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Synthesis, Spectroscopy, and Solid-State Structural Characterization of the Hexanuclear Copper Macrocycle [$Cu_6Cl_6(\mu\text{-PCHP})_6$]**

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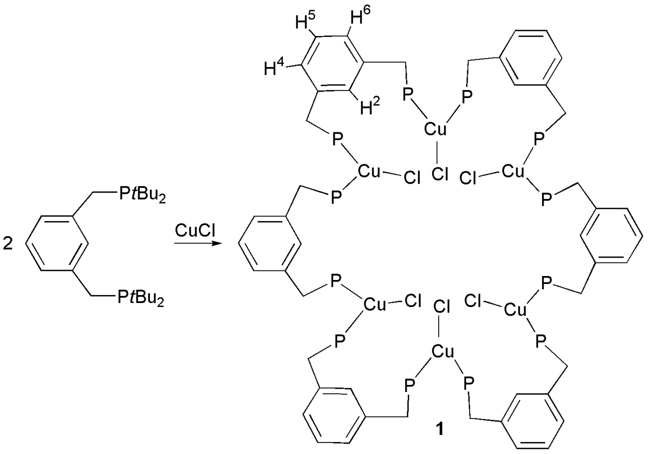
The study of late-transition-metal complexes with electron counts of d^8–d^{10} has been of significant interest as a result of their interesting photophysical and photoredox chemistry.[1–7] Extensive study of d^{10} systems has allowed an increased understanding of, and control over, photophysical properties, and it has been suggested that the rich luminescent behavior of many closed-shell systems arises from weak metal–metal interactions.[1–3, 5, 8, 9] Increasing interest in the preparation and study of late-transition-metal polynuclear systems stems, in part, from possible applications as therapeutic agents (e.g., photocleavage of DNA), photovoltaics, photocatalysts, and tunable chemical sensors.[2, 10–12] One challenge to both the study and the understanding of the properties of late-transition-metal polynuclear complexes is the controlled preparation of new structural motifs. Tetranuclear copper cubanes have been the focus of some attention for Group 11 transition metals,[4] and other polynuclear copper complexes with variable structural patterns are of interest and have been reported.[13–19] Closely related to work reported herein are penta- and tetranuclear copper macrocycles and recently reported high nuclearity gold systems.[12, 20–22] We now report the synthesis and characterization (including solid-state X-ray diffraction analysis) of a novel hexanuclear copper macrocycle of the type [$Cu_6Cl_6(\mu\text{-PCHP})_6$] (PCHP = 1,3-$(CH_2PtBu_2)_2C_6H_4$).

The reaction of CuCl with the bisphosphane 1,3-$(CH_2PtBu_2)_2C_6H_4$ (PCHP) in a 1:2 stoichiometry yields the hexanuclear complex $Cu_6Cl_6(\mu\text{-PCHP})_6$ (**1**; Scheme 1). Similar to reactions of aryl Cu^I compounds with bis(diphenylphosphanyl)methane in which metal:ligand stoichiometry is important, slow addition of the CuCl to a solution (CH_2Cl_2) of the PCHP ligand is important to the success of the reaction.[23] Complex **1** is a macrocycle that incorporates 48 atoms into the large ring structure (if the aryl moieties are each counted as contributing 3 atoms to the macrocycle) and in which each copper atom is bound by phosphorus atoms from two different PCHP ligands. Complex **1** was characterized by elemental analysis, X-ray crystallography, cyclic voltammetry experiments, as well as UV/Vis, ^1H, ^{13}C, and ^{31}P NMR spectroscopy.



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Scheme 1. Preparation of the macrocycle $Cu_6Cl_6(\mu\text{-PCHP})_6$ (**1**; P = $PtBu_2$).

Broad resonances in the ^1H NMR spectrum of **1** at room temperature in CD_2Cl_2 reveal a fluxional process. At −10 °C sharp resonances are observed with a singlet at $\delta = 8.68$ ppm (aromatic H2), doublets at $\delta = 8.25$ and 7.04 ppm (aromatic H4 and H6), a triplet at $\delta = 7.13$ ppm (aromatic H5), multiplets at approximately $\delta = 3.0$ ppm corresponding to the methylene protons, and four phosphane *t*Bu resonances between $\delta = 1.0$ and 1.8 ppm. The aromatic C2–H2 bonds

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Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

remain intact as indicated by the downfield resonance at $\delta = 8.68$ ppm. However, agostic bonding is unlikely because of the distance from the copper centers.[24] The ^{1}H NMR spectrum obtained at $-10\,^\circ$C is consistent with C_6 molecular symmetry, with all six PCHP ligands equivalent and a lack of mirror symmetry (all methylene protons and *t*Bu groups are inequivalent). At temperatures greater than $-10\,^\circ$C a fluxional process introduces mirror symmetry, as shown by the methylene and *t*Bu protons becoming equivalent in the ^{1}H NMR spectra (consistent with overall D_{6h} symmetry; $\Delta G^{\neq} = 51$ kJ mol^{-1}). At temperatures less than $-10\,^\circ$C the ^{1}H NMR spectra broaden, presumably as a result of the conversion from C_6 to lower molecular symmetry. However, the resonances are broad down to $-70\,^\circ$C, and the slow exchange regime has not been accessed. The ^{31}P NMR spectra (CD_2Cl_2) obtained between $-10\,^\circ$C and room temperature are consistent with the suggested fluxionality of complex **1**. At $-10\,^\circ$C the ^{31}P NMR spectrum of **1** reveals an AB pattern ($^2J_{P,P} = 126$ Hz) with resonances at $\delta = 38.6$ and 36.4 ppm, consistent with C_6 molecular symmetry (that is, the two phosphorus atoms on each copper atom are inequivalent). Warming a solution of **1** in C_6D_6 to $70\,^\circ$C results in coalescence of the signals into a single broad phosphane resonance.

Cyclic voltammetry of complex **1** in dichloromethane reveals an irreversible oxidation at $E_{p,a} = 1.04$ V ($E_{p,a}$ = anodic peak potential; irreversible at scan rates up to 1 V s^{-1}). The observation of a single oxidation could imply little electronic communication between copper redox centers. A second irreversible oxidation is observed at $E_{p,a} = 1.75$ V that is presumably a consequence of the formation of decomposition products. The electronic absorption spectrum of **1** in CH_2Cl_2 reveals maximum absorption at 232 nm ($\varepsilon = 1.07 \times 10^5$ L mol^{-1} cm^{-1}). Similar absorptions of related bisphosphane Cu^I complexes have been attributed to metal–metal 3d → 4s transitions.[25] The emission spectrum of complex **1** in CH_2Cl_2 shows maximum absorption at 354 nm.

The solid-state structure of **1** was studied by X-ray diffraction (Figures 1 and 2).[26] The copper clusters possess crystallographically imposed hexagonal symmetry, and there are two crystallographically distinct cluster molecules per unit cell. The macrocycles are stacked one directly over another to form a cylinder with an open cavity. At the center of the cylinder are infinite chains of disordered acetonitrile molecules, which coincide with the threefold symmetry axis. Disordered CH_2Cl_2 molecules occupy sites within the channel as well as surrounding the periphery of the clusters. There are nine molecules of CH_2Cl_2 and one molecule of MeCN per copper macrocycle. The inside diameter of the cylinder is approximately 4.5 Å while the outside diameter of the macrocycle is approximately 24 Å (Figure 3). No suitable disorder model could be found for the solvent molecules (CH_2Cl_2 and CH_3CN) so their associated electron density was removed with the SQUEEZE function of PLATON (see Supporting Information). The Cu1–P1 and Cu–P2 bond lengths are 2.2598(4) and 2.639(5) Å (2.2591(5) and 2.2627(5) Å for the second unique molecule), and the

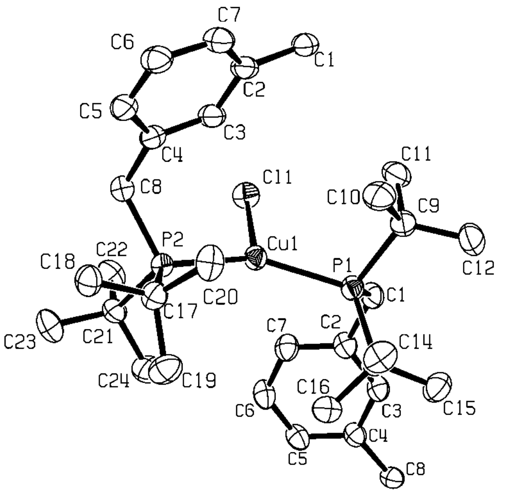

Figure 1. Structure of a section of complex **1** with thermal ellipsoids at the 50% level.

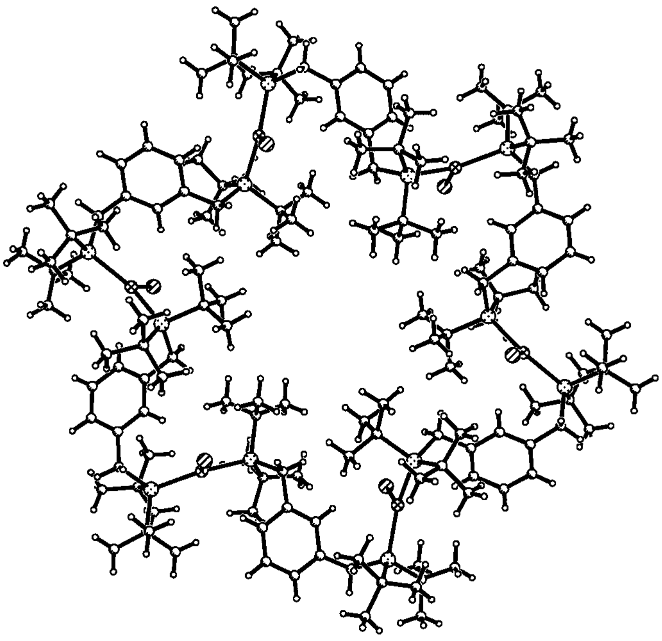

Figure 2. Structure of a single molecule of **1**.

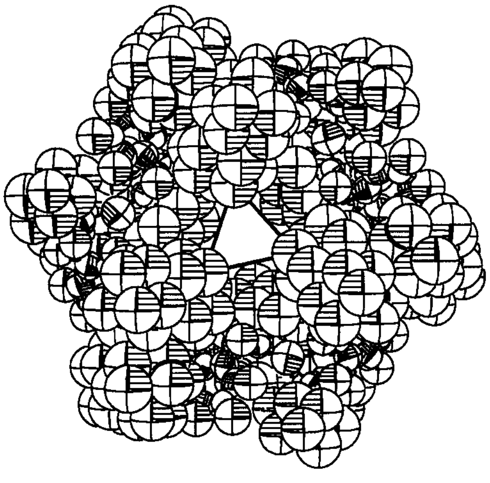

Figure 3. Structure of complex **1** with thermal ellipsoids at the 100% probability level illustrating the inside channel of the solid-state structure.

Cu1−Cl1 bond length is 2.3235(5) Å (2.3293(5) Å for the second unique molecule). The copper coordination geometry is best described as distorted trigonal planar with P2-Cu1-P1, P2-Cu1-Cl1, and P1-Cu1-Cl1 bond angles of 147.100(17), 107.385(16), and 105.46(17)° (146.284(18), 106.747(17), and 106.969(17) for the second unique molecule), respectively. The sum of the bond angles around Cu1 is 359.95(3)° (360.00(3)° for the second unique molecule).

In related Cu^I systems with chelating bis(dicyclohexylphosphanyl)methane ligands, the formation of three-coordinate binuclear complexes with close copper–copper contacts is observed in the solid-state.[25] In contrast, binuclear four-coordinate copper centers with bridging bis(diphenylphosphanyl)methane ligands have longer copper⋯copper separations as do three-coordinate systems with $(i\mathrm{Pr}_2)\mathrm{PCH}_2\mathrm{P}(i\mathrm{Pr})(\mathrm{H})$ ligands.[27, 28] The large bite angle of the PCHP ligand affords the higher nuclearity (compared with the bi- and trinuclear systems discussed immediately above) hexanuclear copper complex **1**, and the unique geometry effectively insulates the complex from close intramolecular Cu⋯Cu interactions. Additionally, the steric bulk of the *t*Bu groups prevents intermolecular Cu⋯Cu interactions in the solid-state (and presumably in solution). Therefore, assignment of the emission to any form of copper⋯copper interaction can be reliably ruled out.

In summary, the new hexanuclear copper complex $[\mathrm{Cu}_6\mathrm{Cl}_6(\mu\text{-PCHP})_6]$ has been synthesized and fully characterized. The novel macrocyclic structure is a result of the large bite angle of the PCHP ligand, as indicated by an X-ray crystallographic study. In addition, the solution-phase dynamics of complex **1** have been studied by variable-temperature NMR spectroscopy.

Experimental Section

1:. The $1,3\text{-}(\mathrm{CH}_2\mathrm{P}t\mathrm{Bu}_2)_2\mathrm{C}_6\mathrm{H}_4)$ ligand (0.4144 g, 1.05 mmol) was dissolved in CH_2Cl_2 (ca. 30 mL). A CuCl suspension (0.0523 g, 0.528 mmol in CH_2Cl_2 (ca. 20 mL) was added dropwise to this solution. The resulting mixture was stirred overnight, and the solvent volume was then reduced under vacuum to approximately 10 mL. The product was precipitated upon addition of hexanes (approximately 10 mL) and isolated by vacuum filtration through a medium porosity frit. The resulting white solid was washed with hexanes and diethyl ether and dried under vacuum (0.160 g, 0.054 mmol, 61 %). Full characterization details can be found in the Supporting Information.

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[26] Crystal data for **1**: Crystals were grown by slow diffusion of hexanes into a solution of **1** in CH_2Cl_2. Colorless block ($0.30 \times 0.26 \times 0.22$ mm^3), rhombohedral, space group $R\bar{3}$, $a = 41.098(2)$, $c = 20.5124(13)$ Å, $V = 30005(3)$ Å^3, $\rho_{\mathrm{calcd}} = 1.251$ g cm^{-3}, $2\theta_{\max} = 54.98°$, $\mathrm{Mo}_{\mathrm{K}\alpha}$, $\lambda = 0.71073$ Å, 173(2) K, of 62796 reflections collected, 15284 are independent and 11493 have $I > 2\sigma(I)$, Residuals $[I > 2\sigma(I)]$: $R1 = 0.0325$, $wR2 = 0.0811$. The structure was solved and refined using SHELXTL-plus V5.10 (SHELXTL-Plus V5.10, Bruker Analytical X-Ray Systems, Madison, WI, **1998**). Solvent molecules found in the voids of the structure were found to be disordered. There are CH_2Cl_2 molecules located close to metal–organic clusters, which are moderately disordered. There also appears to be highly disordered MeCN molecules located along the center of the tubular cavity. All electron density associated with the solvent molecules was artificially removed with the SQUEEZE function of the PLATON program. (A. L. Spek, *Acta. Crystallogr. Sect. A* **1990**, *46*, C34; A. L. Spek, PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, **2000**). This electron density was the equivalent to 54 CH_2Cl_2 and 6 MeCN molecules, which were included in the final calculation of molecular weight, density, and associated parameters per unit cell, leaving a void of 8818 Å^3. CCDC-176679 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit @ccdc.cam.ac.uk).

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