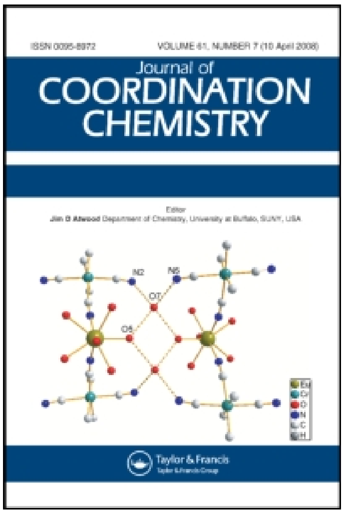

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Synthesis, crystal structure and properties of a 1D copper(II) complex with 1,5,9-triazacyclododecane bridged by *p*-benzenebicarboxylate

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A 1D complex $[\{[Cu_2([12]aneN_3)_2(p\text{-paa})(H_2O)_2](ClO_4)_2\}[Cu_2([12]aneN_3)_2(p\text{-paa})_2]]_n$ ($[12]aneN_3 = $ 1,5,9-triazacyclododecane, *p*-paa = *p*-benzenebicarboxylate) has been synthesized and structurally characterized. The complex contains two different binuclear copper(II) moieties. One part includes a binuclear copper(II) unit and non-coordinated perchlorate anions. A neutral binuclear copper(II) part which forms a zigzag chain structure via the bridging *p*-paa ligand completes the unit-cell. Elemental analysis, IR, UV-Vis spectra and magnetic properties for the complex have also been determined. Magnetic susceptibilities in the solid state are measured over the temperature range from 77 to 300 K, showing a weak antiferromagnetic coupling with a best fit $J_1 = -3.09\,\text{cm}^{-1}$, $J_2 = -5.279\,\text{cm}^{-1}$, $g = 2.099$ and $R = 1.226 \times 10^{-5}$.

Keywords: Copper(II); Crystal structure; Triazamacrocycle ligand; Properties

1. Introduction

Although the chemistry of aza-macrocycles is well established [1–4], the development of new synthetic methodologies and applications continues to be of interest due to the polyfunctional macrocyclic ligands' specific coordination behavior, high selectivity, pH dependence and formation of stable complexes with a large variety of metal ions [5–8]. However, studies on 1,5,9-triazacyclododecane ([12]aneN3) and its derivatives have been limited compared with other macrocyclic ligands [9]. Studies using [12]aneN3 have shown that this larger macrocyclic ligand shows interesting biomimetic properties in some of its complexes [10].

[12]aneN3 with a dangling nitrogen-donor arm can yield metal complexes in which the ligand not only binds metal ions selectively but also provides complexes with different geometries [11]. In this article, we select the 12-membered triazamacrocycle

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ligand [12]aneN3 based on the "macrocyclic effect" of the aza macrocycles [12] and synthesize a 1D complex containing copper(II) with *p*-paa; its synthesis, crystal structure, spectroscopic properties and magnetic properties are reported here.

2. Experimental

2.1. *Materials and instrumentation*

The macrocycle ligand [12]aneN3 was prepared as previously described [13]. All reagents and materials used for synthesis were reagent grade and used without further purification.

Carbon, hydrogen and nitrogen analyses were performed on a Perkin-Elmer 240C analyzer. An infrared spectrum (KBr pellet) of the complex was recorded on a FT-IR NEXUS 670 (Nicolet) spectrophotometer in the range 400–4000 cm^{-1}. The UV-Vis spectrum was measured on a Jasci V-570 UV-Vis spectrophotometer in the 200–2000 nm region. The magnetic susceptibility data were recorded using a Quantum Design MPMS–7 SQUID Magnetometer in the temperature range from 77 to 300 K at an applied magnetic field of 5 KG.

2.2. *Preparation of the title complex*

Single crystals of the title complex suitable for single-crystal structure analysis were synthesized as follows. A solution containing NaOH 0.080 g (2 mmol) in water (15 mL) was dropped into a water solution (15 mL) of $Cu(NO_3)_2 \cdot 3H_2O$ 0.214 g (1 mmol). After stirring for 15 min, a blue precipitate of $Cu(OH)_2$ was formed. The product was filtered off, washed with ethanol, and dried at room temperature. *p*-paa 0.083 g (0.5 mmol) was added to the blue suspended solution obtained by the freshly precipitated $Cu(OH)_2$ dissolved in 30 mL methanol. The resulting mixture was filtered after stirring vigorously for 2 h. Then a solution of [12]aneN3 (0.5 mmol) in methanol (10 mL) was added dropwise to the blue filtrate. A transparently blue solution was generated at once which was filtered after stirring for 24 h. Deep blue crystals suitable for X-ray crystallographic analysis were obtained by slow evaporation of the filtrate for a few weeks. Anal. Calcd for the title complex (%): C, 42.43; H, 5.89; N, 10.04; Found: C, 42.20; H, 6.00; N, 10.08.

2.3. *X-ray crystallography*

Single-crystal X-ray studies were performed on a Bruker SMART 1000 CCD diffractometer equipped with graphite monochromator situated in the incident beam for data collection. The determination of unit cell parameters and data collections were performed with Mo-Kα radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods and semi-empirical absorption corrections were applied using the SHELXS-97 program [14]. The final refinement was performed with the SHELXL-97 program [15] by full-matrix-least squares methods on F^2 with anisotropic thermal parameters for non-hydrogen atoms. The hydrogen atoms were generated theoretically onto atoms to

Table 1. Data collection and processing parameters for the complex.

Empirical formula	$C_{60}H_{100}C_{12}Cu_4N_{12}O_{22}$
Formula weight	1666.58
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	*P*2/c
Unit cell dimensions (Å, °)	
a	16.350(7)
b	16.130(7)
c	14.045(6)
β	90.996(7)
Volume (Å^3)	3704(3)
Z	2
Calculated density (Mg m^{-3})	1.494
Absorption coefficient (mm^{-1})	1.284
F(000)	1740
Crystal size (mm^3)	$0.28 \times 0.22 \times 0.10$
θ range for data collection (°)	1.25–25.00
Limiting indices	$-19 \le h \le 18$, $-19 \le k \le 15$, $-16 \le l \le 15$
Reflections collected	15558
Independent reflections	6265 [$R_{(\text{int})} = 0.0618$]
Absorption correction	Semi-empirical from equivalents
Data collection Diffractometer used	BRUKER SMART 1000
Max. and Min. transmission	1.000000 and 0.816735
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	6265/162/479
Goodness-of-fit on F^2	1.056
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0517$, $wR_2 = 0.1113$
R indices (all data)	$R_1 = 0.1054$, $wR_2 = 0.1446$
Largest diff. peak and hole (e Å^{-3})	0.503 and −0.539

$R = \Sigma w(|F_o| - |F_c|)^2$; $w = 1/(\sigma^2(F) + 0.0001F^2)$.

which they are attached and refined isotropically with fixed thermal factors. Further details about crystal data and structure refinement are summarized in table 1. Selected bond lengths and angles are listed in table 2.

3. Results and discussion

As shown in figure 1(a) and (b), the complex contains two different binuclear copper(II) units. Figure 1(a) gives binuclear copper(II) part filled with a binuclear copper(II) unit and non-coordinated perchlorate anions. The two Cu(II) centers are pentacoordinate (CuN_3O_2) defined by three nitrogen atoms of the triazamacrocycle ligand and one hydroxyl oxygen atom of a *p*-paa bridging carboxylate group together with a water molecule. In pentacoordinate compounds, the geometry of the complex can be described by a structural index parameter τ such that $\tau = (\beta - \alpha)/60^\circ$, where β and α are the two largest angles ($\beta > \alpha$) [16]. Thus, the geometric parameter τ is applicable to pentacoordinate structures as an index of the degree of trigonality, within the structural continuum between trigonal bipyramidal ($\beta - \alpha = 60^\circ, \tau = 1$) and square pyramidal ($\beta - \alpha = 0^\circ, \tau = 0$). Thus, the coordination geometry around Cu(2) (or Cu(2A)) in the complex can be described as a trigonally-distorted, rectangular pyramid which τ value

Table 2. Selected bond lengths (Å) and angles (°) for the complex.[a]

Cu(1)–O(1)	1.956(3)	Cu(1)–O(3)	2.023(3)
Cu(1)–N(3)	2.124(4)	Cu(1)–N(1)	2.015(4)
Cu(1)–N(2)	2.088(4)	Cu(2)–O(7)	1.968(4)
Cu(2)–N(4)	1.998(5)	Cu(2)–N(6)	2.053(5)
Cu(2)–O(5)	2.000(4)	Cu(2)–N(5)	2.101(5)
O(1)–Cu(1)–N(1)	171.2(2)	O(7)–Cu(2)–N(4)	178.6(2)
O(1)–Cu(1)–O(3)	92.2(2)	O(7)–Cu(2)–O(5)	90.2(2)
N(1)–Cu(1)–O(3)	89.6(2)	N(4)–Cu(2)–O(5)	88.5(2)
O(1)–Cu(1)–N(2)	88.5(2)	O(7)–Cu(2)–N(6)	93.4(2)
N(1)–Cu(1)–N(2)	85.3(2)	N(4)–Cu(2)–N(6)	88.0(2)
O(3)–Cu(1)–N(2)	146.8(2)	O(5)–Cu(2)–N(6)	134.1(2)
O(1)–Cu(1)–N(3)	98.4(2)	O(7)–Cu(2)–N(5)	91.6(2)
N(1)–Cu(1)–N(3)	89.1(2)	N(4)–Cu(2)–N(5)	88.5(2)
O(3)–Cu(1)–N(3)	110.3(2)	O(5)–Cu(2)–N(5)	119.6(2)
N(2)–Cu(1)–N(3)	102.5(2)	N(6)–Cu(2)–N(5)	106.1(2)
C(7)–N(3)–Cu(1)	113.1(4)	C(18)–N(4)–Cu(2)	111.0(5)
C(6)–N(3)–Cu(1)	114.1(3)	C(26)–N(4)–Cu(2)	108.5(4)
C(1)–N(1)–Cu(1)	111.1(6)	C(20)–N(5)–Cu(2)	112.2(5)
C(9)–N(1)–Cu(1)	113.9(3)	C(21)–N(5)–Cu(2)	110.9(4)

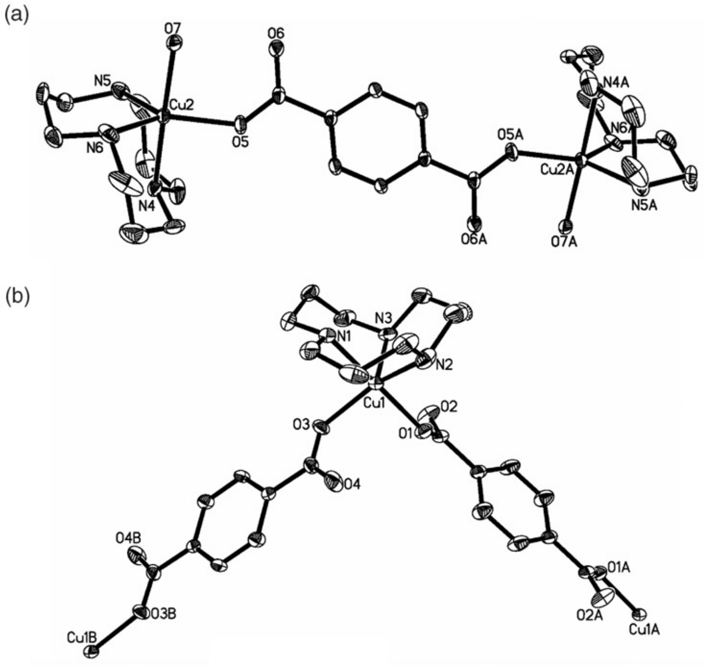

Figure 1. (a) Perspective view of $[Cu_2([12]aneN_3)_2(p\text{-paa})(H_2O)_2]$ with the atom-numbering scheme. Thermal ellipsoids represent 30% probability and hydrogen atoms are omitted for clarity. (b) Perspective view of the $[Cu_2([12]aneN_3)_2(p\text{-paa})_2]_n$ unit with the atom-numbering scheme. Thermal ellipsoids represent 30% probability; hydrogen atoms are omitted for clarity. (c) The 1-D chain structure of the complex. (d) The packing structure with chair conformation of the complex.

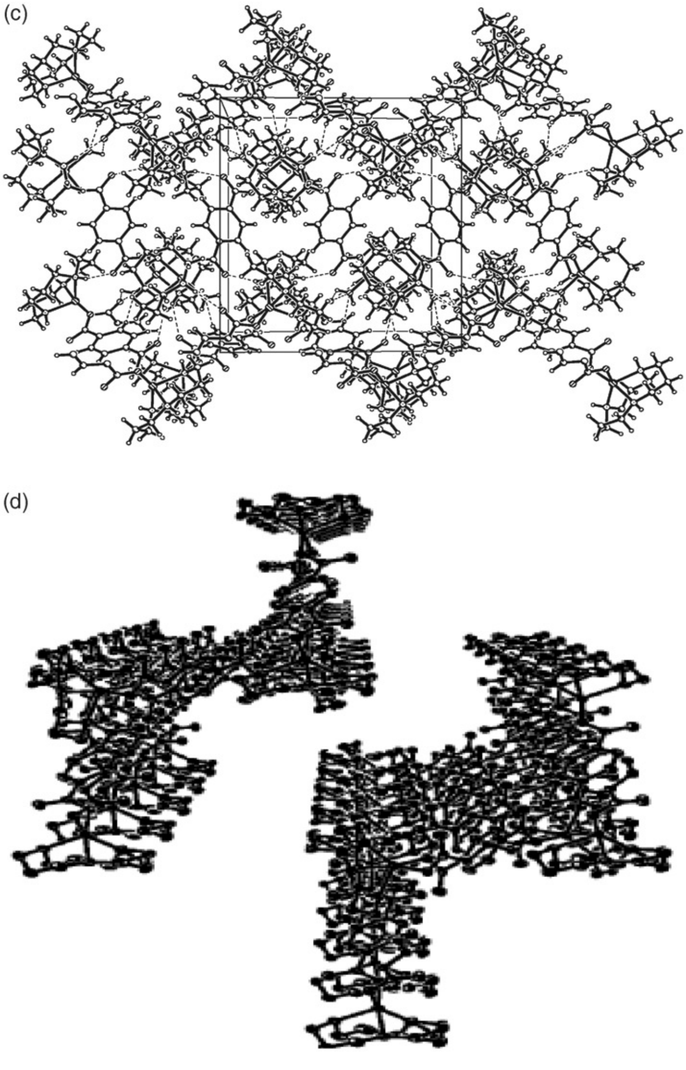

Figure 1. Continued.

of 0.225, with N(5), N(6), O(5) occupying the equatorial positions and N(4), O(7) occupying the apical positions. The Cu(2) is 0.0605 Å above the plane. In another neutral binuclear copper(II) unit (shown in figure 1b), the two Cu(II) centers are also pentacoordinate (CuN_3O_2) defined by three nitrogen atoms of the 1,5,9-triazacycledodecane ligand and two hydroxyl oxygen atoms from bridging carboxylate groups of two different *p*-paa ligands. For Cu(1) (or Cu(1A)), the τ value is 0.35, indicating a distorted trigonal bipyramid with N(2)–N(3)–O(3) in the equatorial position and N(1), O(1) in the apical position. The *p*-paa ligand coordinates to two copper metals via the bridging carboxylate groups giving rise to a zigzag chain structure (shown in figure 1c).

Table 3. Hydrogen-bonds (Å) and angles (°) for the complex.

D–H	d(D–H)	d(H···A)	⟨DHA	d(D···A)	A [symmetry operations]
N3–H3C	0.900	2.081	144.81	2.864	O2
N4–H4C	0.900	2.306	157.06	3.155	O10
N5–H5C	0.900	2.482	137.49	3.204	O2 [x, $-y$, $z-1/2$]
N6–H6C	0.900	2.090	164.53	2.967	O4 [x, y, $z-1$]
N1–H1C_a	0.910	2.318	155.56	3.169	O8
N2–H2C_a	0.910	2.171	160.91	3.046	O6 [x, y, $z+1$]
O7–H7D	0.850	2.650	123.44	3.198	O1 [x, y, $z-1$]

Although the tridentate macrocycle ligand adopts a facial coordination, bonds of Cu(1)–N(1), Cu(1)–N(2) and Cu(1)–N(3) are slightly longer than these of Cu(2)–N(4), Cu(2)–N(5) and Cu(2)–N(6), respectively, which may be partly responsible for different coordination environments of the coppers with *p*-paa ligands. There exist multiple hydrogen bonds between N–H, O–H groups of the tridentate macrocycle ligands and the *p*-paa ligand (table 3), i.e. N3–H3C and N5–H5C groups act as hydrogen donors and the uncoordinated O2 from the *p*-ppa ligand is a hydrogen acceptor. A chair conformation in space is obtained by two 1D zigzag chains connecting with each other via hydrogen bonds of coordinated water and uncoordinated carboxylic oxygens of *p*-paa ligands (shown in figure 1d).

3.1. *IR spectrum*

IR spectrum of the complex displays a medium and broad absorption band at about 3250 cm^{-1}, for the stretching vibrations of coordinated water. The ν(N–H) stretching frequency of the macrocycle ligand is indicated by two medium absorption bands at 2950 and 2860 cm^{-1}, respectively. Very strong and sharp absorption bands at about 1640 and 1415 cm^{-1} can be assigned to the antisymmetric stretching vibrations and symmetric stretching vibrations of *p*-ppa carboxylate groups. The value of $\Delta\nu_{as-s}$ ($\Delta\nu_{as-s} = \nu_{as}(COO) - \nu_s(COO)$) is larger than 200 cm^{-1} indicating a monodentate bridging coordination mode of *p*-ppa [17]. This result was consistent with the crystal structure. The strong and broad band at 1150 cm^{-1} is assigned to the ν_{ClO} stretch of perchlorate. All of these results are consistent with the crystal structure.

3.2. *Electronic spectrum*

The electronic spectrum shows very strong absorption bands at 279 nm for the complex, attributed to π–π* charger transfer of the ligand itself. The shoulder at 295 nm of the complex can be ascribed as $Cu^{II} \rightarrow L$ MLCT charge-transfer transition. In addition, a broad absorption centered at 650 nm can be designated as the typical d–d electronic-transfer absorptions: $^2B_1 \rightarrow {}^2E$ and $^2B_1 \rightarrow {}^2B_2$ in Cu^{II} (3d^9) ground state, in accord with the trigonal bipyramidal geometry of the complex [18].

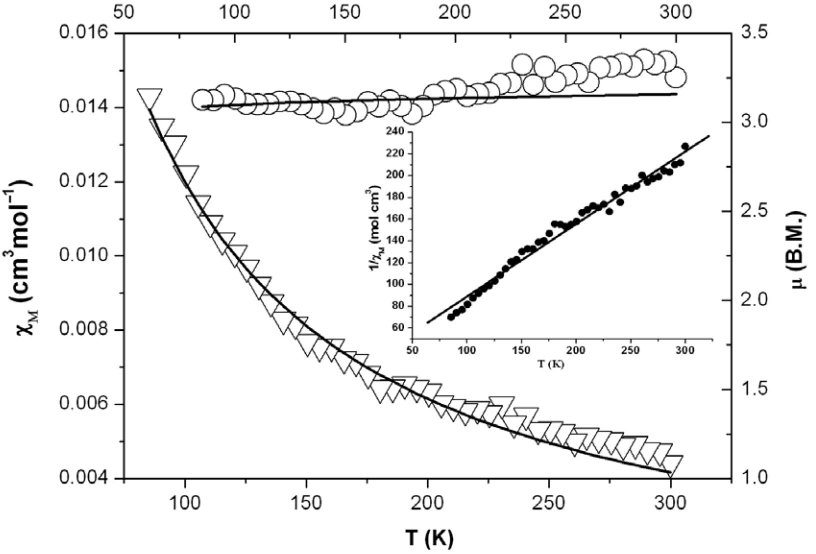

Figure 2. Thermal variations of the magnetic susceptibility μ_{eff} of the complex, where (o) plots for observed result μ_{eff} and solid lines for fitting calculations.

3.3. *Magnetic properties of the complex*

The magnetic properties of a powder sample of the complex are represented as χ_M and μ_{eff} *versus* T (figure 2). At room temperature, the μ_{eff} value is 3.39 cm^3 mol^{-3} K, a little less than isolated copper(II) ions (3.46 cm^3 mol^{-3} K). As can be seen, μ_{eff} slowly decreases as the temperature is lowered reaching 3.25 cm^3 mol^{-3} K at 77 K, typical of antiferromagnetic behavior.

Due to a binuclear copper part and a 1D chain part existing in the unit-cell, we chose a simple measure to deal with χ_M, which can be regarded as the total value of χ_{chain} and χ_{Bi}. According to Fisher [19], the magnetic susceptibility data χ_{chain} and χ_{Bi} are analyzed quantitatively by equations (1) and (2) respectively. $N\alpha$ is the temperature independent paramagnetism, $N\alpha = 120 \times 10^{-6}$ cm^3 mol^{-1}. The best-fit parameters are $J_1 = -3.09$ cm^{-1}, $J_2 = -5.279$ cm^{-1}, g = 2.099 and R = 1.226×10^{-5}.

$$\chi_{\text{chain}} = \frac{Ng^2\beta^2}{KT}\left[\frac{0.25 + 0.074975X + 0.075235X^2}{1.0 + 0.9931X + 0.1721X^2 + 0.757825X^3}\right]$$
$$X = \frac{|J_1|}{KT} \tag{1}$$

$$\chi_{\text{Bi}} = \frac{2Ng^2\beta^2}{KT}\left[3 + \exp\left(\frac{-2J_2}{KT}\right)\right] + N\alpha$$
$$N\alpha = 120 \times 10^{-6} \tag{2}$$

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 629938 for the title complexes. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44 1223336 033; Email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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