Host-guest interactions in a series of self-assembled $As_2L_2Cl_2$ macrocycles

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Supplementary Information

Synthesis:

^{1}H NMR spectra were measured using a Varian INOVA-300 spectrometer operating at 299.935 MHz. *J* values are given in Hz. Commercially available reagents were used as received.

4,4'-bis(mercaptomethyl)biphenyl ($H_2$1). Procedure is modified from that which was previously reported.[1] 4,4'-bis(chloromethyl)biphenyl (2.00 g, 7.96 mmol) was dissolved in solution of absolute ethanol (30 mL) and acetone (4 mL). Thiourea (1.31 g, 17.2 mmol) was added and the solution was heated to reflux for 3 hours. The off-white precipitate was filtered, washed with acetone, and dried under vacuum (3.01g, 7.46 mmol, 93%). A 3-neck round bottom flack was charged with this precipitate (1.04 g, 2.58 mmol), equipped with a stir bar and condenser, and placed under a N_2 atmosphere. Degassed 2M NaOH (30 mL) was added via cannula and the mixture was heated to 80 °C for 4 hours. The cloudy solution was cooled to room temperature and degassed 4M HCl (20 mL) was added via cannula. Precipitate formed as the acid was added and pH paper was used to verify that the solution was acidic (pH < 3). The reaction mixture was extracted with CH_2Cl_2 (3 × 20 mL) and the combined organics were dried over sodium sulfate and evaporated to dryness to yield a white powder (373 mg, 1.51 mmol, 59%). δ_H(300 MHz; $CDCl_3$; Me_4Si) 7.54 (d, 4 H, CH, *J* 4.5), 7.39 (d, 4 H, CH, *J* 7.8), 3.79 (d, 4 H, CH_2, *J* 7.5), 1.80 (t, 2 H, SH, *J* 7.5); δ_C(75 MHz; $CDCl_3$) 140.4, 139.7, 128.6, 127.5, 28.9, which matched the values reported in the literature.

1,4-dimethoxy-2,5-bis(mercaptomethyl)benzene ($H_2$3). Procedure is modified from that which was previously reported.[2] 1,4-bis(methoxy)-2,5-bis(chloromethyl)benzene (251 mg, 1.07 mmol) and thiourea (275 mg, 3.62 mmol) were heated to reflux in acetone (40 mL) for 4 h. The solvent was evaporated to yield an off-white salt. The salt was transferred to a 3-neck round-bottom flask and placed under N_2. Degassed 2M NaOH (50 mL) was transferred via cannula onto the salt and the solution was stirred under N_2 at 80 °C for 7 h. This solution was acidified using 6M HCl under N_2, then extracted with CH_2Cl_2 (4 x 20 mL). The organic layer was washed with water (25 mL) and brine (25 mL) and the solvent was evaporated to yield a white solid (120 mg, 0.521 mmol, 49%). δ_H(300 MHz; $CDCl_3$; Me_4Si) 6.81 (s, 2 H, CH), 3.85 (s, 6 H, CH_3), 3.71 (d, 4 H, CH_2, *J* 7.9), 1.96 (t, 2 H, SH, *J* 7.9), which matched the values reported in the literature.

Volume Calculations using GRASP[3]:

The cavity volume of the [$(As_23_2Cl_2)_2$·toluene] dimer was also calculated using the software package GRASP and found to be 164 Å^3. The large apertures in the plane of the sulfur atoms were "capped" for the calculation by the addition of a non-covalently

bound anthracene units on each side. This "capping" is expected to cause the volume to be slightly underestimated.

Disorder in Crystal Structures:

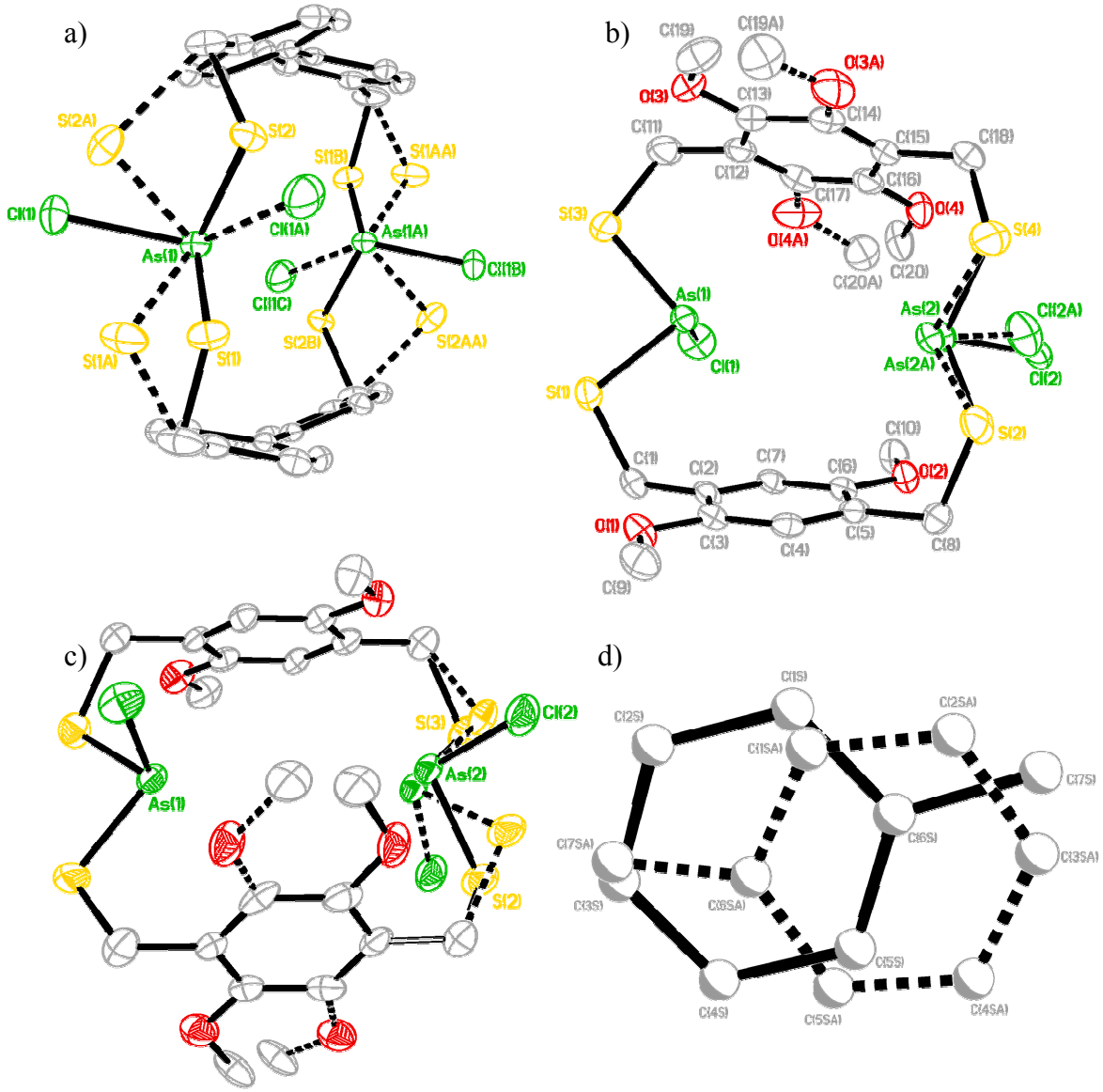

Fig. S1. ORTEP (30% probability ellipsoids) representations of the disorder of the macrocycles in the X-ray crystal structures of (a) $As_2\mathbf{1}_2Cl_2$, (b) $[(As_2\mathbf{3}_2Cl_2)_2{\cdot}p\text{-xylene}]$, and (c) $[(As_2\mathbf{3}_2Cl_2)_2{\cdot}\text{toluene}]$. Ball and stick representation of the disorder of (d) toluene in the X-ray crystal structure of $[(As_2\mathbf{3}_2Cl_2)_2{\cdot}\text{toluene}]$.

Measurement of bend in biphenyl ligand:

The bend of the biphenyl ligands in the X-ray crystal structure of $As_2\mathbf{1}_2Cl_2$ was compared to that of 4,4'-substituted biphenyl moieties in other molecules. To measure this bend, the ligand was represented as a set of five lines, drawn between the following

carbons: C1-C2, C2-C5, C5-C8, C8-C11, C11-C14. The angles formed at the intersections of these lines were measured using the Bruker SHELXTL 6.10 software[4]. A Cambridge Crystal Structure Database[5] search yielded 91 structures containing the 4,4'-substituted biphenyl moiety and the measurement procedure was repeated on a selection of on similar structures. These measurements yielded angles similar to those found in $As_2\mathbf{1}_2Cl_2$.

References:

[1] T. Nakamura, J. J. Ren, K. M. Zhu, S. Kawara and B. K. Jin, *Anal. Sci.*, 2006, **22**, 1261-1264.

[2] Henkel & Cie GmbH. *Br. Pat.*, 807,720, 1959; *Chem. Abstr.*, 1995, **123**, 2870.

[3] A. Nicholls, K. A. Sharp and B. Honig, *Proteins: Struc., Func. and Genet.*, 1991, **11**, 281-296.

[4] Bruker SMART (Version 5.631), SAINT (Version 6.63) and SHELXTL (Version 6.10), 2000, Bruker AXS Inc., Madison, Wisconsin, USA.

[5] Conquest Version 1.7, February 2005 Release.