Supramolecular aggregation in dithia-arsoles: chlorides, cations and N-centred paddlewheels†

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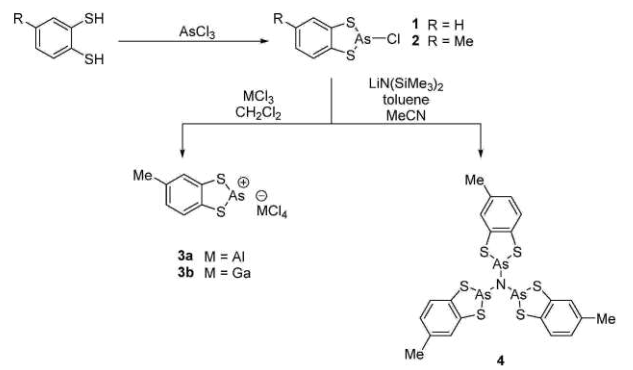
The benzo-fused dithia-chloro-arsole derivative $C_6H_4S_2AsCl$ (1) is found to crystallise in the triclinic space group P¯1 with 17 mole-cules in the asymmetric unit whereas the tolyl derivative, $MeC_6H_3S_2AsCl$ (2) is polymorphic with the α-phase crystallising in the monoclinic space group $P2_1/c$ with a single molecule in the asymmetric unit and the β-phase adopting a triclinic structure with two molecules in the asymmetric unit. Reaction of these dithia-chloro-arsole derivatives with $LiNIJSiMe_3)_2$ in a 3 : 1 mole ratio afforded the unique paddlewheel structure $(MeC_6H_4S_2As)_3N$ (4).

The first two-coordinate Lewis acidic phosphorusIJIII) cation was reported by Dimroth and Hoffmann in 1964.[1] Since then the field of phosphenium chemistry has considerably grown, in part due to the use of these complexes as ligands to coordi-nate to transition metals.[2–7] On the other hand, examples of analogous arsenium compounds are less common in the liter-ature,[8,9] although a number of examples are known ($[R_2E]$ijX], E = P, As, Sb).[10–13] Due to the simultaneous presence of a lone pair and a vacant p-orbital, the chemistry of these cations re-sembles that of comparable group 14 persistent carbenes, al-beit with stronger π-acceptor and poorer σ-donor character as-sociated with the net positive charge.[14] Despite the poorer donor ability, a number of examples of metal-arsenium com-plexes have been reported affording structures homologous to Fischer carbenes.[15,16] One of the earliest dithia-arsolidinium cations (3a, Scheme 1) to be described was reported by Burford in 1989 but its solid-state structure was never eluci-dated.[17] Whilst dithia-arsolidinium cations have been shown to exhibit Lewis acidic properties towards both pyridine and triphenylphosphine,[8,18] more recent studies into arsenic-containing heterocycles have investigated dithia-chloro-arsole derivatives as potential diagnostic and therapeutic pharma-ceuticals for positron emission tomography (PET).[19]

In the current report we describe a series of structural studies on the dithia-chloro-arsoles, 1 and 2 (Scheme 1). Com-pound 1 is unusual in exhibiting 17 molecules in the asym-metric unit and can be categorised amongst the small num-ber of molecules with particularly high Z′ numbers.[20] While there are relatively large numbers of structures with Z′ > 4, the numbers decrease significantly for Z′ > 8 and are very rare for Z′ > 16 with just 7 reported structures.[21] In addition, we find 2 is polymorphic and compare the structures of 2α, initially reported by Kisenyi et al.,[22] with the new polymorph 2β in relation to 1 and other dithia-chloro-arsoles. Treatment of 2 with the Lewis acids MCl_3 (M = Al, Ga) affords the iso-morphous pair of dithia-arsolidinium cations [3]ijMCl_4] (3a M = Al, 3b M = Ga) in which the cations are located on a crystal-lographic mirror plane. Addition of 2 to $LiNlJSiMe_3)_2$ in a 3 : 1 ratio leads to formation of the paddlewheel complex 4 (Scheme 1) which exhibits supramolecular aggregation through close S⋯S contacts.

Combining benzene-dithiol or 4-methyl-benzene-1,2-dithiol with $AsCl_3$ afforded 2-chloro-benzo-1,3,2-dithia-arsole 1 and the 2-chloro-4′-methyl-benzo-1,3,2-dithia-arsole, 2 in good



Scheme 1 Synthesis of arsenic heterocycles 1–4.

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yields (up to 82%) according to the literature method (lit. 85%).[22] Single crystals of 1 suitable for X-ray diffraction were grown from a saturated solution of THF whereas 2 could be grown as either of two polymorphs from MeOH (2α) or MeCN (2β). Recrystallised yields were not optimised for these struc-tural studies.

Compound 1 crystallises in the triclinic space group $P\bar{1}$ with 17 molecules in the asymmetric unit. The molecular ge-ometries of these 17 crystallographically independent mole-cules are essentially identical and, with no torsional flexibil-ity, this large Z′ structure essentially arises through subtle differences in chemical environment. The molecular struc-ture of 1 reveals the C_2S_2As ring plane adopts an envelope structure with fold angles about the S⋯S vector in the range 8.65–20.30° (mean = 14.28°). All 17 molecules of 1 form di-mers through a four-centre As_2Cl_2 interaction with As⋯Cl contacts (3.360lJ7)–3.580lJ8) Å) that are shorter than the sum of the van der Waals radii (3.60 Å). These comprise 8 crystal-lographically independent dimers and one dimer (containing As11) located about a crystallographic inversion centre (Fig. 1).

This $[As–Cl]_2$ dimer motif has also been observed in the closely related thiazarsole, C_6H_4lJNH)SAsCl.[23] A number of other structures in the CSD also exhibit such $[As–Cl]_2$ mo-tifs.[24] These dimers are then linked via additional As⋯Cl contacts (3.453lJ7)–3.951lJ8) Å) generating a chain motif. This intermolecular interaction comprises a combination of electrostatically favourable $As^{\delta+}\cdots Cl^{\delta-}$ interactions, combined with significant dispersion forces. Computational studies support the presence of strong electrostatic and dispersion contributions to bonding (see ESI†). We also examined the potential for a σ-hole interaction but found no evident σ-hole at arsenic but the presence of a σ-hole on chlorine (see ESI†). The latter appears to form a number of contacts to the π-system of the benzo-ring, although the majority of such C⋯Cl contacts fall beyond the sum of the van der Waals radii.

Recrystallisation of 2 from MeOH afforded crystals of 2α whose structure was the same as that previously reported (DAXLOD).[22] A second polymorph 2β was isolated from MeCN. 2α crystallises in the space group $P2_1/c$ with Z′ = 1 whereas 2β adopts the triclinic space group $P\bar{1}$ with two mole-cules in the asymmetric unit. The molecular structures of 2α and 2β are essentially identical and also show an envelope conformation of the heterocyclic ring analogous to 1. For 2α the fold angle is 23.60° whereas they are 19.44 and 21.51° for the two crystallographically independent molecules in 2β. In the case of 2α there are no As⋯Cl contacts analogous to those observed in 1. Instead the packing appears to be di-rected by As⋯π interactions to the benzo ring ($As\cdots\pi_{centroid}$ = 3.251 Å). These contacts link molecules parallel to the crystal-lographic c-axis via a 2_1 screw axis (Fig. 2). Such As⋯π inter-actions from three-coordinate arsenic have been observed in other systems with As⋯π contacts in the range 3.14–3.47 Å.[25] Conversely 2β exhibits As⋯Cl contacts more reminiscent of the dimers formed in 1. In the first crystallographically inde-pendent dimer the intra-dimer As1⋯Cl1 contact (3.8154(9) Å) falls beyond the sum of the van der Waals radii (3.80 Å), and is longer than those observed in 1. In the second dimer the corresponding intradimer As2⋯Cl2 contact (3.5025(9) Å) falls within the range observed in 1.

Notably both structures now offer additional S⋯Cl intra-dimer contacts of (3.5327lJ12) and 3.4724(12) Å for S2⋯Cl1 and S4⋯Cl2 respectively) which are less than the sum of the van der Waals radii of 3.55 Å (Fig. 2 and ESI†). Additionally, a slight fold of the S–As–S fragment out of the plane of the aromatic backbone is noted to form an 'enve-lope' geometry with fold angles of 23.60lJ4)° and 21.51lJ4)° for 2α and 2β respectively. The melting point of 2α (81–82 °C) is higher than that of 2β (67–69 °C) suggesting it has the higher lattice energy. This is also in agreement with the density rule which infers that structures with higher densities are enthalpically more favourable (densities of 2α and 2β are 1.920 and 1.910 g cm^{-3} respectively).[26]

The synthesis of benzo-fused dithia-arsolidinium cations has previously been reported,[17] but structural studies are no-tably absent. The closely related $[(CH_2)_2S_2As]^+$ cation has been structurally characterised as both $AlCl_4^-$ and $GaCl_4^-$ salts but forms centrosymmetric dimers, $[(CH_2)_2S_2As]_2$ijJ$MCl_4]_2$ (M = Al, Ga). Within these structures, the intra-dimer As⋯S contacts (2.423(2) Å) are comparable with the heterocyclic As–S bonds

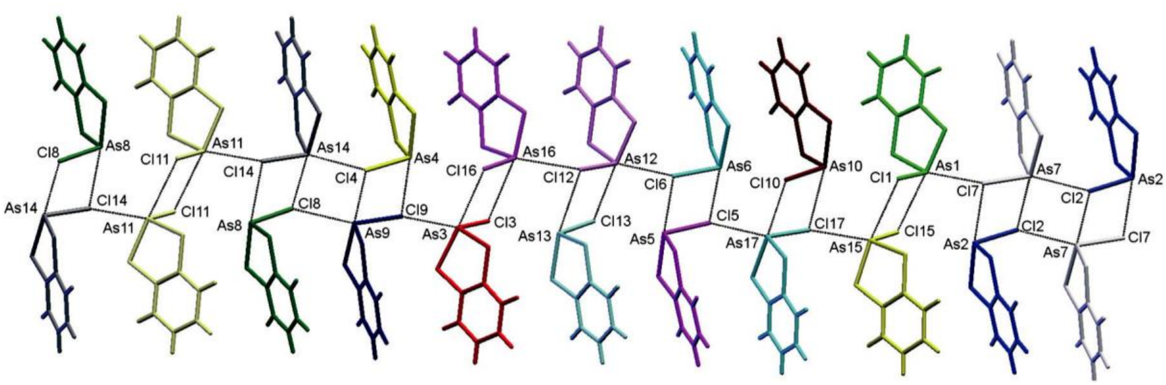

Fig. 1 Dimeric chain-motif of 1 depicting As⋯Cl close contacts. Molecules are colour coded to highlight the 17 crystallographically independent molecules in the asymmetric unit. Crystallographic inversion centers are located within the second dimer from the left and between the last two dimers shown to the right.

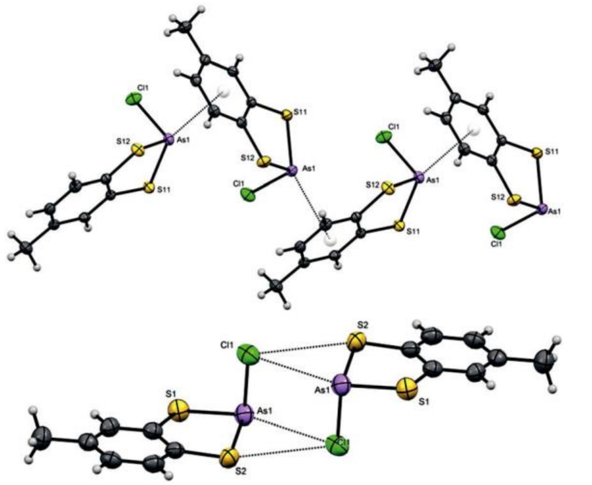

Fig. 2 Solid-state packing of 2 showing As···π$_{centroid}$ contacts within 2α (top) and one of the two crystallographically independent centrosymmetric dimers of 2β with As···Cl contacts (bottom).

(2.181lJ3)–2.326lJ3) Å) and substantially shorter than the sum of the van der Waals radii (3.65 Å).[27] Contrary to these find-ings, we observed the corresponding salts [$MeC_6H_3S_2As$]-ijMCl4] 3a and 3b which were prepared according to the litera-ture method could be recrystallised by slow evaporation from CH_2Cl_2. They were found to be isostructural with two crystal-lographically independent cation–anion pairs in the asym-metric unit with each sitting on a crystallographic mirror plane such that the cations are rigorously planar (see ESI†). The As–S bonds in 3a and 3b (2.1417lJ6)–2.161lJ6) Å) are shorter than those in the corresponding chloride poly-morphs, 1 and 2 (2.188lJ6)–2.233lJ8) Å) as well as the previously reported cation dimer, [$(CH_2)_2S_2As$]$_2$ijGaCl4] (2.181(3) and 2.326(3) Å). The shortening of this bond in related phosphenium cations has previously been ascribed to π-bonding within the formally 10π aromatic fused ring sys-tem.[17] In addition to bond length changes, the S–As–S bond angle expanded upon generating the cation, increasing from 92.448lJ17)° in 2 to 94.38lJ3)–94.81lJ3)° in 3b. Unlike the chlo-ride salts which show a distinct folding of the heterocyclic ring, both 3a and 3b are rigorously planar with the cation and the anion located on a crystallographic mirror plane. In contrast to the previously reported cation in this series which dimerises, [$(CH_2)_2S_2As$]$_2$ijGaCl4]$_2$, there are no close As···S con-tacts evident in 3a or 3b. Instead the two-coordinate arsenic centre forms a range of close cation···anion As···Cl contacts (3.2946lJ10)–3.5376lJ10) Å), less than the sum of the van der Waals radii (3.60 Å).

Substitution chemistry on the chloro-arsoles has been in-vestigated and condensation of ammonium carboxylates has permitted carboxylate derivatives to be prepared.[28] Related substitution with ammonium and sodium salts has led to di-thiocarbamate complexes,[29] and thiolates.[30] Reaction of 2 with lithium bislJtrimethylsilyl)amide in toluene afforded ($MeC_6H_3S_2As$)NlJSiMe$_3$)$_2$ when undertaken in a 1 : 1 molar ra-tio but addition of further 2 in molar ratio. Subsequent addi-tion of two equivalents of compound 2 in MeCN afforded the

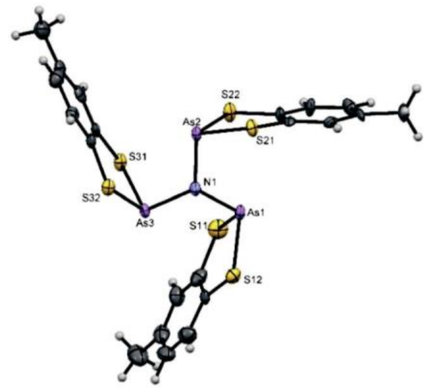

Fig. 3 Solid-state structure of 4. Thermal ellipsoids drawn at 50% probability.

paddlewheel complex ($MeC_6H_3S_2As$)$_3$N (4) (Scheme 1). Crys-tals of 4 suitable for X-ray diffraction were obtained through cooling a saturated CH_2Cl_2 solution to −20 °C, and were found to crystallise in the triclinic space group $P\bar{1}$ (Fig. 3). The crystal structure revealed that the envelope geometry of the five-membered ring as seen in 2 is still preserved, al-though the fold angle is significantly reduced, from 21.51lJ4)° to 13.8lJ13)° for 2β and 4 respectively.

Slight lengthening of the As–S bonds was also found to oc-cur, from 2.099lJ8)–2.2212lJ7) Å in 2β to 2.215lJ3)–2.252lJ3) Å in 4. This increase in the bond length gives a corresponding de-crease in the S–As–S bond angle, although this does not di-rectly correlate to the decreased fold angle. Typical As–N bond distances were found in the solid-state structure (1.843lJ9)–1.862lJ7) Å) with all three As–N–As bond angles be-ing ca. 120°, reflecting an sp^2 hybridised nitrogen centre with the nitrogen atom close to being coplanar with the three arse-nic atoms with the N atom displaced just 0.317(9) Å from the As_3 plane. The unit cell contains two molecules of 4 related about a crystallographic inversion center. These molecules form a dimer with a series of S···S intermolecular interac-tions (3.428lJ4)–3.568lJ4) Å) which are within the sum of the van der Waals radii (3.60 Å) (Fig. 4).

These intermolecular contacts are significantly longer than the intramolecular S···S contacts in S_4N_4 and S_4As_4 which exhibit particularly short S···S distances of 2.580 Å and 2.595 Å respectively.[31] They are however comparable with the

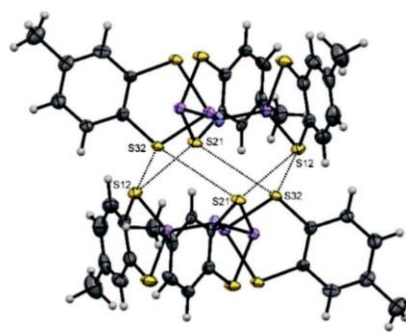

Fig. 4 Solid-state structure of 4 showing intermolecular S···S contacts.

intermolecular S···S contacts in S_8 (orthorhombic α-phase 3.3759lJ4)–3.5023lJ5) Å; monoclinic β-phase 3.275lJ5)–3.600lJ4) and monoclinic γ-phase 3.4012lJ7)–3.5604lJ7) Å).[32]

Conclusions

In this work we have shown that the 3-chloro-benzo-fused 1,3,2-dithia-arsoles exhibit a rich structural chemistry. For ex-ample, 1 contains a rare high Z′ structure with 17 molecules in the asymmetric unit and compound 2 is polymorphic. The melting point and the density rule suggest 2α is the enthalpically preferred polymorph. Structural analyses of the first monomeric dithia-arsolidinium complexes [MeC$_6$H$_3$S$_2$As]-ijAlCl$_4$] and [MeC$_6$H$_3$S$_2$As]ijGaCl$_4$] have shown them to exhibit a rigorously planar 10π aromatic system. Finally, the first ex-ample of an arsenic flanked N-centred paddlewheel structure has been revealed through the addition of 3 equivalents of the tolyl-derived arsole to lithium bislJtrimethylsilyl)amide.

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