This article is published as part of the Dalton Transactions themed issue entitled:

Self-Assembly in Inorganic Chemistry

Guest Editors Paul Kruger and Thorri Gunnlaugsson

Published in issue 45, 2011 of Dalton Transactions



Image reproduced with permission of Mark Ogden

Articles in the issue include:

PERSPECTIVE:

Metal ion directed self-assembly of sensors for ions, molecules and biomolecules Jim A. Thomas Dalton Trans., 2011, DOI: 10.1039/C1DT10876J

ARTICLES:

Self-assembly between dicarboxylate ions and a binuclear europium complex: formation of stable adducts and heterometallic lanthanide complexes James A. Tilney, Thomas Just Sørensen, Benjamin P. Burton-Pye and Stephen Faulkner Dalton Trans., 2011, DOI: 10.1039/C1DT11103E

Structural and metallo selectivity in the assembly of [2 × 2] grid-type metallosupramolecular species: Mechanisms and kinetic control Artur R. Stefankiewicz, Jack Harrowfield, Augustin Madalan, Kari Rissanen, Alexandre N. Sobolev and Jean-Marie Lehn Dalton Trans., 2011, DOI: 10.1039/C1DT11226K

Visit the *Dalton Transactions* website for more cutting-edge inorganic and organometallic research <u>www.rsc.org/dalton</u>

Dalton Transactions

Cite this: Dalton Trans., 2011, 40, 12125

PAPER

Design, synthesis and characterization of self-assembled As_2L_3 and Sb_2L_3 cryptands \dagger

Sean A. Fontenot,[‡] Virginia M. Cangelosi,[‡] Melanie A. W. Pitt, Aaron C. Sather, Lev N. Zakharov, Orion B. Berryman and Darren W. Johnson*

Received 3rd May 2011, Accepted 25th May 2011 DOI: 10.1039/c1dt10817d

The syntheses and X-ray crystal structures of six new self-assembled supramolecular As and Sb-containing cryptands are described. Analysis in the context of previously reported As_2L_3 and Sb_2L_3 cryptands reveals that small differences in ligand geometries result in significant differences in the helicity of the complexes and the stereochemistry of the metal coordination within the assembled complexes. Additionally, a new synthetic route is described which involves exposure of reactants to vacuum to help facilitate self-assembly.

Introduction

Fabrication of complex structures from simple components has been a research topic of great interest in recent years.1 Supramolecular self-assembly processes and dynamic covalent chemistry offer a powerful set of tools for the bottom-up synthesis of complex structures with new properties and emergent functionality.^{2,3} A defining feature of these synthetic strategies is that information contained within relatively simple components determines the formation of much more complex structures. Chemists have compiled an enormous library of self-assembled supramolecular complexes utilizing the directing properties of the transition metals. In comparison, there are relatively few examples of assemblies that were designed to use the main group elements as directing components, showing that main group supramolecular chemistry is still developing the tools for the predictable formation of well-defined structures.⁴ The main group elements generally prefer unusual "coordination" geometries compared to the transition metals, making them attractive targets when seeking novel properties, new topologies and alternative functionalities in selfassembled molecules and materials. However, there exists perhaps a misconception that bonds to main group elements are not labile enough for self-assembly.5 Contradictory to this belief, our lab has shown that thiolate bonds to the Group 15 elements phosphorus, arsenic, antimony and bismuth are sufficiently reversible and can be used to drive the formation of supramolecular assemblies.⁶⁻⁸

[‡] These two authors contributed equally to this work.

This report provides full synthetic details and characterization of new As_2L_3 and Sb_2L_3 cryptands (Table 1). This structural report will discuss in detail how small changes to the ligand can greatly affect the helicity of the assemblies and the stereochemistry of the pnictogen ions. Additionally, a new route that facilitates the supramolecular syntheses is described, in which brief exposure of the reaction mixture to vacuum is sufficient to complete the selfassembly of the cryptands from an equilibrating mixture of lower order structures.

Results and discussion

Cryptands overview

Our lab has previously shown that E_2L_3 (E = As, Sb) cryptands form in self-assembly reactions between ECl₃, base, and rigid dithiol ligands H₂1, H₂2, or H₂3 (Scheme 1, Chart 1).9-10 Characterization of these dynamic assemblies in solution and in the solid state revealed several structural similarities despite the differences in the rigid spacers between the mercaptomethyl groups of the ligands (ligand backbones). Consistently, each complex features short $E \cdots \pi$ distances, a consequence of the favorable pnictogen- π interactions, typically described as donation of electron density from the π -system of the ligands into the σ^* orbitals of the E atoms.¹¹ The different backbones of ligands H₂1, H₂2, or H₂3 cause subtle variations in the angles and distances between the pnictogen atoms and phenyl rings (Table 2). In order to further explore this interaction, a series of E_2L_3 cryptands were assembled using dithiol ligands with newly designed backbones (H_24-H_28 , Chart 1). Within each ligand, the mercaptomethyl arms were preserved but the size and rigidity of the backbone spacer was varied.

Synthesis of cryptands

 As_2L_3 (L = 1–8) and Sb_2L_3 (L = 1, 2, 8) cryptands were prepared in self-assembly reactions from ECl₃ and dithiolate ligands. The

Department of Chemistry, Materials Science Institute, and the Oregon Nanoscience and Microtechnologies Institute (ONAMI), University of Oregon, Eugene, OR, 97403-1253, USA. E-mail: dwj@uoregon.edu; Tel: 541-346-1695

[†] Electronic supplementary information (ESI) available: Experimental details for ligand and complex syntheses, full details on X-ray crystal structure determinations and refinements. CCDC reference numbers 824398–824403. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1dt10817d

| Table 1 | Crystallographic | data and | refinement | parameters |
|---------|------------------|----------|------------|------------|
|---------|------------------|----------|------------|------------|

| | As_24_3 | As ₂ 5 ₃ | As ₂ 6 ₃ | As ₂ 7 ₃ | As ₂ 8 ₃ | Sb ₂ 8 ₃ |
|--|--------------------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|-----------------------------------|
| Formula | C30 H36 As2 S6 | C54 H42 As2 S6 | C48 H48 As2 S6 | C48 H36 As2 S6 | C36.33 H30.33 As2 C1 S6 | C37.25 H31.38 Cl3 N0 13 S6 Sb2 |
| Formula weight | 738 79 | 1033.08 | 967.06 | 954 97 | 844 59 | 1022.96 |
| T/K | 173(2) | 173(2) | 173(2) | 173(2) | 173(2) | 173(2) |
| Wavelength/Å | 0 71073 | 0 71073 | 0 71073 | 0 71073 | 0 71073 | 0 71073 |
| Crystal system | Monoclinic | Monoclinic | Monoclinic | Monoclinic | Hexagonal | Rhombohedral |
| Space group | P2./n | C^{2}/c | C^{2}/c | C^{2}/c | R3c | R3 |
| a/Å | 144540(6) | 26 660(7) | 30 468(3) | 31,093(2) | 21 3256(7) | 21.0255(7) |
| h/Å | 12 6952(5) | 10.399(3) | 13.6420(12) | 135902(10) | 21.3256(7) | 21.0255(7) |
| c/Å | 17.6319(7) | 20 779(6) | 11.0855(10) | 10.6951(8) | 41 358(3) | 21.0255(7) |
| $\alpha(^{\circ})$ | 90 | 90 | 90 | 90 | 90 | 69.14 |
| $\beta(c)$ | 90 1500(10) | 125 192(7) | 106 3970(10) | 107.090(1) | 90 | 69.14 |
| $\gamma(^{\circ})$ | 90 | 90 | 90 | 90 | 120 | 69.14 |
| V/\dot{A}^3 | 32354(2) | 4708(2) | 4420 2(7) | 4319 7(6) | 16288 8(13) | 7831 4(5) |
| Z | 4 | 4 | 4 | 4 | 18 | 8 |
| $D/g \text{ cm}^{-3}$ | 1 517 | 1 458 | 1 453 | 1 468 | 1 550 | 1 735 |
| μ/cm^{-1} | 2.473 | 1.723 | 1.829 | 1.871 | 2.293 | 1.932 |
| F(000) | 1512 | 2112 | 1992 | 1944 | 7692 | 4038 |
| Crystal size/mm | $0.32 \times 0.06 \times 0.04$ | $0.07 \times 0.06 \times 0.05$ | $0.37 \times 0.14 \times 0.04$ | $0.18 \times 0.16 \times 0.12$ | $0.36 \times 0.28 \times 0.18$ | $0.16 \times 0.16 \times 0.08$ |
| Index ranges | -17 < = h < = 17 | -34 < = h < = 17 | -38 < = h < = 38 | -39 < = h < = 39 | -27 < = h < = 27 | -26 < = h < = 26 |
| | -15 < = k < = 15 | -13 < = k < = 11 | -17 < = k < = 17 | -17 < = k < = 17 | -27 < = k < = 27 | -26 < = k < = 26 |
| | -20 < = 1 < = 20 | -24 < = 1 < = 26 | -14 < = 1 < = 14 | -13 < = 1 < = 13 | -52 < = 1 < = 52 | -26 < = 1 < = 26 |
| Reflections collected | 30492 | 9193 | 24133 | 19714 | 58788 | 88616 |
| Independent Reflections [R] | 5689 [0.0546] | 4993 [0.0856] | 4837 [0.0417] | 4719 [0.0416] | 3969 [0.0307] | 11413 [0.0556] |
| Data/restraints/ Parameters | 5689/0/343 | 4993/0/280 | 4837/0/253 | 4719/0/325 | 3969/0/199 | 11413/0/577 |
| Goodness-of-fit on F^2 | 1.066 | 1.004 | 1.088 | 1.091 | 1.075 | 1.37 |
| $R_1 \ \text{w} R_2 \left[I > 2\sigma(I) \right]$ | 0.0456/0.1025 | 0.0756/0.1014 | 0.0468/0.1210 | 0.0418/0.0884 | 0.0385/0.1041 | 0.0633/0.1789 |
| R_1 , w R_2 (all data) | 0.0651/0.1123 | 0 1626/0 1318 | 0.0670/0.1416 | 0.0616/0.1004 | 0.0447/0.1081 | 0.0810/0.1886 |
| Largest diff. peak and hole/e $Å^{-3}$ | 0.571/-0.289 | 0.752/-0.453 | 1.064/-0.452 | 0.609/-0.233 | 1.145/-0.498 | 1.900/-1.630 |

Table 2 Stereochemical outcomes and selected geometric information for E₂L₃ assemblies

| | $E\cdots\pi$ | Stereochemical | E···E | Twist angle | Degree of | Interior | | | |
|--------------------------------|--------------|------------------------------|-------|------------------|----------------------------------|------------------------|---------|-----------|-----------|
| Complex | $(Å)^a$ | Configuration ^b | (Å) | (°) ^e | Helicity ^{<i>d</i>} (°) | Volume/Å ^{3e} | E-S (Å) | S–E–S (°) | Reference |
| $As_2 1_3$ | 3.30 | \varDelta, Λ | 5.03 | 36.6 | | 38 | 2.25 | 94.6 | 9 |
| $As_2 2_3$ | 3.30 | Δ, Λ, P | 5.11 | 35.7 | 6.0 | 44 | 2.25 | 94.2 | 6 |
| As_23_3 | 3.35 | $\Delta, \Lambda, M + P^{f}$ | 9.19 | 39.1 | _ | 55 | 2.24 | 97.3 | 10 |
| As_24_3 | 3.31 | Δ, Λ | 5.09 | 34.7 | | 38 | 2.25 | 94.1 | |
| As_25_3 | 3.33 | Δ, Δ, P | 9.52 | 33.3 | 29.5 | 90 | 2.25 | 94.8 | |
| As_26_3 | 3.30 | Δ, Δ, M | 11.71 | 27.3 | 54.3 | 67 | 2.24 | 96.1 | |
| As_27_3 | 3.25 | Δ, Δ, M | 12.28 | 23.5 | 65.8 | 64 | 2.24 | 97.5 | |
| $As_2 8_3$ | 3.29 | Δ, Δ, P | 7.55 | 29.2 | 7.7 | 72 | 2.24 | 94.7 | |
| Sb ₂ 1 ₃ | 3.31 | Δ, Δ, P | 4.30 | 43.0 | 12.7 | 36 | 2.43 | 92.0 | 12 |
| $Sb_2 2_3$ | 3.34 | Δ, Λ | 4.83 | 33.7 | _ | 46 | 2.42 | 91.5 | 6 |
| $Sb_{2}B_{3}(1)^{g}$ | 3.31 | Δ, Δ, M | 6.44 | 40.0 | 39.9 | 63 | 2.42 | 91.1 | |
| $Sb_2 8_3 (2)$ | 3.36 | Δ, Δ, M | 7.01 | 29.1 | 9.1 | 74 | 2.44 | 91.3 | _ |

^{*a*} Measured as the average distance between E center and centroid of close contacts with neighboring arene rings. ^{*b*} See Fig. 3–5 for examples of helical domain designations. To simplify discussion, for homoconfigurational cryptands only the Δ , Δ isomers are shown. ^{*c*} Twist of the octahedral coordination environment - estimated as the torsion angle between a sulfur, a centroid defined using the three sulfurs, the E center, and the closest aryl contact. ^{*d*} Reported as an average of the three $-CH_2-As-As-CH_2-$ torsion angles. ^{*e*} Cavities were measured using solvent (0.7 Å) surfaces in WebLab ViewerPro 4.0. Cavity volumes were estimated as the difference between the volume of the E₂L₃ cryptand filled with chloride atoms and the E₂L₃ cryptand with a void cavity. ^{*f*} (Δ , Λ , M)- and (Δ , Λ , P)-As₂L²₃ form as a racemic mixture. ^{*g*} There are two different polymorphs observed in the same crystal, Sb₂**8**₃(1) and Sb₂**8**₃(2).

conditions previously reported for the synthesis of cryptands As_2I_3 (Fig. 1a), Sb_2I_3 (Fig. 1b), Sb_22_3 (Fig. 1d), and As_23_3 (Fig. 1e), involving deprotonation of H_2L with base followed by the addition of ECl₃ (E = As, Sb), also allowed for the preparation of cryptands As_24_3 (Fig. 2), As_22_3 (Fig. 1c), As_25_3 (Fig. 3), and As_26_3 (Fig. 4).^{6,9,10,12} Crystals were grown of each assembly (Table 2),

allowing the direct comparison of these structures by single crystal X-ray diffraction.

Interestingly, base was not necessary for the synthesis of As_27_3 (Fig. 5) which assembled under conditions which normally result in $As_2L_2Cl_2$ macrocycle. Furthermore, As_28_3 would not assemble even with base present. These two surprising results prompted us to



Scheme 1 Self-assembly of As_2L_3 cryptands.



Chart 1 Ligands used in synthesis of cryptands.

consider the role of base in this reaction. Was deprotonation of the ligand with base prior to reaction with arsenic necessary or was the role of the base simply to remove the HCl byproduct of As–S bond formation from the reaction? We previously established that when a 1 : 1 ratio of dithiol ligand and AsCl₃ are combined in the absence of base, two thiol functional groups substitute onto each AsCl₃ molecule, resulting in the formation of As₂L₂Cl₂ macrocycles.¹³ These results show that base is not necessary for the addition of these first two ligands. However, even if this reaction is carried out in the presence of excess ligand, substitution of a third thiol ligand onto As does not occur before As₂L₂Cl₂ precipitates from solution



Fig. 2 Stick representations of the X-ray crystal structures of the As_24_3 cryptand: (a) side-view showing the ligand domain and (b) top-view down the As-As axis showing one of the As(III) coordination domains.



Fig. 3 Stick representations of the X-ray crystal structures of Δ, Δ, P isomer of the As₂**5**₃ cryptand: (a) side-view showing the *P* configuration in the ligand domain and (b) top-view showing Δ configuration of one of the As(III) coordination domains.

after several days (except in the case of As_27_3). Each substitution of thiolate onto $AsCl_3$ results in the formation of an equivalent of HCl and one theory to explain our observations is that equilibrium with HCl causes the reaction to stop after two substitutions have been made at each arsenic center. In order to test this hypothesis, a chloroform solution of H₂1 and 2/3 AsCl₃ was heated and exposed to high vacuum at intervals over the course of the reaction (under continuous vacuum all solvent would have evaporated). Under these conditions As_21_3 formed, suggesting that the presence of the HCl byproduct is what limits the addition of ligands onto arsenic. Further support for this theory lies in our previous report



Fig. 1 Stick representations of the X-ray crystal structures of previously reported E_2L_3 cryptands: (a) As_21_3 ,⁹ (b) Sb_21_3 ,¹² (c) As_22_3 ,⁶ (d) Sb_22_3 ,⁶ and (e) As_23_3 .¹⁰ Arsenic is shown in purple, antimony in teal, sulfur in yellow, carbon in black and hydrogen in white.



Fig. 4 Stick representations of the X-ray crystal structures of the Δ , Δ ,M isomer of the As₂6₃ cryptand: (a) side-view showing the M configuration in the ligand domain and (b) top-view showing Δ configuration of one of the As(III) coordination domains.



Fig. 5 Stick representations of the X-ray crystal structures of the Δ , Δ ,M isomer of the As₂7₃ cryptand: (a) side-view showing the M configuration in the ligand domain and (b) top-view showing Δ configuration of one of the As(III) coordination domains.

that heating a mixture of dissolved $As_2L_2Cl_2$ crystals with excess H_2L allows for the formation As_2L_3 .^{13a} Because we started from crystalline $As_2L_2Cl_2$ in that case, only two equivalents of HCl were formed while making As_2L_3 , instead of the six equivalents formed when cryptand was prepared directly from AsCl₃ and H_2L .

The removal of HCl by vacuum allows for cryptand formation while avoiding the use of potentially harsh and complicating bases. To test the scope of this new vacuum-enabled synthetic technique, H₂8 was mixed with AsCl₃ in chloroform at 50 °C and the reaction vessel was exposed to high vacuum for a few seconds every 1.5 h. Within a few hours ¹H NMR spectroscopy revealed no free H₂8 and that As₂4₂Cl₂ and a new highly symmetric species were both present in solution. After one more day of heating, the new high-symmetry species was the dominant product. Crystals were grown by layering this chloroform solution with hexanes and the structure revealed that the main product of the reaction was the As₂8₃ cryptand (Fig. 6a). Similarly, Sb₂8₃ was prepared using vacuum-enabled synthesis (Fig. 6b-c). Both As₂8₃ and Sb₂8₃ could not be prepared by other routes, suggesting that this relatively gentle synthetic route may allow for the preparation of new, largerorder assemblies. Additionally, this further supports that $As_2L_2Cl_2$ macrocycles are intermediates in cryptand formation.^{7,8}



Fig. 6 Stick representations of the X-ray crystal structures of the $E_2 \mathbf{8}_3$ cryptands: (a) $As_2 \mathbf{8}_3$, (b) $Sb_2 \mathbf{8}_3(1)$, and (c) $Sb_2 \mathbf{8}_3(2)$. (b) and (c) are isomeric forms of $Sb_2 \mathbf{8}_3$ which cocrystallize.

Discussion of cryptand size and shape

Single crystals of each cryptand were grown and the structures were obtained using X-ray diffraction (Fig. 1-6). Comparison reveals several structural features that are general for this class of E_2L_3 cryptand. In each case, the $E \cdots \pi$ interaction causes the arsenic or antimony atoms to be positioned within the cryptand cavities. Consequently, their lone pairs of electrons point toward one another making the cavities uniquely Lewis basic. As expected, the distance between the pnictogen centers in each complex depends on the distance between the thiolate functionalities on the ligands (Table 2). In the arsenic structures, As · · · As distances range from 5.03 Å for As_2I_3 , the shortest cryptand, to 12.28 Å for As₂7₃, the longest cryptand (Table 2). While this result is not surprising for the rigid cryptands, (As₂1₃, As₂2₃, As₂4₃, As₂5₃, As_27_3 , and As_28_3) some flexibility is expected for As_23_3 and As_26_3 . Indeed, As_23_3 exhibits this flexibility as the ligands are folded into the cavity, destroying the C_3 symmetry of the complex and giving a shorter than expected As ... As distance of 9.19 Å. All other cryptands have apparent C_3 symmetry. Despite the inherent ligand flexibility within As_26_3 , in the solid state the ligand is fully extended and the C_3 symmetry of the complex is maintained. This bonding arrangement allows for the expected *anti* conformation for the phenyl rings on the ethylene spacer.

Similarly, Sb...Sb distances trend with ligand length (Table 2). Compared to As... π , the relatively stronger Sb... π interaction can provide for shorter E... π contacts although this is not observed here due to the constraints imposed by the rigid ligand framework and the relatively longer Sb–S bonds.^{7,14} The stronger Sb... π interaction may cause twisting of the ligands in Sb₂1₃ to allow for shorter contacts than would be present without twisting. Due to the naphthalene group on H₂2, twisting within E₂3₃ assemblies is limited sterically: while the S...S distances in H₂1 and H₂2 are the same, the Sb...Sb distances for Sb₂1₃ (4.30 Å) and Sb₂2₃ (4.83 Å) differ by > 0.5 Å. This is remarkable because the As...As distances in As₂1₃ and As₂2₃ vary by < 0.1 Å. This larger difference in distances within the antimony cryptands is manifested by the tight helical twist found in the Sb₂1₃ complex.

As expected, cavity volumes trend roughly with ligand length: the volume increases in concert with the $S \cdots S$ distance (Table 2). However, the ligands in As_23_3 are folded into the cavity, resulting in a smaller than expected volume in the solid state (51 Å³). The cavities in As_26_3 and As_27_3 are also smaller than expected, a result of the relatively narrow ligands not completely enclosing a welldefined cavity. The volumes of the corresponding As- and Sbcontaining cryptands are approximately equal.

The S–E–S bond angles and E–S bond distances were measured and the averages for each complex are listed in Table 2. The E– S bond distances do not vary much from complex to complex, averaging 2.24 Å for As–S bonds and 2.44 Å for Sb–S bonds. The S–E–S angles vary slightly more. In the arsenic complexes, the individual (not average) angles range from 90.6° to 103.0° with an average of 95.4°. In the antimony complexes, these angles range only from 89.7 to 94.4° with an average angle of 92.6°. As₂3₃ has the most diverse set of observed angles which is not surprising given the lack of symmetry in the complex.

The degree of helicity in the cryptands was measured as the offset of the methylene carbons on each ligand (Table 2, Fig. 7). It was found to range from 6° (nearly untwisted) for As_22_3 to 65° for As_27_3 . In general, greater $E \cdots E$ distances have larger degrees of helicity, but this can vary greatly depending on ligand orientation. This is evidenced by the structures of co-crystallized Sb₂8₃(1) and Sb₂8₃(2) in which the methylene carbons are offset by pitches 39.9° and 9.1°, respectively, but only differ in Sb...Sb distances by 0.05 Å.

Discussion of pnictogen- π interactions

Lewis acid/base adducts formed by interactions between pnictogens and arene rings have been rigorously studied by Schmidbaur and co-workers, although only recently have they been used in a supramolecular context as a structural motif in the design of larger, higher order assemblies.^{9–14,16} Pnictogen- π interactions are defined as short contacts (less than the sum of the respective van der Waals radii) between the trivalent metalloid center and arene carbon atoms; the attractive interaction is measured between the pnictogen-center and the centroid of these close contacts. η^2 coordination is typically observed, though in some cases hapticity can be as high as η^6 when sterically demanding ring substituents center the metal over the ring.^{11,17} In the crystal structure of each cryptand, short $As \cdots \pi$ contacts are observed (Table 2). The apparent C_3 symmetry of all of the structures except As_23_3 results in approximately equal $E \cdots \pi$ contacts between each metal center and each ligand. The cryptand with the shortest average $E \cdots \pi$ contacts (3.25 Å) is As_27_3 , while As_25_3 had the longest average contacts (3.33 Å). This very narrow range of contact distances does not correlate to the $E \cdots E$ distance or the length of the ligand spacer. Additionally, the hapticity observed for each structure (η^2) was not affected by the length of the ligand.

Analysis of chirality in E₂L₃ cryptands

If considered a chelate, the pnictogen- π contact completes a fivemembered chelate-type ring that contains arsenic or antimony, the thiolate sulfur, the methylene carbon, and the two aryl carbons (*ipso* and *ortho*) involved in the η^2 -E··· π interaction. The bidentate nature of the primary/secondary coordination spheres creates a distorted octahedral coordination environment around the pnictogen center. In the solid state, the coordination environments of all observed E₂L₃ cryptands possess a conformational chirality which can be described with established stereochemical conventions. The absolute configuration of the pnictogen coordination domain is defined by the direction of torsional twist observed along the C₃ axis. A clockwise twist is designated as Δ and a counter-clockwise twist is designated as Λ (Fig. 3–5).^{18,19}

As₂1₃, As₂4₃, and Sb₂2₃ cryptands are "mesocates" - one pnictogen center is Δ and the other is Λ and the ligand domain is not significantly twisted - there is very little, if any, degree of helicity (Fig. 7).^{20a} On the other hand, Sb₂1₃, Sb₂8₃, As₂8₃ and As₂5₃–As₂7₃ are helicates in which helicity is observed in the ligand domain and both pnictogen centers have identical stereochemistry. The ligands of As₂3₃ adopt an asymmetric conformation in the solid state, resulting in the crystallization of a racemic pair of helices: Δ , ΔM -As₂3₃ and Δ , ΔP -As₂3₃. Here, M designates a left-handed twist in the ligand domain and P designates a right-handed twist (Fig. 3–5).¹⁰ All helical structures crystallize as racemic mixtures of enantiomers (Δ , Δ and Λ , Λ). For the sake of simplicity, only Δ , Δ isomers are shown and discussed. These complexes are examples of chiral structures originating from coordination assemblies lacking chiral components.^{20,21}



Fig. 7 Illustrations of degree of helicity and twist angle of pnictogen coordination domains. (a) Degree of helicity was measured as an average of the three $-CH_2$ -E-E- CH_2 - torsion angles; -CH2- carbon atoms highlighted green; (b) twist angle was estimated as the torsion angle between a sulfur, a centroid defined using the three sulfurs, the E center, and the closest aryl contact.

In general, there are three origins of helicity in metallosupramolecular architectures: 1) helical induction by intramolecular effects, 2) axial chirality in the ligands, and 3) helical induction by intermolecular interactions.^{18,19,22} Presumably, cryptands adopt the degree of helicity necessary to reach a conformation in which interactions that promote twisting of the ligand domain are balanced with interactions that oppose twisting. Interactions that promote twisting in the ligand domain include favorable ligandligand interactions and $E \cdots \pi$ interactions. An $E \cdots \pi$ distance of about 3.3 Å is remarkably preserved across all observed cryptands. This is evidence that the $E \cdots \pi$ interaction is significant to the conformation and, thus, the stereochemistry of these cryptands. Steric interactions between individual components of an assembly could be considered interactions which would oppose helical twisting. For instance, in the smaller, non-helical cryptands such as As₂1₃, twisting is limited by the unfavorable steric interactions which would result from short As ... As distances. The bulky ligands of the non-helical As_22_3 and As_24_3 cryptands exacerbate the effects of the interactions opposing twisting due to unfavorable steric clash between neighboring ligands in the cryptand. For As_25_3 , As_26_3 , and As_27_3 , these cryptands are large enough to allow twisting up to the point that steric interactions predominate.

With the exception of the highly asymmetrical As₂**3**, the observed helical structures have E centers of identical chirality (*i.e.* Δ, Δ or Λ, Λ) while the non-helical structures possess Δ, Λ configurations. Since Δ and Λ configurations of the pnictogen coordination environments are energetically equal, it is reasonable to suspect that the helicity in the ligand domain (or lack thereof) gives rise to the relative configurations (pairing or non-pairing) of chirality of the E centers and not the other way around.

Since helicity results in the coordination environments of the E centers being offset from one another (i.e., the sulfur atoms are not eclipsed), in order for the two E centers in helical cryptands to have equivalent environments, they must have identical stereochemical configurations. We observe that a small degree of helicity may allow for Δ , Λ configuration of the E coordination domains. For example, $As_2 2_3$ has a small (6°) degree of helicity yet maintains Δ , Λ configuration. A unique coupling relationship exists between the stereochemical domains. In related dinuclear assemblies (e.g., double, triple, and quadruplestranded metallohelicates) the helicity is coupled to the absolute stereochemical configuration of each metal center. For instance, in the bis-chatecolate structures studied by Raymond and coworkers, the metal coordination domains of *P*-helices all have Δ , Δ configurations as a result of strong mechanically coupling between the metal centers.²² In our structures, the *absolute* stereochemistry of the E coordination domains is decoupled from that of the helical domain. However, the coupling of the *relative* stereochemistry of the two E coordination domains to the ligand domain is still intact. In cryptands with significant helical twist, the E coordination domains have the same stereochemistry, while in non-helical cryptands, the E coordination domains have opposite stereochemistry (the cryptands are "meso"). The unrestricted rotation around the sulfur-methylene bonds seems to be sufficient to decouple the absolute stereochemistry of the ligand domain from that of the As and Sb coordination domains. In related metallohelicates, the ligands are much more rigid and no similar rotation is possible.21,22

Experimental

General

Complete schemes, experimentals and citations for the ligand syntheses and techniques used for single crystal growth are provided in the ESI. Caution: arsenic compounds are highly toxic and should be handled with care!

X-ray crystallography

Diffraction intensities were collected at 173(2) K on a Bruker Apex CCD diffractometer using Mo-K α radiation $\lambda = 0.71073$ Å. Absorption corrections were applied by SADABS.²³ 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. H atoms were refined in calculated positions in a rigid group model. Solvent molecules, CHCl₃ in As₂8₃ and CH₃CN in Sb₂8₃, are disordered around -3 axis and were treated by SQUEEZE.24 Corrections of the X-ray data by SQUEEZE (343 and 23 electron/cell, respectively for $As_2 \mathbf{8}_3$, $Sb_2 \mathbf{8}_3$) are close to the required values of 348 and 22 electron/cell for six and one molecules, respectively, in the full unit cells. In $A_{5_2}6_3$ elongations of thermal ellipsoids for some carbon atoms in ligands perpendicular to C-C bonds were found. Such elongations seem to be related to a disorder for these carbon atoms. Some structural features in $Sb_2 8_3$ also indicate that the molecules in this structure are flexible or could be disordered as well. As results some of C-C bond distances in Sb₂8₃, As₂5₃ and As₂6₃ were not able to be measured precisely. All calculations were performed by the Bruker SHELXTL (v. 6.10) package.²⁵

Conclusions

In this report, the X-ray crystal structures of six new As_2L_3 and Sb_2L_3 supramolecular cryptands were analyzed in the context of previously reported As- and Sb-cryptands. A new vacuumenabled synthesis allowed for the formation of two of these new assemblies which could not be prepared by other routes. Comparing the stereochemistries of these assemblies revealed that in cryptands with significant helicity, the As and Sb coordination environments showed identical stereochemistry (*i.e.*, Δ , Δ or Λ , Λ), whereas all non-helical cryptands were also mesocates (Δ, Λ) configuration) as expected. Surprisingly, the mechanical coupling in these cryptands is not sufficient to dictate helicity: P helicates can give rise to either Δ, Δ or Λ, Λ metal center configurations showing the stereochemical domains are decoupled, which is unusual in such metallohelicates. The degree of helicity determines the stereochemical relationship between the As and Sb coordination environments. The pnictogen- π interaction is an anchoring point for a chelate ring and influences the degree of helicity and overall stereochemistry in the observed cryptands. This reinforces the conclusion that pnictogen- π interactions are important supramolecular forces in directing the conformations of main group element-containing structures and, thus, are important to the design of these complexes.

Acknowledgements

We gratefully acknowledge funding from the National Science Foundation (CAREER award CHE-0545206). D.W.J. is a Cottrell Scholar of Research Corporation for Science Advancement. This material is based upon work supported by the U.S. Department of Education under Award No. P200A070436 (V.M.C.) and an NSF Integrative Graduate Education and Research Traineeship (M.A.P., O.B.B., and S.A.F., DGE-0549503).

Notes and references

- (a) D. L. Caulder and K. N. Raymond, Acc. Chem. Res., 1999, 32, 975;
 (b) S. Leininger, B. Olenyuk and P. J. Stang, Chem. Rev., 2000, 100, 853;
 (c) M. W. Hosseini, Acc. Chem. Res., 2005, 38, 313;
 (d) D. J. L. Tranchemontagne, Z. Ni, M. O'Keeffe and O. M. Yaghi, Angew. Chem., Int. Ed., 2008, 47, 5136;
 (e) Z. Wang and S. M. Cohen, Angew. Chem., Int. Ed., 2008, 47, 4699.
- 2 M. Hutin, D. Schultz and J. R. Nitschke, *Chimia*, 2008, **62**, 198; R. J. Sarma and J. R. Nitschke, *Angew. Chem., Int. Ed.*, 2008, **47**, 377.
- 3 D. Fiedler, D. H. Leung, R. G. Bergman and K. N. Raymond, *Acc. Chem. Res.*, 2005, **38**, 351.
- 4 M. A. Pitt and D. W. Johnson, Chem. Soc. Rev., 2007, 36, 1441.
- 5 S. R. Batten, S. M. Neville and D. R. Turner, *Coordination Polymers: Design, Analysis, and Application*, RSC Publishing, Cambridge, 2009, p 7.
- 6 V. M. Cangelosi, L. N. Zakharov and D. W. Johnson, Angew. Chem., Int. Ed., 2010, 49, 1248.
- 7 V. M. Cangelosi, T. G. Carter, J. L. Crossland, L. N. Zakharov and D. W. Johnson, *Inorg. Chem.*, 2010, 49, 9985.
- 8 V. M. Cangelosi, T. G. Carter, L. N. Zakharov and D. W. Johnson, Chem. Commun., 2009, 5606.
- 9 W. J. Vickaryous, R. Herges and D. W. Johnson, *Angew. Chem., Int. Ed.*, 2004, **43**, 5831.
- 10 M. A. Pitt, L. N. Zakharov, K. Vanka, W. Thompson, B. Laird and D. W. Johnson, *Chem. Commun.*, 2008, 3936.
- 11 (a) H. Schmidbaur, W. Bublak, B. Huber and G. Müller, Angew. Chem., 1987, 99, 248; (b) H. Schmidbaur, R. Nowak, B. Huber and G. Müller, Organometallics, 1987, 6, 2266; (c) T. Probst, O. Steigelmann, H. Riede and H. Schmidbaur, Chem. Ber., 1991, 124, 1089; (d) J. Zukerman-Schpector, A. Otero-de-la-Roza, V. Luaña and E. R. T. Tiekink, Chem. Commun., 2011, 47, 7608.

- 12 W. J. Vickaryous, L. N. Zakharov and D. W. Johnson, *Main Group Chem.*, 2006, 5, 51.
- 13 (a) W. J. Vickaryous, E. R. Healey, O. B. Berryman and D. W. Johnson, *Inorg. Chem.*, 2005, 44, 9247; (b) V. M. Cangelosi, L. N. Zakharov, S. A. Fontenot, M. A. Pitt and D. W. Johnson, *Dalton Trans.*, 2008, 3447; (c) V. M. Cangelosi, A. C. Sather, L. N. Zakharov, O. B. Berryman and D. W. Johnson, *Inorg. Chem.*, 2007, 46, 9278.
- 14 (a) A. Schier, J. M. Wallis, G. Müller and H. Schmidbaur, Angew. Chem., Int. Ed. Engl., 1986, 25, 757; (b) H. Schmidbaur, R. Nowak, A. Schier, J. M. Wallis, B. Huber and G. Müller, Chem. Ber., 1987, 120, 1829; (c) H. Schmidbaur, J. M. Wallis, R. Nowak, B. Huber and G. Müller, Chem. Ber., 1987, 120, 1837; (d) H. Schmidbaur, R. Nowak, O. Steigelmann and G. Müller, Chem. Ber., 1990, 123, 1221.
- 15 H. Schmidbaur and A. Schier, Organometallics, 2008, 27, 2361.
- 16 N. R. Lindquist, T. G. Carter, V. M. Cangelosi, L N. Zakharov and D. W. Johnson, *Chem. Commun.*, 2010, 46, 3505.
- 17 H. Schmidbaur, T. Probst, B. Huber, O. Steigelmann and G. Müller, Organometallics, 1989, 8, 1567.
- 18 (a) M. Albrecht, Top. Curr. Chem., 2004, 248, 105; (b) C. Piguet, G. Bernardinelli and G. Hopfgartner, Chem. Rev., 1997, 97, 2005.
- 19 G. A. Hembury, V. V. Borovkov and Y. Inoue, *Chem. Rev.*, 2008, **108**, 1.
- 20 (a) M. Albrecht, Chem.-Eur. J., 2000, 6, 3485; (b) M. Albrecht and R. Fröhlich, Bull. Chem. Soc. Jpn., 2007, 80, 797.
- 21 (a) D. L. Caulder, R. E. Powers, T. N. Parac and K. N. Raymond, Angew. Chem., Int. Ed., 1998, 37, 1840; (b) R. M. Yeh, J. Xu, G. Seeber and K. N. Raymond, Inorg. Chem., 2005, 44, 6228.
- 22 (a) M. Meyer, B. Kersting, R. E. Powers and K. N. Raymond, *Inorg. Chem.*, 1997, **36**, 5179; (b) R. M. Yeh, M. Ziegler, D. W. Johnson, A. J. Terpin and K. N. Raymond, *Inorg. Chem.*, 2007, **40**, 2216; (c) J. Xu, T. N. Parac and K. N. Raymond, *Angew. Chem., Int. Ed.*, 1999, **38**, 2878.
- 23 G. M. Sheldrick, Bruker/Siemens Area Detector Absorption Correction Program, Bruker AXS, Madison, WI, 1998.
- 24 P. Van, der Sluis and A. L. Spek, Acta Crystallogr., Sect. A: Found. Crystallogr., 1990, 46, 194.
- 25 SHELXTL-6.10 "Program for Structure Solution, Refinement and Presentation", BRUKER AXS Inc., 5465 East Cheryl Parkway, Madison, WI 53711–5373 USA.