Multiple weak supramolecular interactions stabilize a surprisingly twisted As$_2$L$_3$ assembly†

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A combined crystallographic, DFT and NMR spectroscopic study of a flexible As$_2$L$_3$ assembly reveals temperature dependent conformational behavior in solution and a highly asymmetric structure stabilized by As–π and edge-to-face aromatic interactions.

Supramolecular chemistry based on metal–ligand coordination is a rapidly advancing field that has provided access to a wide variety of structures through information programmed into the coordination preferences of metal ions.[1,2] These coordination assemblies frequently display emergent properties such as guest encapsulation,[3] with some metal–ligand assemblies exhibiting changes in size through a non-dissociative mechanism that has been described as "breathing".[4]

Interest in main-group supramolecular chemistry has flourished in recent years, as the main group elements provide access to unique coordination geometries otherwise unavailable to researchers preparing novel structures with new properties.[5] In this communication we report a novel arsenic-based supramolecular assembly whose structure is determined by a combination of As–π[6] and edge-to-face aromatic interactions. The NMR spectra of this assembly are highly temperature dependent, suggesting that the ligand scaffold expands and contracts in response to temperature changes, in effect "breathing."

Previous work in this laboratory has focused on the preparation of dinuclear arsenic assemblies bridged by rigid ligands, such as 1,4-dimercaptomethylbenzene, which accommodates the preference of trivalent arsenic for trigonal pyramidal coordination.[7,8] This assembly was found to be thermodynamically and kinetically stable under a variety of harsh conditions and in the presence of competing metal ions and ligands, presumably due to the strength of the As–S bonds (~81 kcal mol^{-1}).[9] Furthermore, the endo-hedrally-directed lone pairs and short As–π contacts suggested the potential for unique host–guest interactions.[10]

A longer ligand containing two phenyl rings, 4,4′-dimercapto-methyldiphenylmethane (H$_2$L), was prepared through modifications of literature methods.[11] Diphenylmethane was chosen as a spacer due to its ubiquity in supramolecular systems—it provides an expanded cavity to host structures and has a moderate degree
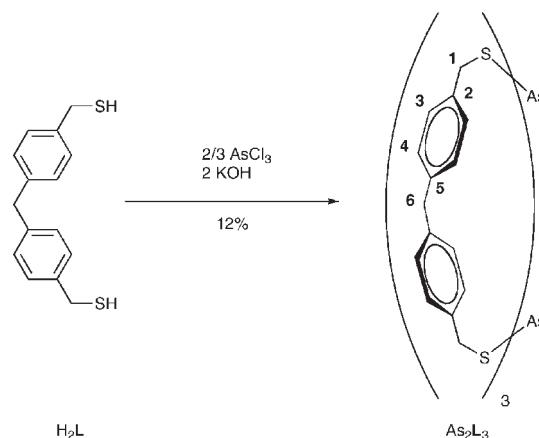
Scheme 1 Synthesis of As$_2$L$_3$ assembly; the included numbering scheme will be used later in discussing the structure.

of flexibility.[12] The corresponding As$_2$L$_3$ assembly was then prepared (Scheme 1) by slow addition of AsCl$_3$ in benzene or THF to a solution of the ligand and KOH in methanol.[13]

Slow evaporation of either chloroform or dichloromethane solutions of As$_2$L$_3$ yielded clear, colorless blocks whose identity was confirmed through X-ray crystallography.§ The As$_2$L$_3$ structure (Fig. 1a) features four close contacts of varying distances between As(III) and the nearest carbon on the phenyl rings of
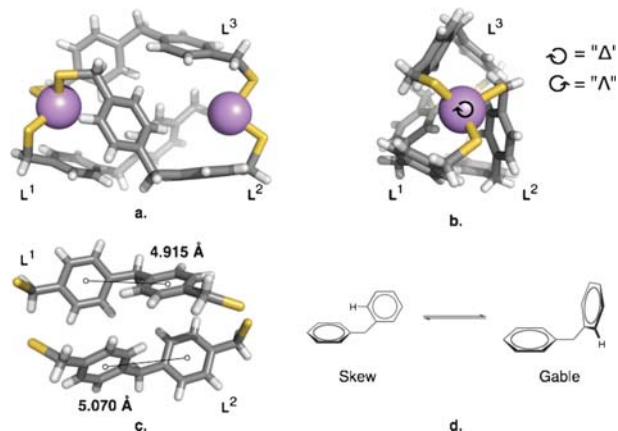
Fig. 1 Three-dimensional structure of As$_2$L$_3$. (a) Crystal structure shown as wireframe; spheres represent arsenic atoms. (b) Crystal structure, looking down As···As axis. Note the Δ axial chirality (clockwise twist) of As(III) facing the viewer. (c) Cutaway view of two lower strands showing centroid–centroid distances. (d) Schematic of equilibrium between skew (crowded) and gable (remote) geometries in diphenylmethane.

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ligand strands L^1 and L^2. This observation is in agreement with calculations showing that the geometry of the As–π interaction is strong (at least 7.4 kcal mol^{-1}) yet has variable directionality.[7] The solid-state structure of this complex is surprisingly distorted in comparison to geometries predicted by MM3 calculations and the majority of self-assembled metal–ligand complexes that exhibit a high degree of symmetry in both solution and the solid state,[2] including those containing the diphenylmethane spacer.[14] Instead, the three ligands are unevenly distributed about the metal centers—an arrangement best described as a distorted mesocate, as the –CH$_2$S– groups maintain opposite twists about the two metal centers. For the purposes of this study, the counterclockwise twisted As(III) center will be described as Λ, while the clockwise As(III) center will be described as Δ. We will therefore refer to the As$_2$L$_3$ assembly as a $\Delta\Lambda$ mesocate; since the space group $P2_1/n$ is centrosymmetric, equal amounts of the structure shown in Fig. 1 and its mirror image are present. In the view along the As$\cdots$As axis in Fig. 1b, the Δ twist faces the reader. The angles between the mean planes of the phenyl rings about the Δ metal center are 48.5(1), 49.8(1), and 85.2(1)°, while those about the Λ center are 35.1(1), 46.7(1), and 80.9(1)°. The rings are twisted so as to direct the edges toward the interior of the complex, effectively filling any empty space inside.

Calculations and long-range NMR couplings have shown that there are two predominant solution conformations of diphenylmethane, defined by the pair of dihedral angles relating the bridging methylene protons and the *ortho* aromatic protons. These conformations have been described as skew and gable[15] (Fig. 1d) and are thought to exist in dynamic equilibrium in solution. Crystalline diphenylmethane, however, is exclusively skew—this conformation suggests an attractive intramolecular edge-to-face aromatic interaction. Two ligand strands (L^1 and L^2) exhibit this type of interaction in which the centroids of the rings are near the ideal offset¶ of 5.025 Å,[16] (Fig. 1c) in nearly perpendicular skew conformations. The third ligand strand (L^3) is also skew, but not to the same degree as the other two strands. This is a relatively rare example of an "imploded" supramolecular structure similar to the imploded cryptophane observed by Holman *et al.*,[17] which contracts in the absence of an appropriate guest.

DFT optimization of As$_2$L$_3$ (with a 6-31+G* basis set for all atoms and the B3LYP functional[18]) produces two remarkably similar minima which differ in energy by only 4.1 kcal mol^{-1} (Fig. 2a and b). Neither structure maintains the high degree of symmetry predicted by MM3 calculations. Instead, the phenyl rings are twisted such that the edges point toward the interior of the complex, effectively filling any empty interior space. These calculations predict the "*meso*" As$_2$L$_3$ crystal structure with a surprising degree of accuracy: the As$\cdots$As distance is underestimated by only 0.11 Å, while the average As–π distance is *overestimated* by 0.19 Å (Fig. 2a). The calculated structure places L^1 and L^2 in nearly perpendicular skew arrangements with centroid offsets of 4.96 and 5.01 Å, in nearly perfect agreement with the observed distances. The strong agreement between the calculated structure and the crystal structure is a powerful indicator that the distorted structure is not merely an artifact of crystal packing forces, but is instead the result of a combination of supramolecular interactions.[19]

As$_2$L$_3$ is remarkably stable in solution: no ligand exchange is observed with free ligand and the intact assembly can be ionized
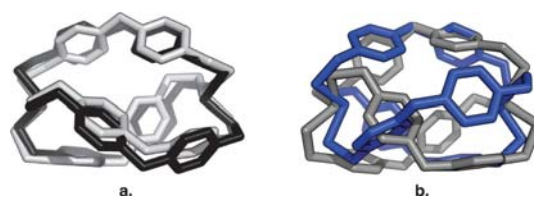

Fig. 2 (a) Overlay of DFT optimized geometry (black) and crystal structure (gray) of As$_2$L$_3$. (b) Overlay of higher-energy DFT geometry (blue) and crystal structure.

from solution with APCI-MS. The ^{1}H-NMR spectrum is surprisingly uncomplicated at room temperature—singlets are observed for both H1 and H6 (Fig. 3; see Scheme 1 for numbering). In addition, there is an accidental chemical shift degeneracy for H3 and H4 as evidenced by the presence of a singlet resonance in the aromatic region instead of the expected set of two doublets. The ^{13}C-NMR spectrum showed a similar degeneracy for C3 and C4.

These uncomplicated spectra indicate dynamic solution behavior on the NMR timescale. The simple aromatic region indicates that the phenyl rings rotate rapidly, and the singlet observed for H6 shows that the solution structure cannot be a static $\Delta\Lambda$ mesocate at the As(III) centers. There must therefore be fast interconversion between $\Delta_1\Lambda_2$ and $\Lambda_1\Delta_2$ isomers on the NMR timescale, either by simultaneous interconversion or through a $\Delta_1\Delta_2$ or $\Lambda_1\Lambda_2$ intermediate with a lifetime too short to observe.

In order to resolve the discrepancy between the solid and solution phase data, variable temperature NMR experiments were carried out. No resolution of either set of methylene protons was observed even at −80 °C (in contrast to other diphenylmethane bridged supramolecular systems[14]), but a strong upfield shift was observed for one aromatic proton, lifting the accidental degeneracy of H3 and H4. H1 also displayed a noticeable upfield shift as the temperature was decreased, consistent with the weak contact with a neighboring aromatic ring observed in the crystal structure. The accidental degeneracy in carbon signals C3 and C4 was also lifted as the temperature decreased. Returning the sample to room temperature reversed the chemical shift change and returned the aromatic protons to their coincidentally degenerate state. In contrast, VT-NMR experiments with the original phenylene spaced assembly[7] showed no appreciable changes at lowered temperature. This is a strong indication that the changes in the NMR spectra are related to changes in conformation along the diphenylmethane spacer rather than activity about the As(III) centers.

The identity of the upfield shifted aromatic proton was confirmed as H3 by low-temperature HMBC and HMQC spectra
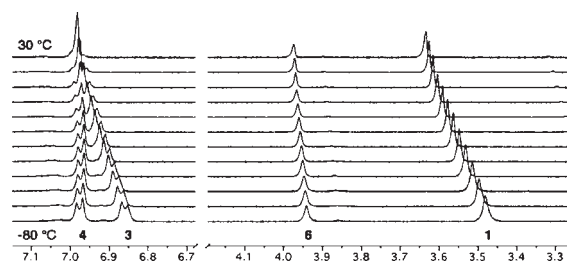
Fig. 3 VT-NMR of As$_2$L$_3$ in CD$_2$Cl$_2$. Spectra are referenced to residual solvent signal and are taken at 10 °C intervals.

(see ESI†). Similar flexible molecules capable of intramolecular edge-to-face aromatic interactions are known to interconvert rapidly between "crowded" and "remote" limiting geometries on the NMR timescale at experimentally accessible temperatures. In that analysis, lower temperatures favor a more crowded geometry, enhancing edge-to-face aromatic interactions and a contracted structure. At higher temperatures, entropy apparently disfavors the edge-to-face interaction, promoting a more remote geometry and an expanded structure; intermediate conformations would be expected over the observed temperature range. In either case, the conformations exist in a fast equilibrium; the observed NMR shift is a weighted average of the populations of all conformers present.[20] For As_2L_3, the remote geometry corresponds to a gable-like conformation of the diphenylmethane spacer at room temperature, while the crowded geometry observed at lowered temperatures corresponds to a more skew-like conformation. As the structure of more expanded conformations is not yet understood, it would be premature to calculate thermodynamic parameters from this data.

In summary, weak forces such as edge-to-face aromatic and arsenic–π interactions play an important role in determining the solution and solid-state structures of supramolecular complexes. In particular, the arsenic–π interaction appears to persist in the presence of flexible ligand scaffolds, showing that it is an important component of arsenic ligand design and can itself be considered an emerging supramolecular interaction. The varying strength and geometry in the crystal structure and the temperature dependence of these weak aromatic interactions in solution have been shown to dramatically affect the structure of a new As_2L_3 assembly with a flexible ligand scaffold. In particular, we have observed expansion and contraction or "breathing" of the host in solution over a range of temperatures. This may have significant implications in the design of expanded arsenic-containing host structures—the addition of conformationally mobile spacer units may play a role in determining the size, shape, and exchange mechanism of guests.

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