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# Synthesis and Characterization of a Novel Tetranuclear Copper(II) Resorc[4]arene Complex Possessing Four Structurally Different Copper Centers

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## Introduction

Complexes that have several metal ions in close proximity are useful in the formation of supramolecular assemblies and metal catalysts. Metal ions offer a vast range of possibilities in the formation of supramolecules[1] and, furthermore, confer upon the resulting compound the properties and strength characteristic of a metal complex. The generation of metal−ligand architectures involves multiple-component recognition events and is achieved by metal ion addition to small bridging ligands[2] or large compounds that have multiple binding sites.[3] The synthesis of metal-assembled cage complexes exemplifies some of the processes involved in the formation of metal-assembled compounds.[4] Recently, we reported the synthesis and structure of a metal-assembled cage that forms in water by dimerization of two iminodiacetic acid functionalized resorc[4]arene-based hemispherical units.[5] Calixarene and resorcinarene molecules, when appended with ligating moieties, may be used to arrange coordinated metal ions in proximity to each other. Although there are numerous examples of metal complexes based on calixarene and resorcinarene ligands,[6] there are few multinuclear metal complexes that have metal ions in proximity to each other and that have metal coordination sites accessible via labile ligand dissociation.[7]

Dinuclear metal catalysts are extensively studied due to their metalloenzyme counterparts.[8] Complexes with more than two metal ions also exist in nature and are used for oxygen activation and photosynthesis.[9] One of the ligands used in model systems for bioinorganic catalysis is bis(pyridylmethylamine) (bpa).[10] Alkylation of the amine nitrogen has resulted in a series of ligands, often possessing further coordinating functional groups (e.g., carboxylate, phenolate, and imidazole moieties),[11] which are suitable for the creation of multinuclear metal complexes of iron and copper.[12] Both mono- and multinuclear metal complexes of bpa or derivatized bpa ligands have been the subjects of catalytic studies in the areas of phosphoester hydrolysis, amino acid−ester hydrolysis,[13] and organic molecule oxidation.[14] Metal complexes with one or two bpa's have been formed and sometimes have coordinatively labile ligands.[15]

In studies exploring the assembly of multinuclear metal complexes, we have synthesized the ligand bpa-res, a resorc[4]arene-based molecule functionalized with four bpa moieties. We have also characterized the multinuclear copper(II) complex

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of this ligand, $[Cu_4bpa\text{-}res(CH_3COO)_3(ClO_4)_2(H_2O)_2](ClO_4)_3$, **1**.[16] The crystal structure of **1** shows an unusual multinuclear complex, where each copper center is structurally different and two of the copper ions form a discrete binuclear complex. In solution, the copper ions of **1** remain coordinated to bpa-res, but exchange perchlorate, water, and acetate molecules.

## Experimental Section

**General Procedures.** All commercial reagents were used as supplied. IR spectra were recorded using a Perkin-Elmer instrument. $^1H$ (300 MHz) and $^{13}C$ (85 MHz) NMR shifts are reported in parts per million and were obtained using a Varian spectrometer. FAB mass spectra were obtained on a JEOL JMS-SX102A operating with Xe ionization, and ESI mass spectra were obtained on a Bruker APEX 47e Fourier transform ion cyclotron resonance mass spectrometer. Elemental analyses were performed by M-H-W Laboratories, Arizona. Magnetic susceptibility measurements over the temperature range 5−300 K were collected on a Quantum Design SQUID magnetometer and include a correction for the diamagnetic contribution calculated from Pascal's constants. *Caution! Perchlorate salts are potentially explosive and should be handled in small quantities.*

**Bpa-res.** To a stirred solution of tetrabromomethylresorc[4]arene[17] (1.0 g, 1.0 mmol) and powdered, anhydrous potassium carbonate (6.0 g, 43 mmol) in xylene (400 mL) was added bis(pyridylmethylamine) (0.84 g, 4.2 mmol), and the resultant mixture was heated under a nitrogen atmosphere (120 °C, 16 h). The cooled solution was filtered to remove undissolved inorganic material and the solvent removed under reduced pressure to yield a yellow oil. Addition of acetonitrile (100 mL) afforded a pale yellow powder that was recrystallized from chloroform−acetonitrile as very fine needles (0.89 g, 62%). $^1H$ NMR ($CDCl_3$): $\delta$ 8.47 (d, 8H, $J_{HH} = 4.8$ Hz, pyH6), 7.66 (td, 8H, $J_{HH} = 7.6$, 1.8 Hz, pyH5), 7.57 (d, 8H, $J_{HH} = 7.5$ Hz, pyH3), 7.12 (m, 16H, ArH, pyH4), 5.15 (d, 4H, $J_{HH} = 7.2$ Hz, $OCH_2O$ outer), 4.93 (q, 4H, $J_{HH} = 7.5$ Hz, C*H*$CH_3$), 3.87 (d, 4H, $J_{HH} = 7.2$ Hz, $OCH_2O$ inner), 1.68 (d, 12H, $J_{HH} = 7.5$ Hz, $CHCH_3$). $^{13}C$ {$^1H$} NMR ($CDCl_3$): $\delta$ 160.4, 154.1, 148.9, 138.7, 136.5, 123.4, 123.1, 122.0, 119.6, 98.9, 60.4, 48.2, 31.3, 16.4. Anal. Calcd for $C_{88}H_{84}N_{12}O_8{\cdot}CHCl_3$: C, 68.65; H, 5.50; N, 10.79. Found: C, 69.25; H, 5.85; N, 10.84. FAB MS: *m/z* = 1437 $M^+$.

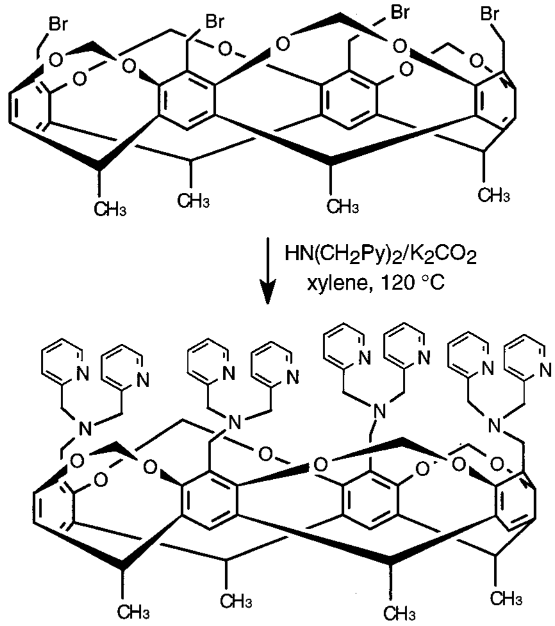
**[Cu₄bpa-res(CH₃COO)₃(ClO₄)₂(H₂O)₂](ClO₄)₃, 1.** The ligand bpa-res (100 mg, 0.0695 mmol) was dissolved in chloroform (2 mL) and added to an acetonitrile (15 mL) and water (5 mL) solution of copper(II) acetate monohydrate (58 mg, 0.29 mmol) and sodium perchlorate (80 mg, 0.656 mmol). The resulting deep blue solution was stirred (1 h), filtered, and layered with isopropyl alcohol. After 2 days, large, deep blue, prismatic crystals of **1** formed (132 mg, 0.0515 mmol, 74%). IR (KBr disk, $cm^{-1}$): 1576, 1405, 1099, 769, 623. Magnetic moment $\mu_{eff} = 1.87\ \mu_B$ at 300 K. Anal. Calcd for **1**, $C_{88}H_{84}N_{12}O_8Cu_4(ClO_4)_5(C_2H_3O_2)_3(H_2O)_5(C_2H_6O)(C_3H_8O)$: C, 46.40; H, 4.60; N, 6.56. Found: C, 46.13; H, 4.82; N, 6.37.

**Table 1.** Crystal Data and Structure Refinement for **1**

| | | | |
|---|---|---|---|
| empirical formula | $C_{99}H_{101}Cl_5Cu_4N_{12}O_{41}$ | $V$ (Å$^3$) | 7266(4) |
| fw | 2545.33 | $Z$ | 2 |
| space group | $P\bar{1}$ | $\rho_{calcd}$ (g cm$^{-3}$) | 1.327 |
| $a$ (Å) | 18.602(3) | $\mu$(Mo K$\alpha$) (mm$^{-1}$) | 0.740 |
| $b$ (Å) | 18.964(4) | $T$ (K) | 293(2) |
| $c$ (Å) | 21.684(9) | $\lambda$ (Å) | 0.710 73 |
| $\alpha$ (deg) | 89.79(3) | R1 [$I > 2\sigma(I)$][a] | 0.1056 |
| $\beta$ (deg) | 88.02(2) | wR2[b] | 0.3058 |
| $\gamma$ (deg) | 71.90(2) | | |

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

**Scheme 1**



**X-ray Structural Determination.** Crystal data and details of the data collection are given in Table 1. In addition, the Supporting Information contains crystallographically determined parameters. The deep blue crystals of **1** rapidly lose solvent when removed from their mother liquor, and therefore the X-ray data collection was performed on a crystal (0.6 × 0.4 × 0.3 mm) glued to the wall of a sealed glass capillary containing mother liquor. The data for **1** were collected using a Siemens R3m/V automated diffractometer with graphite-monochromated Mo K$\alpha$ radiation ($\lambda = 0.710\ 73$ Å). Lattice parameters were calculated using a least-squares procedure involving carefully centered reflections. The solution and refinement were carried out using the SHELXTL PC program package.[18] Of the 13 884 total number of reflections, 13 348 were unique and used for refinement with 1440 parameters. A partial structure was obtained using direct methods, and the structure was completed using Fourier methods. The non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms bound to carbon atoms were calculated, and the hydrogen atoms were allowed to ride on their neighboring carbon atoms during the refinement. There were loosely held solvent water molecules in the structure.

## Results and Discussion

The new bpa-res ligand is synthesized by reacting tetrabromomethylresorc[4]arene with bpa in xylene in the presence of potassium carbonate, and is recrystallized from a chloroform−acetonitrile mixture before use (Scheme 1). The bpa-res ligand has properties of interest to the field of catalysis because it provides (1) a tridentate $N_3$ donor set suitable for the coordina-

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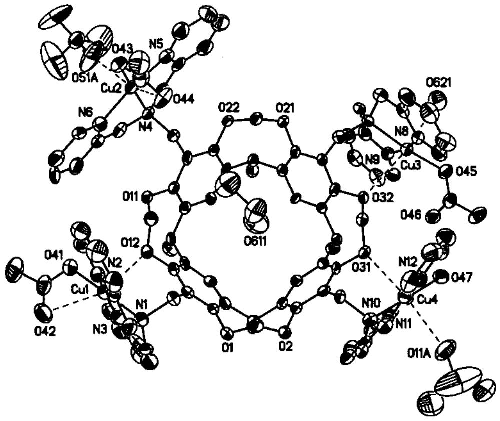

**Figure 1.** Top view of the molecular structure (30% ellipsoids) for **1** showing the coordination of the four copper ions. The dashed lines represent long copper−ligand bonds. Hydrogens, three perchlorate anions, water molecules, and an isopropyl alcohol molecule have been removed for clarity.

tion of catalytically active metal ions such as iron, copper, and zinc, (2) a preorganized template of ligands situated to permit proximity between four metal centers, and (3) a cavity with known molecular recognition properties[19] positioned by a site for multinuclear metal coordination.

Reacting bpa-res with copper(II) acetate monohydrate and adding sodium perchlorate gives the tetranuclear complex $[Cu_4bpa\text{-}res(CH_3COO)_3(ClO_4)_2(H_2O)_2](ClO_4)_3$, **1**. Complex **1** crystallizes in the triclinic space group and exhibits no internal symmetry within the molecule (Figure 1). Along with water molecules of crystallization around **1**, there is an ethanol in the resorc[4]arene bowl. Although it might be expected that the four copper centers would be crystallographically unique, the existence of four, structurally different copper ions, each with a different coordination sphere, is clearly unexpected. In common with all four copper centers is the meridonal coordination of the tridentate bpa moiety. The $Cu-N_{py}$ bonds range from 1.95 to 1.99 Å (average 1.97 Å) and are typical for in-plane $Cu-N_{py}$ bonds. The $Cu-N_{amine}$ bonds are 2.04 (Cu1−N1, Cu2−N4, Cu3−N7) and 2.02 (Cu4−N10) Å and are also typical. Along with the nitrogen ligation in the equatorial plane of the copper atoms is oxygen from acetate (Cu1−O41 1.93 Å, Cu2−O43 1.98 Å, and Cu3−O45 1.96 Å) or water (Cu4−O47 1.96 Å) molecules. Two of the acetates are coordinated in a bidentate manner, while the other is monodentate and part of a hydrogen-bonded network ($O47_{water}\cdots O46_{acetate}$ 2.51 Å) between Cu3 and Cu4.

All four copper atoms also have copper−oxygen equatorial bonds that are longer than the axial bonds. For example, the equatorial $Cu-O_{acetate}$ bonds are 2.61 (Cu1−O42) and 2.51 (Cu2−O44) Å, the $Cu-O_{water}$ bond is 2.59 Å (Cu3−O62), and the $Cu-O_{perchlorate}$ bonds are 2.45 (Cu2−O51A) and 2.64 (Cu4−O11A) Å. Also of note are the equatorial $Cu-O_{ether}$ bonds that are from three of the copper atoms to the etheric oxygens of the resorcinarene ligand (Cu1−O12 2.51 Å, Cu3−O32 2.73 Å, Cu4−O31 2.63 Å). Although very long, these three $Cu-O_{ether}$ bonds are typical for apical, etheric, oxygen ligand atoms to copper(II).[20] During the formation of **1**, acetate ions are present in 2-fold excess, so the reason Cu2 is without acetate cannot be attributed to a deficiency in acetate ions.

It is of interest to note that two of the copper centers (Cu3 and Cu4) within the tetranuclear complex are turned toward each other due to a $Cu3-O_{aacetate}-H_2O-Cu4$ bonding network. This generates in the solid state a discrete, asymmetric, binuclear complex. The Cu3···Cu4 distance of 6.37 Å is too long for a simple monatomic ligand to bridge, but can be spanned by a suitable bridging group. Internuclear distances between copper atoms across the resorcinarene bowl are longer and approximately 14 Å. The hydrogen-bonding network is expected to be broken in polar solvents.

An additional structural feature of **1** is the orientation of each Cu(bpa) moiety with respect to the bowl. For those copper centers possessing bonds to ether atoms of the bowl, the orientation of the Cu(bpa) fragment is perpendicular, resulting in one pyridyl arm positioned above the upper rim of the bowl and one below. However, Cu2 behaves differently, orientating itself parallel to the bowl, such that both of its pyridyl arms reside above the upper rim. This directs the fourth copper coordination site in the equatorial plane upward and away from the bowl, in a position suitable to receive additional ligands. Conceivably, by introducing a bridging ligand, two hemispherical resorcinarenes may be assembled into a cage complex.

To further investigate the solution behavior of **1**, we undertook a mass spectrometric study using electrospray ionization. Singly charged ionic species exemplifying the number of counteranions observed in the crystal were not detected. However, intense triply charged species centered at *m*/*z* 676 and 688 attributed to the ions $[Cu_4L(ClO_4)(OAc)_4]^{3+}$ and $[Cu_4L(ClO_4)_2(OAc)_3]^{3+}$, respectively, and a doubly charged species at *m*/*z* 1023, $[Cu_4L(OAc)_6]^{2+}$, were observed. A range of other triply charged and doubly charged species containing various amounts of acetate and perchlorate were also detected, but as small signals. This study serves to demonstrate that in solution the acetate and perchlorate ions are easily displaced, suggesting **1** may be suitable for the generation of larger resorcinarene-based metal assemblies.

The room-temperature magnetic moment per copper center is 1.87 $\mu_B$ and is typical for copper(II). The magnetic susceptibility of **1** over the temperature range 5−300 K obeys Curie law and shows no significant indication of intra- or intermolecular couplings; that is, all four copper centers behave as magnetically isolated. Significant magnetic exchange interactions are not expected to occur between copper centers in the discrete binuclear complex $Cu-O_{acetate}-H_2O-Cu$ that exists within the tetranuclear complex.

In summary, the bpa-res ligand, capable of bringing together four metal ions, has been synthesized and its copper complex structurally characterized. The copper complex has four metal ions in proximity to each other and to a molecular recognition site.

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**Supporting Information Available:** An X-ray crystallographic file in CIF format and magnetic data for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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