	1.963(3)
Cu(3)–N(7)	2.039(3)	Cu(3)–N(4)	2.101(3)
Cu(3)–Cl(2)	2.3855(11)	Cu(4)–O(1)	1.932(2)
Cu(4)–O(4)	1.970(3)	Cu(4)–N(8)	1.984(3)
Cu(4)–N(12)	1.997(3)	Cu(4)–Cl(3)	2.6575(11)
Bond angles			
Cu(3)–O(1)–Cu(4)	12.01(13)	Cu(3)–O(1)–Cu(1)	103.89(11)
Cu(4)–O(1)–Cu(1)	115.99(12)	Cu(3)–O(1)–Cu(2)	115.16(12)
Cu(4)–O(1)–Cu(2)	106.36(11)	Cu(1)–O(1)–Cu(2)	103.41(12)
Cu(1)–Cl(1)–Cu(2)	76.20(3)	Cu(1)–Cl(2)–Cu(3)	78.36(3)
Cu(2)–Cl(3)-Cu(4)	77.13(3)		



Scheme 1 Schematic representation of the synthesis of HL

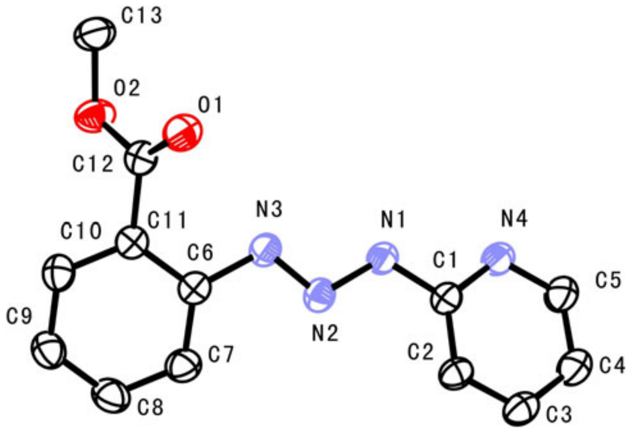


Fig. 1 ORTEP view of ligand (HL)

and 115.99(12)° for Cu(2)–O(1)–Cu(3) and Cu(1)–O(1)–Cu(4). This distortion is attributed to the steric bulk of the chelating ligands, which contract each of the two copper centers within the tetranuclear unit (Cu(l), Cu(2) and Cu(3), Cu(4)), associated with a reduction of the corresponding Cu–O–Cu bond angles.

In complex **1**, Cu(1) and Cu(2) are both coordinated by two nitrogen atoms from L^-, one μ_4–O atom, and two chloride atoms, respectively. The Cu–N bond lengths fall in the range 1.967(4)–2.014(3) Å for Cu(1)–N, and 1.964(3)–2.022(3) Å for Cu(2)–N. The Cu–Cl bond lengths are within the range of 2.3319(11)–2.4228(11) Å for Cu(1), and 2.2957(10)–2.5920(12) Å for Cu(2), respectively. Cu(1) and Cu(2) are connected by one μ_4–O bridge and one chloride bridge, with the bond angle Cu(1)-Cl(3)-Cu(2) of 76.20(3)°.

Cu(3) and Cu(4) are both coordinated by three nitrogen atoms from two L^- ligands, one μ_4–O atom, and one chloride atom. The Cu–N bond lengths are 1.963(3)–2.101(3) Å and the Cu–Cl distances are 2.3855(11) and 2.6575(11) Å, respectively. Pairs Cu(1), Cu(3) and Cu(2), Cu(4) are connected by one μ_4–O bridge and one chloride bridge with bond angles Cu(1)–Cl(2)–Cu(3) of 78.36(3)° and Cu(4)–Cl(3)–Cu(2) of 77.13(3)°.

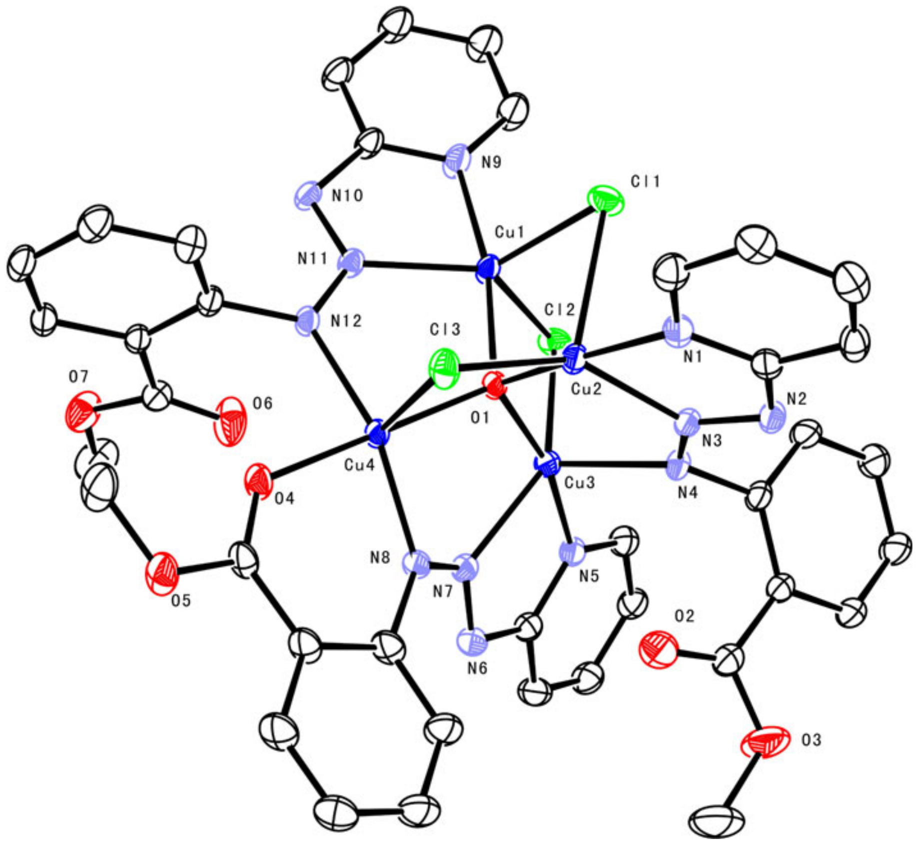
Magnetic properties of 1

Magnetic susceptibility data for a solid sample of **1** was collected in the temperature range 2–300 K (Fig. 3). Complex **1** has a low room-temperature magnetic moment ($\mu_{eff} = 1.09\ \mu_B$ (300 K)), indicating significant antiferromagnetic coupling between the copper(II) centers. Three different exchange pathways can occur in complex **1**, involving Cu–N–Cu, Cu–O–Cu, and Cu–Cl–Cu. Considering the relatively large average Cu–Cl distances in **1** and the well-known magneto-structural correlations for equivalent Cu–Cl–Cu systems [22], a significant contribution of the Cu–Cl–Cu pathway in **1** can be excluded. It was found that for (μ-carboxylato)copper(II) systems, only those compounds which exhibit an approximately square planar copper coordination show a strong contribution of the carboxylato ligand to the overall exchange [23–25]. The effect of other bridging ligands such as Cl should only slightly modulate the extent of coupling.

To explain the magnetic behavior of complex **1**, its structure can consequently be reduced to a central Cu_4N_6O core which can be described as O(1)-connected Cu_2N_2 rings, as shown in Fig. 4. The Cu–Cl–Cu and Cu–N–N–Cu pathways in **1** are assumed to have only a second-order effect upon the magnetic exchange between the copper centers. The tetranuclear copper(II) complex can be formally divided into two dinuclear Cu_2N_2O subunits. The intradimer coupling via the oxygen atom is assumed to be larger than the interdimer exchange interactions. Hence initially a molecular field model [26] was used to approximate the case where interdimer magnetic coupling (i.e., the exchange between the di-μ-oxo-bridged copper centers) is expected to dominate the relatively weaker interdimer coupling.

The experimental data can be fitted by the following model. The spin Hamiltonian for complex **1**, assuming interaction in each pair can be properly described in terms

Fig. 2 ORTEP view of **1.** THF molecules are omitted for clarity



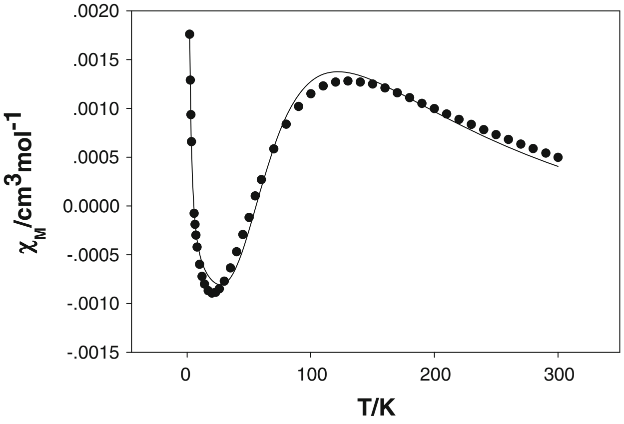


Fig. 3 Plot of the temperature dependence of the χ_M for complex **1** at 5000 Oe

of the Heisenberg Hamiltonian of the form $H = -J_{ij}S_i{\cdot}S_j$, is given in Eq. 1.

$$H = -2[J_{12}S_1 \cdot S_2 + J_{13}S_1 \cdot S_3 + J_{14}S_1 \cdot S_4 + J_{23}S_2 \cdot S_3 + J_{24}S_2 \cdot S_4 + J_{34}S_3 \cdot S_4] \quad (1)$$

For an arrangement of copper(II) ions as shown in Fig. 4, Eq. 1 simplifies directly to Eq. 2.

$$H = -2[J_{12}(S_1 \cdot S_2 + S_3 \cdot S_4) + J_{13}(S_1 \cdot S_3 + S_1 \cdot S_4 + S_2 \cdot S_3 + S_2 \cdot S_4)] \quad (2)$$

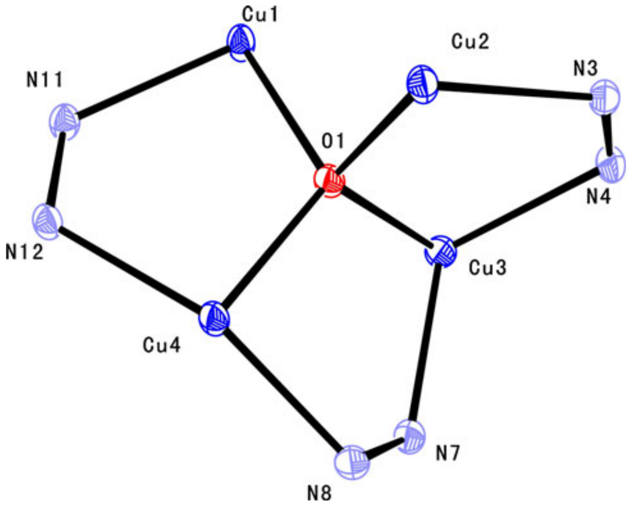


Fig. 4 Connection of the [$Cu_4N_6(\mu_4$–O)] core

with $S_A = S_1 + S_2$, $S_B = S_3 + S_4$, $S_T = S_A + S_B$, and $S =$ 1/2, specifying S_T, S_A, S_B, and S uniquely defines an eigenstate of the Hamiltonian which will be represented by the notation |T, SA, SB> and which has the energy given by Eq. 3.

$$E(S_T, S_A, \mathrm{SB}) = -J_{12}[S_A(S_A+1) + S_B(S_B+1) - 4S(S+1)] - J_{13}[S_T(S_T+1) - S_A(S_A+1) - S_B(S_B+1)] \quad (3)$$

The susceptibility can then be expressed theoretically by Eq. 4, with $x = J_{12}/\mathrm{kT}$ and $y = J_{13}/\mathrm{kT}$;

$$\begin{aligned}\chi_{\mathrm{Cu}_4} = {} & (1 - x_p)\frac{\mathrm{N}g^2\mu^2}{\mathrm{kT}}\{[10\exp(2x) + 2\exp(-2x) \\ & + 4\exp(-2y)]/[5\exp(2x) + 3\exp(-2x)\exp(-4x) \\ & + 6\exp(-2y) + \exp(-4y)]\} \\ & + \exp\left(\frac{\mathrm{N}g^2\mu^2}{3\mathrm{kT}}\right)S(S+1) + \mathrm{TIP} \qquad (4)\end{aligned}$$

The best parameters obtained using standard least-squares fitting were $J_{12} = 597\ \mathrm{cm}^{-1}$, $J_{13} = -355\ \mathrm{cm}^{-1}$ for **1**.

For symmetrical oxygen-bridged copper(II) compounds, a linear relationship has been found between magnetic exchange coupling and the Cu–O–Cu angle [27]. The exchange interaction for bis-(μ-hydroxo)copper(II) complexes is generally ferromagnetic for Cu–O–Cu angles less than 97.5°. An opening of the Cu–O–Cu angle is connected with a transition from ferromagnetic to antiferromagnetic coupling. Melnik [27] found that in the case of bis (μ-hydroxo)-bridged copper(II) complexes an increase of 1.5° in the Cu–O–Cu angle is associated with an increase in antiferromagnetic coupling of $\approx 80\ \mathrm{cm}^{-1}$. The Cu–O–Cu angles in the $\mathrm{Cu_2ON_2}$ ring of **1** are 103.41–115.99°, which are larger than 97.5°, and we observe strong antiferromagnetic coupling between copper(II) ions in the title complex **1**.

In summary, the present study shows that the 1,3-RR′-triazene ligand gives a polynuclear Cu(II) complex. Currently we are exploring this further, as well as the reactions of HL with other metals.

Supplementary data

CCDC 757905 and 758980 contain the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

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