

# Synthesis and Structure of a Novel Tetranuclear Copper(II) Resorcin[4]arene-based Complex

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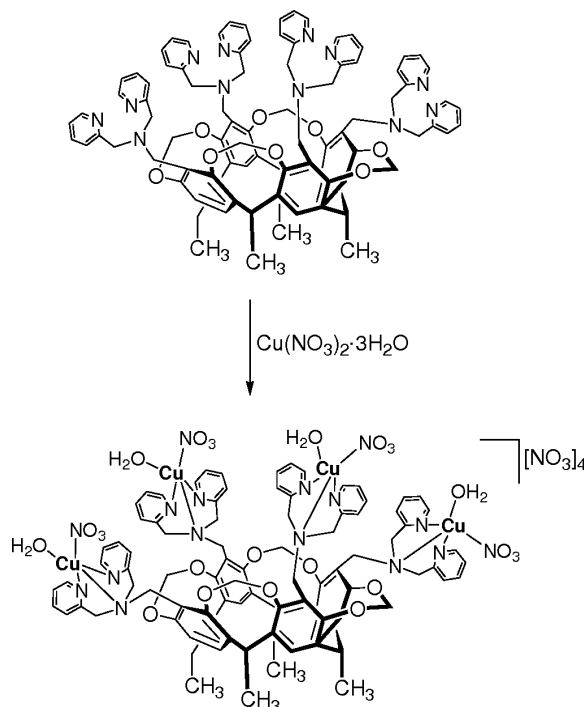
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The preparation, spectroscopic properties and crystal structure of a tetranuclear copper(II) resorcin[4]arene-based complex with the cap-bpa ligand [cap = resorcin[4]arene-based cavitand, bpa = bis(pyridyl)methylamine] are reported. The orientation of each (bpa)Cu fragment in the complex is perpendicular to the cap bowl. All four copper centers are only coordinated to the tridentate bpa moiety.

**Key words:** Resorcinarene, Cavitand, Synthesis, Crystal Structure, Copper(II) Complex

## Introduction

Resorcin[4]arenes are cavity-containing macrocyclic compounds that attract considerable interest in the field of host-guest and supramolecular chemistry as building blocks for the design of selective cation receptors and carriers [1]. It is then understandable that resorcin[4]arenes have been used as templates for the synthesis of some metal cage complexes, due to their crown-shaped structure and their ability to be functionalized with metal-coordinating ligands [2]. Derivatives of the resorcin[4]arenes with  $\text{Ph}_2\text{P}$  and  $\text{PhP}$  units show strong coordinating ability, complexing transition metals such as Cu, Ag, and Au, to give transition metal-rimmed bowl complexes, which have the potential to accept small guest molecules and to include ions [3]. Dimerization of two iminodiacetic acid functionalized resorcin[4]arene-based hemispherical units occurred by assembling at the redox-active  $\text{Fe(II)}$ . The resulting molecular cages containing iron, as a model for metalloproteins, have a molecular recognition site, along with a reactive metal center [4]. Some copper and zinc complexes with functionalized resorcin[4]arene-based dithiocarbamate (dtc) cavitands may lead to the construction of nanosized structures *via* metal-ligand self-assemblies [5]. Recently, resorcin[4]arene-based molecules functionalized with four pyridylmethylamine moieties have also been used to coordinate  $\text{Cu}^{2+}$ ,  $\text{Pd}^{2+}$ , and  $\text{Pt}^{2+}$  ions to form cavity-containing metallo-supramolecular frameworks which can encapsulate guest molecules or act



Scheme 1.

as catalysts [6]. In studies exploring the assembly of multinuclear metal complexes with functionalized resorcin[4]arene-based ligands, we selected the labile ligand bis(pyridylmethyl)amine (bpa) to act as functional moieties in the resorcin[4]arene-based cavitands (cap) [7]. The reason is that the functional cap-bpa lig-

Table 1. Crystal data, data collection parameters and details of the structure refinement.

Empirical formula	C <sub>87</sub> H <sub>94</sub> N <sub>20</sub> O <sub>39</sub> Cu <sub>4</sub>
Formula weight	2297.98
Color, habit	light green, block
Crystal size [mm <sup>3</sup> ]	0.28 × 0.22 × 0.16
Crystal system	orthorhombic
Space group	<i>Pnma</i>
<i>a</i> [Å]	22.622(4)
<i>b</i> [Å]	28.863(6)
<i>c</i> [Å]	17.656(3)
<i>V</i> [Å <sup>3</sup> ]	11528(4)
<i>Z</i>	4
Density (calc.) [g cm <sup>-3</sup> ]	1.32
Absorption coefficient [mm <sup>-1</sup> ]	0.81
Temperature [K]	294(2)
<i>F</i> (000) [e]	4736
Radiation	MoK <sub>α</sub> (λ = 0.71073 Å)
Reflections collected	87230
Independence reflections	14733 ( <i>R</i> <sub>int</sub> = 0.1042)
Reflections with ( <i>I</i> ≥ 2σ( <i>I</i> ))	3821
Weighting scheme	$w = [\sigma^2(F_o^2) + 0.2000P^2 + 0.0000P]$ where $P = (F_o^2 + 2F_c^2)/3$
Parameters refined	648
Final <i>R</i> indices (all data)	<i>R</i> 1 = 0.1634, <i>wR</i> 2 = 0.2728
Goodness of fit (GoF)	1.064
Final difference peaks [e Å <sup>-3</sup> ]	+0.915, -0.538

$$R1 = \sum ||F_o| - |F_c|| / \sum |F_o|; wR2 = [\sum w(|F_o|^2 - |F_c|^2)^2 / \sum w|F_o|^2]^2]^{1/2};$$

$$GoF = [\sum w(|F_o| - |F_c|)^2 / (N_{obs} - N_{param})]^{1/2}.$$

and can provide a tridentate N<sub>3</sub> donor set suitable for the coordination of catalytically active metal ions such as palladium, silver, copper, and zinc [8]. The results of the synthesis and structure of a tetranuclear copper(II) resorcin[4]arene-based complex with the cap-bpa ligand are presented in this paper (Scheme 1).

## Experimental

### General

All manipulations were conducted using Schlenk techniques under an atmosphere of nitrogen. The cap-bpa ligand was prepared according to the literature method [7]. The IR spectrum was measured on a Digilab FTS-40 spectrophotometer. The mass spectrum was obtained on a Finnigan TSQ-700 spectrometer. The magnetic moment for the solid sample was measured by a Sherwood magnetic susceptibility balance at r. t.

### Synthesis

To a solution of the ligand cap-bpa [7] (150 mg, 0.105 mmol) in THF (20 mL) was added a solution of Cu(NO<sub>3</sub>)<sub>2</sub> · 3H<sub>2</sub>O (106 mg, 0.439 mmol) in methanol (8 mL) at r. t. The resulting green solution was stirred for 2 h and filtered. Diffusion of hexane after 3 d gave deep green block crystals in a yield of 72%

Table 2. Selected bond lengths (Å) and bond angles (°) for complex 1.

Cu(1)–N(1)	2.000(9)	Cu(1)–N(2)	2.002(9)
Cu(1)–N(3)	1.971(10)	Cu(2)–N(4)	2.025(9)
Cu(2)–N(5)	1.979(12)	Cu(2)–N(6)	1.939(13)
Cu(1)–O(5)	1.970(9)	Cu(2)–O(6)	1.996(10)
Cu(1)–O(7)	2.380(17)	Cu(2)–O(10)	2.388(13)
O(5)–Cu(1)–N(3)	97.5(5)	O(5)–Cu(1)–N(1)	177.2(3)
N(3)–Cu(1)–N(1)	84.2(4)	O(5)–Cu(1)–N(2)	96.0(4)
N(3)–Cu(1)–N(2)	166.3(5)	N(1)–Cu(1)–N(2)	82.4(4)
O(5)–Cu(1)–O(7)	89.2(5)	N(3)–Cu(1)–O(7)	92.5(5)
N(1)–Cu(1)–O(7)	93.0(4)	N(2)–Cu(1)–O(7)	85.4(5)
N(6)–Cu(2)–N(5)	167.9(7)	N(6)–Cu(2)–O(6)	98.1(6)
N(5)–Cu(2)–O(6)	93.9(5)	N(6)–Cu(2)–N(4)	83.1(6)
N(5)–Cu(2)–N(4)	84.9(5)	O(6)–Cu(2)–N(4)	173.4(4)
N(6)–Cu(2)–O(10)	90.7(4)	N(5)–Cu(2)–O(10)	89.3(4)
O(6)–Cu(2)–O(10)	91.3(4)	N(4)–Cu(2)–O(10)	95.2(4)

(142 mg). – IR (KBr disc, cm<sup>-1</sup>): ν<sub>O–H</sub> 3358 (br), ν<sub>N=O</sub> 1281(m), 1302(s), 1388(s). – Magnetic moment μ<sub>eff</sub> = 1.89 μ<sub>B</sub> at 294 K. – MS (FAB): *m/z* = 2011 ([cap-bpaCu<sub>4</sub>(NO<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)<sub>4</sub>] – 1), 1940 ([cap-bpaCu<sub>4</sub>(NO<sub>3</sub>)<sub>4</sub>]), 1691 ([cap-bpaCu<sub>4</sub>]). – Anal. found: C 47.1, H 4.61, N 11.2; calcd. for C<sub>88</sub>H<sub>84</sub>N<sub>12</sub>O<sub>8</sub>Cu<sub>4</sub>(NO<sub>3</sub>)<sub>8</sub>(H<sub>2</sub>O)<sub>6</sub>(C<sub>6</sub>H<sub>14</sub>)(CH<sub>4</sub>O): C 47.3, H 4.73, N 11.6.

### Crystal structure determination

Crystallographic data were collected on a Bruker SMART diffractometer equipped with a CCD area detector, using graphite-monochromated MoK<sub>α</sub> radiation (λ = 0.71073 Å) at r. t. Data in the frames corresponding to an arbitrary hemisphere of data were integrated with SAINT [9]. Data were corrected for Lorentz and polarization effects and were further analyzed by using XPREP. An empirical absorption correction based on the measurement of redundant and equivalent reflections and an ellipsoidal model for the absorption surface was applied with use of SADABS [10]. The structure solution and refinement (by full-matrix least-squares methods on *F*<sup>2</sup>) were performed with SHELXTL [11]. All copper atom positions were confirmed upon the first refinement. Other non-hydrogen atoms were located from subsequent difference Fourier syntheses. All copper atoms and the non-hydrogen atoms of the cap-bpa ligand were refined anisotropically. Several nitrate anions were refined isotropically due to disorder, and the nitrogen and oxygen atoms of the nitrate anions were refined with fixed N–O bond lengths. The coordinated water molecules and the disordered solvent molecules were also refined isotropically and the corresponding oxygen and carbon atoms were treated without hydrogen atoms. The crystallographic and structure refinement data are given in Table 1, selected bond lengths and angles are listed in Table 2.

Crystal data (excluding structure factors) for the structure in this paper have been deposited as supplementary publication no. CCDC-259393. Copies of the data can be obtained

free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

## Results and Discussion

The cap-bpa ligand with four tridentate  $N_3$  units was prepared by reacting tetrabromo-methylresorcin[4]arene with bpa in the presence of potassium carbonate as a base [7]. Treatment of the ligand cap-bpa in THF solution with  $Cu(NO_3)_2 \cdot 3H_2O$  in methanol gave solely the tetranuclear copper(II) complex  $[cap-bpaCu_4(NO_3)_4(H_2O)_4][NO_3]_4$ , **1**, in a yield of 72%. The green crystalline product **1** easily loses solvents making collection of X-ray diffraction data difficult. Complex **1** appears to be air-stable and is soluble in most polar solvents. The r.t. magnetic moment of **1**  $1.89 \mu_B$  is typical for copper(II). The complex gives no obvious EPR signal at r.t. The IR spectrum of the complex reveals absorptions expected for the nitrate moieties. The N=O stretching frequency of  $1281 \text{ cm}^{-1}$  is characteristic of chelating nitrate ligands. The  $[NO_3]^-$  counteranion shows  $\nu_{NO}$  at higher frequencies ( $1302$  and  $1388 \text{ cm}^{-1}$ ) than the  $\kappa^1$ - $NO_3^-$  bonded ligand [12]. A weak broad absorption at  $3358 \text{ cm}^{-1}$  attributed to the water molecule can also be observed in the IR spectrum. The positive ion FAB mass spectrum of the complex shows the three ions  $[cap-bpaCu_4(NO_3)_4(H_2O)_4]^+$ ,  $[cap-bpaCu_4(NO_3)_4]^+$  and  $[cap-bpaCu_4]^+$  with the characteristic isotopic distribution patterns.

The structure of  $1 \cdot C_6H_{14} \cdot MeOH \cdot 2H_2O$  consists of a cationic tetranuclear complex  $[cap-bpaCu_4(NO_3)_4(H_2O)_4]^{4+}$  with crystallographic mirror symmetry, four  $[NO_3]^-$  counter anions and solvent molecules. The structure of the cation  $[cap-bpaCu_4(NO_3)_4(H_2O)_4]^{4+}$  is illustrated in Fig. 1 as a top view. A similar structure of a tetracopper(II) complex with the cap-bpa ligand has been previously reported by Harrison [7]. The structure of Harrison's compound shows differently coordinated copper(II) atoms, however, while the four copper(II) centers of the present structure all have the same coordinative environment. As expected, the tetramethyl-cavitand (cap) unit is present in the bowl-shaped conformation with four bpa units attached to the sides of the cap unit by four methylene bridges. The orientation of each (bpa)Cu fragment is perpendicular to the bowl, resulting in one pyridyl arm of each bpa moiety positioned above the upper rim of the bowl and one below. All four copper centers are only coordinated to the triden-

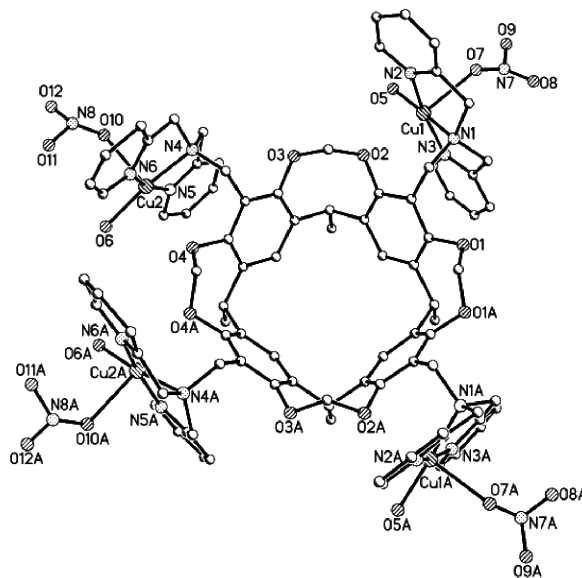


Fig. 1. Top view of the molecular structure of the cation in **1** (atoms with arbitrary radii).

tate bpa moiety. The coordination geometry of each copper atom is a square-pyramid, the four basal atoms coming from three nitrogen atoms of the bpa moiety and one oxygen atom of a water molecule, along with the apical oxygen atom from a  $\kappa^1$ - $NO_3^-$  anion. The Cu– $N_{py}$  bond lengths are in the range of  $1.939(13)$ – $2.002(9) \text{ \AA}$  [average  $1.973(10) \text{ \AA}$ ] and are typical for in plane Cu– $N_{py}$  bonds. The Cu– $N_{amine}$  bonds are  $2.000(9) \text{ \AA}$  [Cu(1)–N(1)] and  $2.025(9) \text{ \AA}$  [Cu(2)–N(4)] and are also normal. The water molecules *trans* to the amines bind to the central copper atoms with  $O_{water}$ –Cu– $N_{amine}$  bond angles of  $177.2(3)$  and  $173.4(4)^\circ$ . The Cu– $O_{water}$  bonds are with  $1.970(9) \text{ \AA}$  [Cu(1)–O(5)] and  $1.996(10) \text{ \AA}$  [Cu(2)–O(6)] typical for the Cu–O bond in the basal plane of a copper(II) ion. The average distance between the copper atom and the apical oxygen atom of the binding nitrate is  $2.384(15) \text{ \AA}$ , which is obviously longer than the basal Cu–O bonds, but slightly shorter than the apical Cu–O bonds for Cu– $O_{perchlorate}$  ( $2.51$ – $2.61 \text{ \AA}$ ) and Cu– $O_{acetate}$  ( $2.45$ – $2.64 \text{ \AA}$ ) in the related complex [7]. The average bond angle involving the apical oxygen atoms of  $90.8(5)^\circ$  is typical for the square-pyramidal copper(II) coordination geometry [13]. The average separation between two adjacent copper atoms is  $7.842 \text{ \AA}$ , which is too long for electron spin–spin coupling, thus ruling out magnetic exchange interactions between the copper centers in the complex.

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