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Synthesis of an Unprecedented Bicapped Adamantoid $[Cu_6(\mu_2\text{-}I)(\mu_3\text{-}I)_4(\mu_4\text{-}I)(m\text{-}tolyl_3P)_4(CH_3CN)_2]$ Cluster

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The reaction of copper(I) iodide with tri-*m*-tolylphosphine (*m*-tolyl$_3$P) in acetonitrile yielded the cluster $[Cu_6(\mu_2\text{-}I)(\mu_3\text{-}I)_4(\mu_4\text{-}I)(m\text{-}tolyl_3P)_4(CH_3CN)_2]$ (**1**), with a bicapped adamantoid geometry. In this compound, four Cu atoms are coordinated to four terminally bonded *m*-tolyl$_3$P ligands, two Cu atoms are bonded to two CH_3CN ligands, and iodide ligands have μ_2-I, μ_3-I, and μ_4-I bonding modes. This compound has four CuI_3P and two CuI_3N cores, and geometry around each Cu center is distorted tetrahedral.The polarizable iodide ligand and the position of the methyl group in the phenyl ring attached to the P atom appear to have played the pivotal role in the formation of monomeric bicapped adamantoid geometry, which is unique in copper chemistry.

Organophosphorus compounds, such as tertiary phosphines (PR_3), phosphole (DMPP), and bis(diphenylphosphino)methane (dppm), react with copper(I) halides to form tetranuclear complexes of stoichiometry $[(PR_3)CuX]_4$ {PR_3 = PPh_3, X = Cl (**2**),[1a] Br (**3**),[1b] I (**4**);[1c] PR_3 = PEt_3, X = Cl (**5**),[2a] Br (**6**),[2a] I (**7**);[2b] PR_3 = $PMePh_2$, X = I (**8**),[2c] PR_3 = *t*-Bu$_3$P, X = Br (**9**)[2d]}, $[(DMPP)CuI]_4$ (**10**),[3] and $[(dppm)_2Cu_4I_4]$ (**11**).[4]

Compounds **2** and **5**−**10** have cubane structure, while **3**, **4**, and **11** have steplike structure. The solvated compound $[(PPh_3)CuBr]_4\cdot 2CHCl_3$ (**12**) also has steplike structure.[1c] However, for compounds **3** and **4,** cubane isomers are also known.[1d] Triethylarsine also formed a cluster, $[(Et_3As)CuI]_4$ (**13**), with cubane structure, similar to that of **7**.[2b]

As a part of our research activity to understand the formation of clusters, or polymeric networks, with transition metals,[5,6] we decided to observe the effect of the position of the methyl group in the phenyl ring, attached to the P atom, and thus carried out reactions of tritolylphosphines with copper(I) iodide in acetonitrile. The construction of supramolecular metal complexes containing copper(I) and silver(I) is a very interesting area, in view of formation of unusual metal clusters and multidirectional networks, some of which display conducting properties.[7]

In this Communication, we report an unprecedented bicapped adamantoid copper(I) cluster, $[Cu_6(\mu_2\text{-}I)(\mu_3\text{-}I)_4(\mu_4\text{-}I)(m\text{-}tolyl_3P)_4(CH_3CN)_2]$ (**1**), obtained by the reaction of copper(I) iodide with tri-*m*-tolylphosphine in acetonitrile. The reaction of tri-*m*-tolylphosphine (*m*-tolyl$_3$P) with copper(I) iodide in acetonitrile solvent yielded an intriguing product with empirical composition $Cu_3I_3(m\text{-}tolyl_3P)_2(CH_3CN)$ (**A**). The X-ray crystal determination of compound **A** has shown that it exists as $[Cu_6(\mu_2\text{-}I)(\mu_3\text{-}I)_4(\mu_4\text{-}I)(m\text{-}tolyl_3P)_4(CH_3CN)_2]$ (**1**), with a bicapped adamantoid structure (Figure 1).[8,9] The

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(8) Synthesis of **1**: A solution of tri-*m*-tolylphosphine (0.040 g, 0.13 mmol) in dry acetonitrile (20 mL) was added to a solution of copper(I) iodide (0.025 g, 0.13 mmol) in 10 mL of dry acetonitrile, and the mixture was stirred for 6 h and filtered. Colorless crystals of **1** were obtained by slow evaporation at room temperature in a few days. Mp: 180−190 °C. Anal. Calcd for $C_{88}H_{90}Cu_6I_6N_2P_4$: C, 43.40; H, 3.48; N, 1.15. Found: C, 43.16; H, 3.68; N, 0.90.

(9) Crystallographic data for **1**: $C_{88}H_{90}Cu_6I_6N_2P_4$, $M = 2442.29$, F-centered cubic, $a = 26.3990(7)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 18397.7(8)$ Å^3, $T = 193.0$ K, space group cubic $Fd\bar{3}$ (No. 203), $\rho_{calcd} = 1.759$ g cm^{-3}, $Z = 8$, μ(Mo Kα) = 3.488 mm^{-1}, 44553 reflections measured on a Rigaku/MSC Mercury CCD 1000 diffractometer, unique 29636 ($R_{int} = 0.048$). The final R_1 was 0.023 for 13831 reflections [$I > 2.0\sigma(I)$], and wR_2 was 0.067 (all data). ^{1}H and ^{31}P NMR spectra were recorded in $CDCl_3$ at 300.40 and 121.50 MHz frequencies on a FT-NMR AL-300 MHz JEOL spectrometer.

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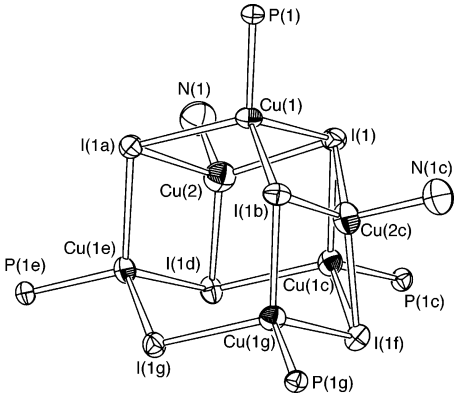

Figure 1. Structure of bicapped adamantoid cluster **1** without *m*-tolyl and CH_3 groups.

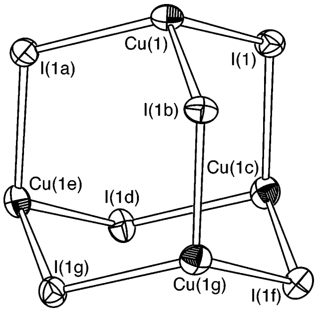

Figure 2. Structure of bicapped adamantoid cluster **1** without Cu(2) and Cu(2c) atoms and other ligands.

Cu(2) and Cu(2c) atoms are the capping atoms to which CH_3CN ligands are bonded.[9] Each ring of adamantane is formed by three Cu and three bridging iodide ligands. Two Cu(2)−NCMe moieties are disordered into four positions, and the Cu(2) atoms occupy two of four Cu_3I_3 faces of the adamantane framework Cu_4I_6 (Figure 2) of cluster **1**.

Cluster **1** has one (μ_2-I), four (μ_3-I), and one (μ_4-I) bonding modes of iodide ligands {Cu−I = 2.584(1) Å, 2.690(1) Å}, with terminal bonding by *m*-tolyl$_3$P {Cu−P = 2.257(1) Å} and CH_3CN {Cu−N = 2.077(5) Å} ligands, and these bond distances are similar to literature reports.[10,11] The geometry around each Cu center is distorted tetrahedral with bond angles in the range 102−116°. The proton NMR spectrum of cluster **1** in $CDCl_3$ has shown the methyl protons of the aryl ring at δ =2.21 ppm and those of CH_3CN at 2.02 ppm. Aryl ring protons absorbed at δ = 7.59m (6H, *o*-CH), 7.31m (3H, *p*-CH), and 7.15m (3H, *m*-CH). The ^{31}P NMR spectrum of this cluster in $CDCl_3$ solvent has shown one peak at δ = 17.6 ppm, with a coordination shift of $\delta_{\text{complex}} - \delta_{\text{ligand}} = 24.2$ ppm.[10,11]

The polarizable iodide ligand and the position of the methyl group in the phenyl ring attached to the P atom appear to have played the pivotal role in the formation of copper(I) compounds, with variable nuclearities of copper and different bonding modes of iodide ligands (cf. **1**, **16**, **17**). The formation of monomeric bicapped adamantoid geometry is the first example in copper chemistry. It is also a rare cluster compound among other metal complexes.[1−7,12] The formation of adamantoid cluster **1** is the consequence of the *m*-methyl group in the phenyl ring which alters the Lewis basicity of the tri-*m*-tolylphosphine ligand and the bridging properties of the iodide ligand. The investigations demonstrate the role of substituents in an aryl ring coupled with the effect of an anion in a coordinating solvent like acetonitrile.

It may be interesting to compare the formation of **1** with the analogous structures reported in the literature. If we remove Cu(2) and Cu(2c) atoms from compound **1**, along with the CH_3CN and *m*-tolyl$_3$P ligands, the species $[Cu_4I_6]^{2-}$ will be formed with adamantane structure, formed by the three six-membered rings (Figure 2). The dianion of $[MePh_3P]_2[Cu_4I_6]$ **(14)** has adamantane geometry, similar to that of **1,** but without Cu(2), Cu(2c) atoms and other ligands (Figure 2).[13] Alternatively, one can imagine the formation of **1** from **14** by coordinating each Cu center to four neutral *m*-tolyl$_3$P ligands, and replacing $MePh_3P^+$ cations by two $Cu(CH_3CN)^+$ species, which cap two adamantane faces, via coordination to iodide ligands, as shown in Figure 1. Similarly, the removal of the Cu(2) atom, along with all the phosphine ligands, from cluster **1** shall form the species $[Cu_5I_6(CH_3CN)_2]^-$, the same as that in $[Cs(18c6)_2][Cu_5I_6(CH_3CN)_2]$[14] (**15**). In the anion $[Cu_5I_6(CH_3CN)_2]^-$, the CH_3CN ligands are coordinated to Cu(1) and Cu(2c) in **1**.

It may be mentioned here that the related isomeric phosphines, namely, tri-*o*-tolylphosphine (*o*-tolyl$_3$P) and tri-*p*-tolylphosphine (*p*-tolyl$_3$P), with copper(I) iodide, formed an iodo-bridged dimer $[Cu_2(\mu_2\text{-}I)_2(o\text{-tolyl}_3P)_2]$ (**16**), similar to literature reports, $[Cu_2(\mu_2\text{-}I)_2(o\text{-tolyl}_3P)_2]\cdot$toluene, $[Cu_2(\mu_2\text{-}I)_2(o\text{-tolyl}_3P)_2(CH_3CN)_2]\cdot CH_3CN$,[15] or cubane, $[Cu_4(\mu_3\text{-}I)_4(p\text{-tolyl}_3P)_4]$ **(17)**, similar to **2** and **5−10** as discussed above.

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Supporting Information Available: X-ray crystal data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org. The CCDC number for this CIF is 229703.

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