Supramolecular Chemistry

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Supramolecular “Transmetalation” Leads to an Unusual Self-Assembled P_2L_3 Cryptand**

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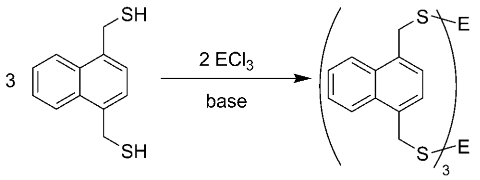
Transmetalation is common in biochemical,[1] inorganic,[2] and organometallic synthesis,[3] but has been largely overlooked by supramolecular chemists as a synthetic technique for preparing discrete assemblies.[4] The self-assembly of complex, multi-component metal–organic supramolecules[5] occurs by the breaking and reforming of reversible metal–ligand bonds[6] and in some cases through dynamic covalent chemistry.[7] These dynamic bonds also allow for the reshuffling of components within “fully formed” complexes, as revealed by ligand exchange studies.[8] The introduction or removal of guest molecules can cause rearrangement to higher or lower-order structures, which also necessitates the breaking and reforming of bonds.[9] Transmetalation, which can occur upon the addition of a second type of metal, is a less common display of the dynamic nature of these assemblies.[8c,10] Here, we report a “transmetalation” reaction of an antimony-containing cryptand with arsenic and, remarkably, phosphorus to provide a previously unattainable P_2L_3 cryptand. In this reaction, P–S bonds behave reversibly like typical metal–ligand bonds within supramolecular assemblies suggesting a potentially new motif for dynamic covalent chemistry.

A rigid dithiol ligand, 1,4-bis(mercaptomethyl)naphthalene ($H_2\mathbf{L}$),[11] was treated with a pnictogen trichloride (ECl_3, E = As, Sb, Bi) and base resulting in self-assembly to the corresponding cryptands, $E_2\mathbf{L}_3$ (Scheme 1). While our group has previously prepared As-[12] and Sb[13]-containing cryptands by a similar synthetic route, this is one of the first known examples of a Bi-containing supramolecular complex.[14] X-ray quality crystals were grown by layering chloroform solutions of each cryptand with acetonitrile (Figure 1).[15]



Scheme 1. The self-assembly of E_2L_3 (E = As, Sb, Bi) cryptands.

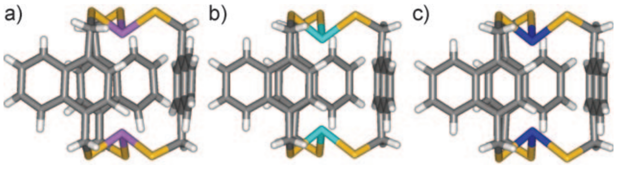


Figure 1. X-ray crystal structures of a) $As_2\mathbf{L}_3$, b) $Sb_2\mathbf{L}_3$, and c) $Bi_2\mathbf{L}_3$. Arsenic atoms are shown in purple, antimony in teal, bismuth in blue, sulfur in yellow, carbon in gray and hydrogen in white.

The structure of each cryptand is very similar, with apparent C_{3h} symmetry and only slight variations in ligand position. In each case, the pnictogen atoms are positioned within the cavity, with the lone pairs of electrons on the two atoms pointing toward each other. The E···E distance decreases from $As_2\mathbf{L}_3$ (5.11 Å) to $Sb_2\mathbf{L}_3$ (4.83 Å) to $Bi_2\mathbf{L}_3$ (4.68 Å), and the difference is compensated for in the increasing E–S bond distances and S-E-S angles. In each case, the pnictogen atoms are also involved in attractive E···π interactions,[16] as evidenced by E···C_{aryl} contacts of less than the sum of the van der Waals radii.[17] In solution, these cryptands display similar, but distinct, ^{1}H NMR resonances with splitting (*ABq* for the methylene protons), which suggests that the ligands are “locked” into place as they are seen in the crystal structure, rather than flipping back and forth quickly (see Supporting Information, Figure S1).

To compare the stability of the complexes, transmetalation reactions were carried out and monitored by ^{1}H NMR spectroscopy. Crystals of $Sb_2\mathbf{L}_3$ were dissolved in $CDCl_3$ and two equivalents of $AsCl_3$ were added (Scheme 2). Within 30 min, all the $Sb_2\mathbf{L}_3$ was consumed and a white solid precipitated out of solution which was likely a coordination polymer incorporating both Sb and As. NMR spectroscopy identified two of the initial soluble reaction products (Figures 2 and S2). The first is the previously reported $As_2\mathbf{L}_2Cl_2$ macrocycle,[11] which is converted to $As_2\mathbf{L}_3$ as the precipitate redissolves and more ligand becomes available for reaction. This suggests that $As_2\mathbf{L}_2Cl_2$ is an intermediate in the self-assembly of $As_2\mathbf{L}_3$. The second species, a heterometallic $AsSb\mathbf{L}_3$ cryptand,[18] is relatively short-lived as the Sb atom is quickly replaced with As. After 5 days, the only species left in solution are $As_2\mathbf{L}_3$ and trace $As_2\mathbf{L}_2Cl_2$.

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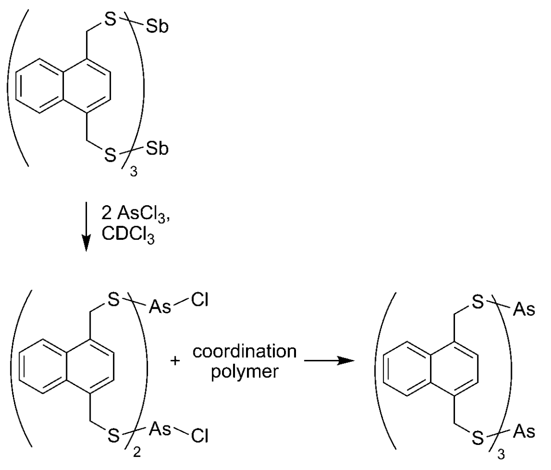

Scheme 2. Transmetalation of $Sb_2\mathbf{L}_3$ to $As_2\mathbf{L}_3$.

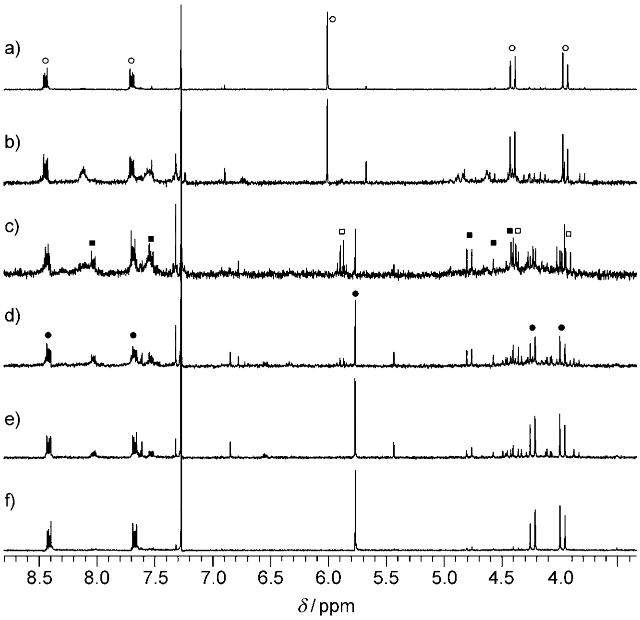

Figure 2. ^{1}H NMR spectra for the reaction of $Sb_2\mathbf{L}_3$ (a) with $AsCl_3$ after b) 10 min, c) 32 min, d) 85 min, e) 7 h, and f) 5 d. $Sb_2\mathbf{L}_3$ is marked ○, $AsSb\mathbf{L}_3$ □, $As_2\mathbf{L}_2Cl_2$ ■, and $As_2\mathbf{L}_3$ ●.

Similarly, $Bi_2\mathbf{L}_3$ was treated with $AsCl_3$ and $SbCl_3$. In each case, a reaction occurred immediately resulting in a white precipitate. Over time, $As_2\mathbf{L}_2Cl_2$ and $Sb_2\mathbf{L}_2Cl_2$ were formed and identified by NMR spectroscopy, but the precipitate never completely redissolved and the reaction was not driven to completion as in the case of $Sb_2\mathbf{L}_3 \rightarrow As_2\mathbf{L}_3$. A control reaction was carried out in which an excess of $SbCl_3$ was added to $As_2\mathbf{L}_3$, but no reaction occurred even after several days at elevated temperatures. Given that self-assembly reactions such as these are typically under thermodynamic control, it seems that $As_2\mathbf{L}_3$ is more stable than $Sb_2\mathbf{L}_3$ which is more stable than $Bi_2\mathbf{L}_3$. While the energies of E^{III}–S bonds have not been reported, they are likely the driving force for this transmetalation. The presumed byproduct of transmetalation is ECl_3 (where E is the metal that was removed) and E^{III}–Cl bonds *decrease* in strength moving from As–Cl to Sb–Cl to Bi–Cl.[19]

The success of this transmetalation reaction led us to believe that this route might allow access to P-containing supramolecular complexes, which we have been unable to prepare by any other route. $Sb_2\mathbf{L}_3$ was dissolved in $CDCl_3$, PBr_3 was added to the NMR tube, and a white solid precipitated out of solution. While this precipitate did not completely redissolve, several new resonances appeared in the ^{1}H NMR spectrum after two days which correspond to $P_2\mathbf{L}_3$ (Figure S3). Crystals of this cryptand were grown by layering this solution with acetonitrile (Figure 3). The X-ray structure[20] reveals that the phosphorus atoms are located slightly within the cavity with their lone electron pairs pointing inwards, filling the same position as the metals Sb and Bi and the metalloid As. While no favorable P···π interactions are expected, the P···C_{aryl} close contacts (3.25 and 3.54 Å) are less than the sum of the van der Waals radii (3.6 Å). The geometry of the ligand is well suited for this bis(trithiophosphite): all of the ligands are in a preferred *gauche* conformation[21] and the S-P-S angle (96.5°) is only slightly smaller than that for other reported trithiophosphites.[22] With a P···P distance of 5.49 Å, $P_2\mathbf{L}_3$ has a small, empty cavity.[23] Attempts to fill that cavity with BH_3 or Au^+[24] have thus far resulted in no reaction and $P_2\mathbf{L}_3$ is surprisingly air-stable for a trithiophosphite. This suggests that P's lone pairs are not inverting in solution, but are locked into their endohedral positions as observed in the crystal structure, in effect protecting the phosphorus atoms from further reaction or decomposition. Currently, we are working to expand the size of the cavity and use similar cryptands as *trans*-directing phosphine ligands.

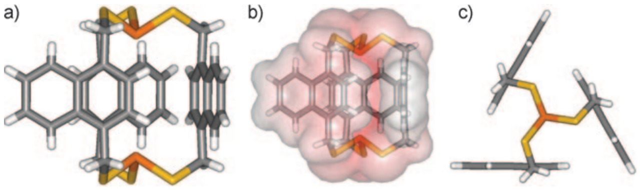

Figure 3. X-ray crystal structure of $P_2\mathbf{L}_3$: a) side view with b) van der Waals surface; c) top view. Phosphorus atoms are shown in orange.

We have shown in a supramolecular context that thiolate ligands prefer As over Sb over Bi. Surprisingly, an Sb-containing cryptand can be "transmetalated" with P, resulting in a previously inaccessible $P_2\mathbf{L}_3$ cryptand in which P acts like the "metal" in a metal–ligand self-assembly reaction. All of the $E_2\mathbf{L}_3$ cryptands have a propeller twist due to intramolecular edge-to-face aromatic interactions, yet are achiral due to an internal plane of symmetry (C_{3h} point group). Heterometallic analogs would provide interesting examples of chiral supramolecular assemblies, and in the case of P-containing cryptands, these chiral assemblies could act as *trans*-directing ligands for a metal guest. The facile transmetalation of these stable, yet labile, supramolecular main group assemblies suggests that transmetalation is another synthetic method for supramolecular chemists seeking to prepare otherwise inaccessible assemblies. Such hosts offer applications in molecular machines,[10b] catalysis, and sensing.[10a] Furthermore, the As- and P-based assemblies are unusually stable compared to mononuclear analogs. If the Bi-containing cryptands display similar stability, are applications as materials precursors, catalysts, and radiopharmaceuticals[25] possible?

Experimental Section

All synthetic procedures can be found in the Supporting Information.

X-ray crystallography: Diffraction intensities for $\mathrm{As}_2\mathbf{L}_3$, $\mathrm{Sb}_2\mathbf{L}_3$, $\mathrm{Bi}_2\mathbf{L}_3$, and $\mathrm{P}_2\mathbf{L}_3$ were collected at 173(2) K on a Bruker Apex CCD diffractometer using $\mathrm{Mo}_{K\alpha}$ radiation $\lambda = 0.71073$ Å. Space groups were determined based on systematic absences. Absorption corrections were applied by SADABS.[26] Structures were solved by direct methods and Fourier techniques and refined on F^2 using full-matrix least-squares procedures. All non-H atoms were refined with anisotropic thermal parameters. All H atoms in $\mathrm{As}_2\mathbf{L}_3$, $\mathrm{Sb}_2\mathbf{L}_3$, and $\mathrm{Bi}_2\mathbf{L}_3$ were refined in calculated positions in a rigid group model. H atoms in $\mathrm{P}_2\mathbf{L}_3$ were found from the F-map and refined with isotropic thermal parameters. In the crystal structures of $\mathrm{Sb}_2\mathbf{L}_3$, $\mathrm{Bi}_2\mathbf{L}_3$, and $\mathrm{P}_2\mathbf{L}_3$ there is a solvent molecule, $\mathrm{CH_3CN}$, disordered over two positions related by a mirror plane which was treated by SQUEEZE.[27] Corrections of the X-ray data by SQUEEZE (41, 38, and 44 electrons per cell, respectively, for $\mathrm{Sb}_2\mathbf{L}_3$, $\mathrm{Bi}_2\mathbf{L}_3$, and $\mathrm{P}_2\mathbf{L}_3$) are close to the required values of 44 electrons per cell for two molecules in the full unit cells. All calculations were performed by the Bruker SHELXTL (v. 6.10) package.[28] CCDC 753593 ($\mathrm{As}_2\mathbf{L}_3$), 753594 ($\mathrm{Bi}_2\mathbf{L}_3$), 753595 ($\mathrm{P}_2\mathbf{L}_3$), and 753596 ($\mathrm{Sb}_2\mathbf{L}_3$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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