Coinage-Metal Supramolecules

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Supramolecular Tetrahedra of Phosphines and Coinage Metals**

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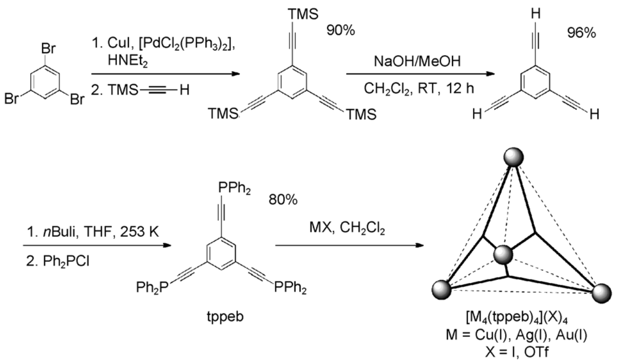
Supramolecular metal–ligand clusters, sometimes referred to as metal–organic polyhedra (MOPs), have been a major area of chemical research for at least 20 years.[1] The groups of Stang,[2] Raymond,[3] Fujita,[4] and many others have discovered an incredibly wide array of such molecules.[5] Many of the assemblies have demonstrated spectacular host–guest chemistry, including the ability to catalyze chemical reactions.[6] These clusters have also been linked together or assembled in such a way as to generate solid-state materials, such as metal–organic frameworks (MOFs, or "crystalline molecular flasks").[7] Despite the vast literature on these types of self-assembled structures, such constructs have only been rarely assembled from soft Lewis base ligands derived from second-row heteroatoms (for example, sulfur and phosphorus). Such ligands would be expected to form a distinct class of assemblies in conjunction with lower oxidation-state metal ions or metalloids. Indeed, Johnson and co-workers have successfully used thiol-based ligands to obtain self-assembled clusters based on P^{III}, As^{III}, Sb^{III}, and Bi^{III}.[8] Herein, we present a unique series of tetrahedral clusters derived from a rigid tris(diphenylphosphine) ligand and the soft Lewis acid coinage-metal ions of Group 11. To best of our knowledge, this is the first time isostructural supramolecular structures of a platonic solid (tetrahedron) have been prepared with all members of a transition metal group of the periodic table.

Some supramolecular assemblies have been described with multidentate phosphine ligands. Of particular note is work from the groups of Yip[9] and James,[10] both of whom have prepared self-assembled structures from M^I-phosphine interactions (M = Ag, Au). From a variety of rigid, multidentate phosphine ligands these groups have constructed rings, helicates, and a small, adamantoid-shaped cluster. The use of Ag^I and Au^I has also engendered some of these supramolecular species with luminescent properties.[11] Furthermore, Hahn and co-workers have also prepared cylinder-typed supramolecular structures combining polydentate N-heterocyclic carbene (NHC) ligands with coinage-metal ions by metal-controlled self-assembly.[12] Despite the impressive progress made by these groups and others, no large, three-dimensional structures, reminiscent of the platonic solids described with many other metal–ligand systems, have been reported. The supramolecular tetrahedra prepared herein (Scheme 1) with Cu^I, Ag^I, and Au^I are the first to realize this challenging target in metal–ligand self-assembly.



Scheme 1. Synthesis of the ligand tppeb and $[M_4(tppeb)_4]X_4$ clusters. TMS = trimethylsilyl.

By analogy to the many rigid, threefold-symmetric ligands that have been successful used to prepare discreet supramolecular complex ions,[13] the ligand 1,3,5-tris((diphenylphosphino)ethynyl)benzene (tppeb) was prepared as described previously (Scheme 1).[14] Combining a Group 11 metal iodide (CuI, AgI, AuI) with the tppeb ligand using a 1:1 stoichiometry in CH_2Cl_2 solvent results in the isolation of a pale yellow solid (after removal of solvent) in high yield (96, 95, and 86 % for Cu, Ag, and Au, respectively). ^1H NMR analysis confirms that the isolated solids are a high-symmetry species (see below).

The isolated powders could be recrystallized by various methods. Slow diffusion of Et_2O into a saturated solution of the material in $CHCl_3$, CH_2Cl_2, or acetone gave colorless crystals in high yield (ca. 90 % from the powder) within one day. However, these crystals were not of suitable quality for single-crystal X-ray diffraction. Alternatively, layering of Et_2O or *n*-pentane over these same solutions in $CHCl_3$, CH_2Cl_2, or acetone gave crystals of similar quality. Crystals suitable for single-crystal X-ray diffraction were produced from a saturated (prepared hot) DMF solution of the clusters, although the yields obtained were lower and the crystallization was slower. The single-crystal X-ray structure of the three clusters was determined, all of which crystallized in the chiral space group $P2_12_12_1$ (Supporting Information, Table S1), revealing that this series of supramolecules were essentially isostructural (Figure 1). In all of the clusters, the phosphine ligands occupy a pyramidalized, threefold-symmetric coordination geometry around the M^I coinage metal. The overall geometry of the M^I ions is tetrahedral, with the apical site

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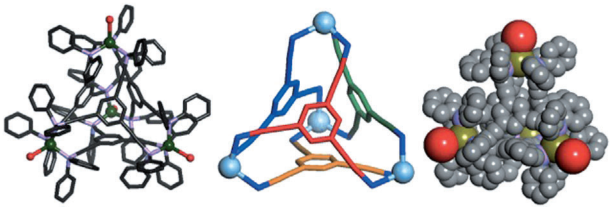

Figure 1. Crystal structure of the $[M_4(tppeb)_4]I_4$ clusters. Each cluster is shown in a distinct depiction: the complete $[Cu_4(tppeb)_4]I_4$ cluster is shown as sticks (left); to emphasize the cluster geometry, the $[Ag_4(tppeb)_4]I_4$ cluster is shown with phenyl groups removed and each ligand in a different color (middle); and the $[Au_4(tppeb)_4]I_4$ cluster is shown as a space-filling model (right).

occupied by a tightly bound iodide ligand (Figure 1). A minor difference between the clusters is the range of the metal–phosphine distances, which are 2.28–2.31 Å, 2.49–2.52 Å, and 2.37–2.41 Å in the Cu, Ag, and Au clusters, respectively. Similarly, the metal–iodide distances are about 2.60, 2.76 Å, and 2.82 Å in the Cu, Ag, and Au clusters, respectively. The metal–phosphine and metal–iodide bond distances are in good agreement with those of metal–phosphine and metal–iodide bonds in other four-coordinate phosphine-based metal(I) iodide complexes.[15] There do not appear to be any strong interactions, such as hydrogen bonding, between the clusters and the solvate molecules (DMF) present in the crystals. No solvent guests are found inside of the clusters, which are too small to accommodate such guests (< 60 Å^3).

A critically important feature of supramolecular coordination clusters is their persistence in solution, and not just in the solid state. It is in solution that many such clusters demonstrate their most interesting reactivity. Therefore, ESI-MS, ^{1}H NMR, and ^{31}P NMR analysis of the $[M_4(tppeb)_4]I_4$ clusters was performed to determine their stability in solution. Samples of all three clusters dissolved in CH_2Cl_2 and diluted with acetone yielded high-resolution ESI-MS spectra that unambiguously showed the persistence and elemental composition of these clusters in solution. As shown in Figure 2, the positive-ion mode ESI-MS spectrum of $[Ag_4(tppeb)_4]I_4$ shows several peaks indicative of the fully intact supramolecule. The base peak at m/z 3773.9502 corresponds to the $[M{+}Na]^+$ exact mass, which confirms the molecular formula of the cluster and is further supported by the simulated isotopic spectrum of this peak (Figure 2). The $[M{+}Na]^+$ base peak indicates a strong association of the iodide ligands with the cluster, suggesting that in solution the complex is best considered as a neutral molecule (that is, $Ag_4(tppeb)_4I_4$ as opposed to the complex ion $[Ag_4(tppeb)_4]I_4$). Additional peaks are seen in the ESI-MS corresponding to $[M{+}K]^+$ (m/z 3787.9175), $[M{-}I{+}acetone]^+$ (m/z 3680.0117), and $[M{-}I]^+$ (m/z 3623.0429), all providing conclusive evidence for the stability of $[Ag_4(tppeb)_4]I_4$ in solution (Supporting Information, Figure S1). Similar positive-ion mode ESI-MS were obtained for $[Cu_4(tppeb)_4]I_4$ and $[Au_4(tppeb)_4]I_4$. For $[Cu_4(tppeb)_4]I_4$, a $[M{+}Na]^+$ (m/z 3595.0447) base peak was also observed (Supporting Information, Figure S2), while for $[Au_4(tppeb)_4]I_4$ a $[M{+}Na]^+$ (m/z 4129.1965) peak was observed (Supporting Information, Figure S3), but it was not the base peak, as this complex showed significantly more fragmentation in the spectrum.

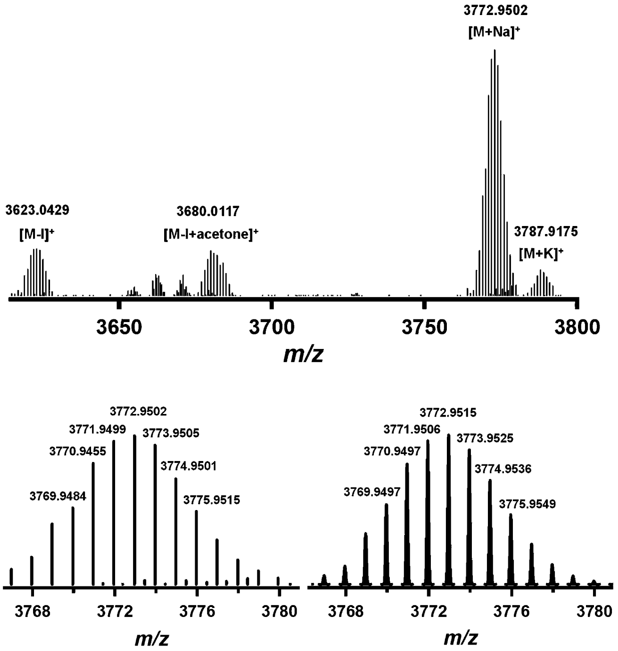

Figure 2. High-resolution ESI-MS of the $[Ag_4(tppeb)_4]I_4$ cluster: The positive-ion mode measured spectrum (top), magnification of the $[M+Na]^+$ base peak (bottom left), and the simulated $[M+Na]^+$ (bottom right) spectrum.

Along with the aforementioned ESI-MS data, ^{1}H NMR and ^{31}P NMR spectroscopy confirmed the robust nature of these $[M_4(tppeb)_4]I_4$ clusters in solution. Figure 3 shows the ^{1}H and ^{31}P NMR spectra of free tppeb and of $[Cu_4(tppeb)_4]I_4$. In the ^{1}H NMR spectrum, the proton signals of free tppeb appear at 7.37–7.41 (for H_a and H_b) and 7.64–7.68 (for H_c and H_d). In contrast, the ^{1}H NMR spectrum of $[Cu_4(tppeb)_4]I_4$ shows a significant shift of the resonances and thus was easily distinguishable from the free ligand. The signals of H_{ortho} (H_c' and H_c'') were observed at $\delta = 7.83$ and 7.97 ppm as broad multiplets. Indeed, all of the ^{1}H NMR resonances of the cluster indicate an asymmetry between the two phenyl rings on each phosphorous atom (two distinct environments, $H_{meta} = H_b'$ and H_b'' at $\delta = 6.82$, 7.35 ppm; $H_{para} = H_a'$ and H_a'' at $\delta = 7.09$, 7.39 ppm), which is consistent with X-ray structure of the clusters (peak assignments were facilitated by a COSY NMR experiment; Supporting Information, Figure S4). The singlet at 7.57 ppm is attributed to the protons of the central benzene ring in tppeb (H_d). In the ^{31}P NMR spectrum of $[Cu_4(tppeb)_4]I_4$, the peak of free tppeb (-34.02 ppm) is no longer present and a new resonance at 8.06 ppm was observed (Figure 3). For $Ag_4(tppeb)_4]I_4$, similar patterns were observed in ^{1}H and ^{31}P NMR spectra (Supporting Information, Figure S5) with all of the chemical shifts being quite similar, except the protons of central benzene moiety (H_d), which exhibit more upfield shifts ($\delta = 7.19$ ppm) than those of $[Cu_4(tppeb)_4]I_4$. Unfortunately, efforts to obtain ^{1}H NMR of $[Au_4(tppeb)_4]I_4$ were not successful owing to poorer solubility of this cluster. However, ^{31}P NMR in hot [D$_7$]DMF solution gave a resonance at 7.19 ppm consistent

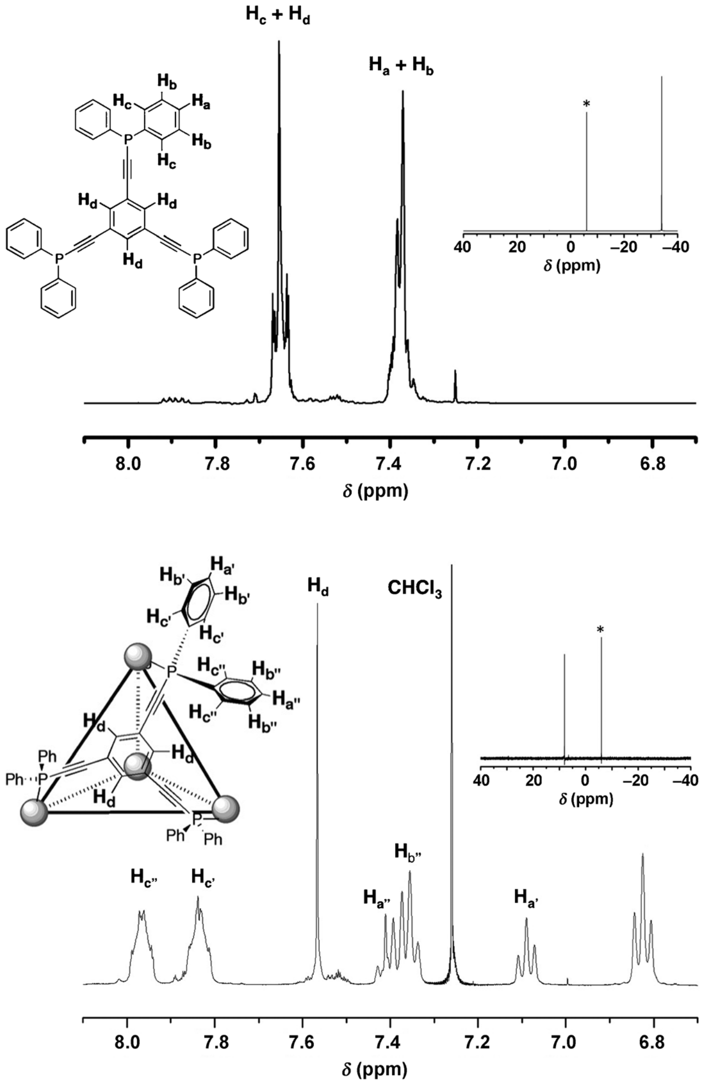

Figure 3. ^{1}H and ^{31}P NMR (inset) spectra of free tppeb (top) and of $[Cu_4(tppeb)_4]I_4$ (bottom). The PPh_3 reference is labeled with an asterisk.

with the spectra of the other clusters (Supporting Information, Figure S6).

As noted above, the $[M_4(tppeb)_4]I_4$ series of compounds appear to behave as neutral clusters, based on the strong association of the halide ligand with the Group 11 metal ions. This is supported by both the X-ray structures and positive-ion mode, high-resolution ESI-MS of all three clusters. Based on this observation, it was hypothesized that synthesizing these supramolecules from a metal salt with a weakly coordinating anion could modulate the composition and charge of the cluster. This would provide an unusual but simple way to control the physiochemical properties of these self-assembled systems. Indeed, combining AgOTf with tppeb under similar reaction conditions as described above gave the $[Ag_4(tppeb)_4](OTf)_4$ cluster in high yield (97%). $[Ag_4(tppeb)_4](OTf)_4$ was also crystallized and the compound was found to be similar structure with the other $[M_4(tppeb)_4]I_4$ clusters reported herein (Supporting Information, Figure S7). However, some differences are noted in $[Ag_4(tppeb)_4](OTf)_4$ from the $[M_4(tppeb)_4]I_4$ clusters. $[Ag_4(tppeb)_4](OTf)_4$ also crystallizes in a noncentrosymmetric space group, $P6_3$, with the cluster sitting on a threefold symmetry axis such that that one third of the cluster resides in asymmetric unit. There are two distinct Ag^I centers in asymmetric unit. One Ag^I ion is tightly bound to one of oxygen atoms of a triflate counter ion (2.43 Å) and three phosphorous atoms of the tppeb ligands (2.46, 2.48, and 2.50 Å, respectively). The other Ag^I ion is bound to three identical phosphorous atoms (Ag–P distance 2.51 Å) generated by threefold symmetry; however, no close contact between this Ag^I ion and a triflate anion is present, suggesting that indeed the effective charge of the cluster can be modulated by changing the counterion. Interestingly, this Ag^I center still shows a tetrahedral geometry despite a vacant apical coordination site, with P-Ag-P bond angles of about 109.8°, which is close to ideal tetrahedral geometry. The formation of the cluster in organic solution was confirmed by ^{1}H NMR spectroscopy (Supporting Information, Figure S8); however, the spectrum is not as well resolved as for $[Ag_4(tppeb)_4]I_4$, perhaps suggesting lower stability in solution. This observation is supported by ESI-MS experiments on $[Ag_4(tppeb)_4](OTf)_4$, which did not yield the expected ions. This is also consistent with a hypothesis that with weakly bound anions a more labile cluster species is produced that cannot survive under the ESI ionization conditions.

In conclusion, a new class of supramolecular metal–ligand clusters has been prepared. These clusters have several unusual features, including being comprised of metal–phosphine bonds, utilizing Group 11 coinage metals, modulation of composition/charge by employing of different counteranions, and formation an isostructural series over an entire group of the periodic table. These findings suggest that these and related clusters can be prepared that have several modular features that can be controlled by choice of ligand, metal, and counterion. Furthermore, the growing use of coinage metals as catalysts suggest such clusters might serve as unusual scaffolds for new catalyst design.[16] Studies along these lines are presently underway.

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[15] Based on a search of the Cambridge Structural Database (CSD), other four-coordinate phosphine-based metal(I) iodide complexes are ca. 2.30, 2.54, and 2.40 Å for Cu–P, Ag–P, and Au–P, and ca. 2.65, 2.84, and 2.94 Å for Cu–I, Ag–I, and Au–I, respectively.

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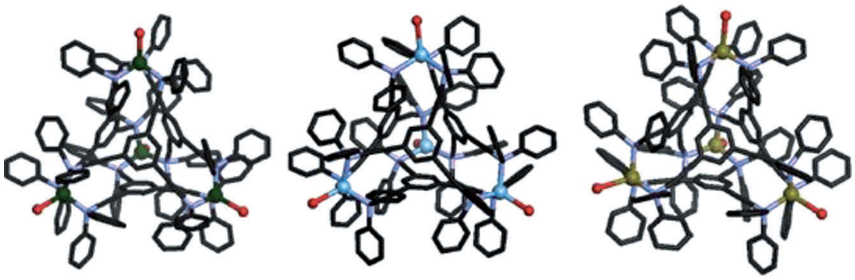

Treasure chests: The Group 11 metals Cu^{I}, Ag^{I}, and Au^{I} form tetrahedral supramolecular clusters with a rigid threefold-symmetric phosphine ligand. These supramolecular clusters, which assemble by metal–phosphine interactions, are the first to form across an entire group of the periodic table. Cu^{+} green, Ag^{+} pale blue, Au^{+} green, I^{-} red, P purple.