

I and suggest that transannular interaction may play a significant role in the latter.

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Preparation and Structure of the $[\text{Cu}_5(\text{C}_6\text{H}_5)_6]^-$ Anion

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The reaction between phenyllithium and cuprous bromide in ethers has been reported to yield phenylcopper, a white, pyrophoric, and presumably polymeric solid.^{1,2} When the reaction is carried out with excess phenyllithium, one gets a solution from which crystalline adducts such as $(\text{PhCu})_4\text{PhLi}\cdot 3.5\text{Et}_2\text{O}$ can be isolated.¹ We have investigated this system and report here the isolation and structure determination of a new pentanuclear copper cluster, $[\text{Cu}_5\text{Ph}_6]^-$, as its $[\text{Li}(\text{THF})_4]^+$ and $[\text{Li}(\text{PMDTA})(\text{THF})]^+$ salts (PMDTA = pentamethyldiethylenetriamine).

$[\text{Li}(\text{THF})_4]^+[\text{Cu}_5\text{Ph}_6]^-$ was prepared by treating a cold (-20°C) suspension of CuBr (1 g, 7 mmol) in diethyl ether with a solution of freshly prepared phenyllithium (9.6 mL, 0.97 M in Et_2O , 9.3 mmol). The yellow suspension was allowed to warm to room temperature, when it formed first a clear yellow solution and then a pale yellow precipitate in a yellow supernatant. The precipitate was isolated and recrystallized from a THF/ Et_2O mixture (50:50) to give pale yellow prisms.³ The corresponding $[\text{Li}(\text{PMDTA})(\text{THF})]^+$ salt was isolated under similar conditions.⁴ Salts of $[\text{Cu}_5\text{Ph}_6]^-$ are somewhat unstable, decomposing at room temperature in several days.

$[\text{Li}(\text{THF})_4]^+[\text{Cu}_5\text{Ph}_6]^-$ crystallizes in the monoclinic space group $P2_1/n$,⁵ with the following unit cell parameters: $a = 17.112$ (10) Å, $b = 13.920$ (6) Å, $c = 21.969$ (4) Å, $\beta = 105.98$ (4)°, $\rho(\text{calcd}) = 1.42$ g cm^{-3} for $Z = 4$. X-ray diffraction data were collected on a Syntex $P2_1$ diffractometer with $\text{Mo K}\alpha$ radiation with a $\theta/2\theta$ scan mode. The positions of the five copper atoms were obtained by direct methods,⁶ and the rest of the structure

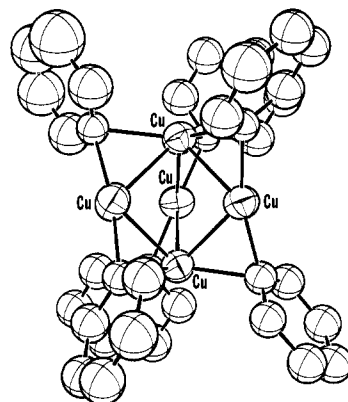


Figure 1. View of the $[\text{Cu}_5\text{Ph}_6]^-$ cluster as found in the $[\text{Li}(\text{THF})_4]^+$ salt.

Table I. Average Distances and Angles in the $[\text{Cu}_5\text{Ph}_6]^-$ Anion

	$[\text{Li}(\text{THF})_4]^+$ salt	$[\text{Li}(\text{PMDTA})-$ $(\text{THF})]^+$ salt
Cu(ax)-Cu(eq), Å	2.452 (4)	2.446 (7)
Cu(eq)···Cu(eq), Å	3.165 (4)	3.137 (8)
Cu(ax)···Cu(ax), Å	3.269 (4)	3.288 (6)
Cu(ax)-C, Å	2.19 (2)	2.14 (3)
Cu(eq)-C, Å	1.99 (2)	1.96 (4)
Cu(ax)-C-Cu(eq), deg	71.6 (7)	73.1 (12)
C-Cu(ax)-C, deg	119.1 (9)	119.5 (14)
C-Cu(eq)-C, deg	166.6 (9)	168.1 (15)

was solved by standard heavy-atom techniques.⁷ Full-matrix least-squares refinement (with Cu atoms assigned anisotropic temperature factors) resulted in a final R factor of 0.071 for 1846 nonzero reflections [$I > 3\sigma(I)$]. The structure analysis of $[\text{Li}(\text{PMDTA})(\text{THF})]^+[\text{Cu}_5\text{Ph}_6]^-$ was carried out in an analogous fashion,⁸ yielding a final R factor of 0.069. The $[\text{Cu}_5\text{Ph}_6]^-$ clusters in the two salts are virtually identical. In the following discussion, distances and angles quoted are averaged over both structure determinations.

The $[\text{Cu}_5\text{Ph}_6]^-$ anion (Figures 1 and 2) has a pentanuclear skeleton that is best described as a "squashed" trigonal bipyramid, with the Cu(ax)-Cu(eq) distances [average 2.449 (9) Å] much shorter than the Cu(eq)-Cu(eq) distances [average 3.151 (6) Å]. The six phenyl groups bridge the Cu(ax)-Cu(eq) edges of the trigonal bipyramid. Distances and angles in the core of the cluster are given in Table I. The $[\text{Li}(\text{THF})_4]^+$ cation has a normal tetrahedral geometry with an average Li···O distance of 1.93 (3) Å, while in $[\text{Li}(\text{PMDTA})(\text{THF})]^+$ the Li^+ ion is coordinated to one O and three N atoms in a distorted tetrahedral fashion.

The three equatorial Cu atoms in $[\text{Cu}_5\text{Ph}_6]^-$ are approximately linearly coordinated [average C-Cu-C angle = 167 (1)°], while the two axial Cu atoms are roughly trigonal planar (the axial Cu atoms are displaced by 0.2 Å from the planes of the three bridging C atoms). The bridging phenyl groups are, as expected,⁹ essentially perpendicular (83°) to the Cu-Cu vectors and are situated in a slightly asymmetric position [average C-Cu(ax) = 2.17 (2) Å, C-Cu(eq) = 1.98 (1) Å]. The gross structure of the cluster is

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(3) $[\text{Li}(\text{THF})_4]^+[\text{Cu}_5\text{Ph}_6]^-$ (Anal. Calcd. for $\text{C}_{52}\text{H}_{62}\text{O}_4\text{Cu}_5\text{Li}$ (mol wt 1074.7): C, 58.1; H, 5.77. Found: C, 57.5; H, 5.25%): IR (Nujol) 3040 w, 1560 w, 1411 m, 1300 w, 1259 m, 1239 w, 1168 w, 1150 w, 1090 m, 1072 m, 1042 s, 912 w, 888 m, 798 m, 718 s, 699 s, 446 m cm^{-1} .

(4) The $[\text{Li}(\text{PMDTA})(\text{THF})]^+$ salt of $[\text{Cu}_5\text{Ph}_6]^-$ was prepared as follows: To a suspension of CuBr (1 g, 7 mmol) in tetrahydrofuran was added at -20°C , dropwise with stirring, a solution of phenyllithium (14.4 mL, 0.97 M in Et_2O , 14 mmol). The suspension was allowed to warm slowly to room temperature with continued stirring, when a clear yellow solution had formed. To this solution was added dropwise pentamethyldiethylenetriamine (1 mL) with vigorous stirring. The clear yellow solution was evaporated in vacuo to dryness and the yellow tarry solid titrated with diethyl ether (30 mL) to remove LiBr . This gave a fine pale yellow powder that recrystallized from tetrahydrofuran-diethyl ether (50:50) (ca. 30 mL). Anal. Calcd. for $\text{C}_{50}\text{H}_{61}\text{ON}_3\text{Cu}_5\text{Li}$ (mol wt 1031.7): C, 57.0; H, 5.91. Found: C, 56.9; H, 5.67. IR (Nujol) 3035 s, 1680 w, 1560 w, 1412 w, 1282 m, 1261 m, 1150 w, 1120 s, 1091 m, 1030 s, 935 w, 910 w, 890 w, 857 w, 832 w, 790 m, 715 s, 698 s, 451 m cm^{-1} .

(5) Space group $P2_1/n$ is an alternative, nonstandard setting of $P2_1/c$ (No. 14) with equivalent positions (x, y, z); ($-x, -y, -z$); ($1/2 + x, 1/2 - y, 1/2 + z$); ($1/2 - x, 1/2 + y, 1/2 - z$).

(6) MULTAN: a system of computer programs for the automatic solution of crystal structures from X-ray diffraction data (Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A* **1971**, *A27*, 368).

(7) Major computations in this work were performed on the USC IBM 370/158 computer using CRYM, an amalgamated set of crystallographic programs developed by R. E. Marsh's group at the California Institute of Technology.

(8) $[\text{Li}(\text{PMDTA})(\text{THF})]^+[\text{Cu}_5\text{Ph}_6]^-$ crystallizes in the monoclinic space group Cc , with $a = 13.752$ (7) Å, $b = 19.647$ (20) Å, $c = 19.797$ (10) Å, $\beta = 98.93$ (4)°, $\rho(\text{calcd}) = 1.30$ g cm^{-3} for $Z = 4$. As in the structure analysis of the $[\text{Li}(\text{THF})_4]^+$ salt, the five Cu atoms were located with direct methods and the rest of the structure was solved by standard techniques. Full-matrix least-squares refinement (Cu atoms anisotropic) yielded a final R factor of 0.069 for 1570 nonzero reflections [$I > 3\sigma(I)$].

(9) Camus, A.; Marslich, N.; Nardin, G.; Randaccio, L. *Inorg. Chim. Acta* **1977**, *23*, 131.

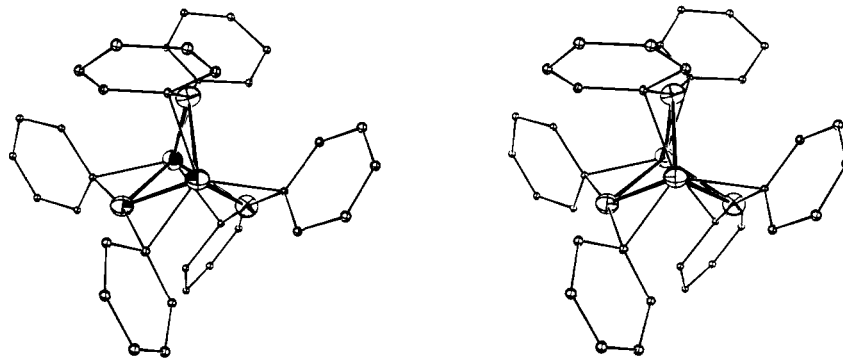
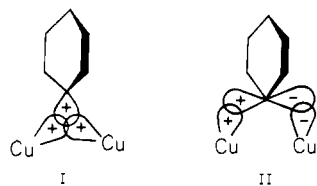


Figure 2. Stereoscopic view of the $[\text{Cu}_5\text{Ph}_6]^-$ cluster as found in the $[\text{Li}(\text{PMDTA})(\text{THF})]^+$ salt. This molecular plot is drawn in a different orientation from the one shown in Figure 1; however, the $[\text{Cu}_5\text{Ph}_6]^-$ clusters in the two salts are virtually identical.

rather similar to that of $[\text{Cu}_5(\text{S}-t\text{-Bu}_6)]^-$.¹⁰

Although many copper/aryl clusters with substituted phenyl groups are known,¹¹⁻¹⁴ this work represents, to our knowledge, the first structural characterization of a copper cluster with unsubstituted phenyl ligands. All previous structure determinations¹¹⁻¹⁴ involved bidentate aryl ligands with lone-pair-containing substituents (such as NMe_2 or OMe).¹⁵ For the parent phenyl ligand, other known bridging structures include those of Al_2Ph_6 ,¹⁶ $\text{Al}_2\text{Ph}_2\text{Me}_4$,¹⁷ $(\text{LiPh-TMED})_2$ ¹⁸ (TMED = tetramethylethylenediamine), $[\text{Li}(\text{TMED})]_2[\text{Mg}_2\text{Ph}_6]$,¹⁹ and the osmium cluster complex $\text{Os}_3(\text{CO})_8(\text{PPh}_2)(\text{Ph})(\text{PPhC}_6\text{H}_4)$.²⁰ In all cases, the perpendicular bridging configuration of the phenyl ring was found.^{11-14,16-20}

The bonding in the copper-phenyl-copper bridge, as pointed out earlier,^{13,21} is probably a combination of three-center interactions involving the two Cu atoms and the carbon sp^2 and p orbitals (i.e., I and II respectively). Interaction II is the factor



most likely responsible for maintaining the phenyl group in a perpendicular orientation, while interaction I implies some degree of Cu-Cu bonding. The question of Cu-Cu interactions in Cu clusters has been discussed by Mehrotra and Hoffmann,²² who concluded that, in many cases, weak Cu-Cu interactions exist. In $[\text{Cu}_5\text{Ph}_6]^-$, one can probably assume that the short $\text{Cu}(\text{ax})-\text{Cu}(\text{eq})$ interactions are weakly bonding but that the long Cu-

$(\text{eq})-\text{Cu}(\text{eq})$ interactions are essentially nonbonding.

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Registry No. $[\text{Li}(\text{THF})_4]^+[\text{Cu}_5\text{Ph}_6]^-$, 81027-54-5; $[\text{Li}(\text{PMDTA})(\text{THF})]^+[\text{Cu}_5\text{Ph}_6]^-$, 81027-56-7.

Supplementary Material Available: Listing of the final atomic parameters for the $[\text{Cu}_5\text{Ph}_6]^-$ anion in $[\text{Li}(\text{THF})_4]^+[\text{Cu}_5\text{Ph}_6]^-$ and in $[\text{Li}(\text{PMDTA})(\text{THF})]^+[\text{Cu}_5\text{Ph}_6]^-$ (2 pages). Ordering information is given on any current masthead page.

Initial Fluorescence Depolarization of Tyrosines in Proteins

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A wide variety of experimental and theoretical techniques are providing an increasingly detailed picture of the internal dynamics of proteins.¹ This information is essential for an understanding at the molecular level of the relationship between structure and function for processes requiring protein flexibility. Both fluorescence depolarization^{2,3} and ¹³C nuclear magnetic resonance (NMR) relaxation experiments⁴⁻⁶ can provide information about fast (picosecond-nanosecond) protein motions. Theoretical studies⁷ using molecular dynamics computer simulation methods have

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