Synthesis and characterisation of the ternary intermetalloid clusters \{M@As_{8}(ZnMes)_{4}\}^{3−} (M = Nb, Ta) from binary [M@As_{8}]^{3−} precursors†

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The development of rational synthetic routes to inorganic arsenide compounds is an important goal because these materials are finding applications in many areas of materials science. In this paper, we show that the binary crown clusters [M@As_{8}]^{3−} (M = Nb, Ta) can be used as synthetic precursors which, when combined with ZnMes, generate ternary intermetalloid clusters with 12-vertex cages, \{M@As_{8}(ZnMes)_{4}\}^{3−} (M = Nb, Ta). Structural studies are complemented by mass spectrometry and an analysis of the electronic structure using DFT. The synthesis of these clusters presents new opportunities for the construction of As-based nanomaterials.

Introduction

Ternary intermetalloid clusters have attracted a great deal of attention in the recent literature due to their complex electronic structures and also their potential role in materials science.1−3 The majority of known clusters in this class are synthesised either by extraction of the corresponding quaternary intermetallic phases or by the reaction of binary Tt/Pn or Tr/Pn Zintl anions with sources of low-valent transition metals, lanthanides or actinides.1−6 Scheme 1a illustrates the extraction of the quaternary solid-state Zintl phase K/Ge/As/M (M = V, Nb, Ta) in ethylenediamine (en) in the presence of the sequestering agent, [2.2.2]crypt, which allows for the crystallization of cluster anions including 12-vertex [M@Ge_{9}As]^{3−} (M = V, Ta), and 14-vertex [M@Ge_{9}As]^{3−} (M = Nb, Ta).7,8 Clusters such as [Zn@Zn_{3}Sn_{2}Bi_{3}@Bi_{3}]^{4+},9 [Ni@Sn_{2}Bi_{3}]^{3−},10 [Pd@Sn_{3}Bi_{4}]^{4+},11 [Pd@Pd_{3}P_{10}Bi_{6}]^{4+},12 and [Eu@Sn_{3}Bi_{6}]^{3−},13 have, in contrast, been accessed by reacting a salt of a binary mixed main group Zintl compound, [K[[2.2.2]crypt]]_{2}[TrBi_{3}]-en (Tr = Ga, In, TI) or [K[[2.2.2]crypt]]_{2}[TrBi_{3}]-en (Tr/Pn = Sn/Sb, Sn/Bi, Pb/Bi)14,15 with various organometallic compounds. A variant on this approach is to use a preformed binary intermetalloid where the central transition metal is already in place, surrounded by a shell of main-group atoms, as a starting material to react with other transition metal salts (Scheme 1b). This protocol has been used, for example, in the synthesis of [[L]MCo@Sn_{9}]^{3−}, from the reaction of [Co@Sn_{9}]^{4+}, extracted from the ternary phase

Scheme 1 (a and b) Selected examples of ternary intermetalloid cluster anions of the general formula \{M_{m}@E_{x}E_{y}^{2}\}^{3−} synthesised by different methods. (c) This work.
“K₂Co₃Sn₉”, with group 10-containing precursors such as [Ni(CO)₃(PPh₃)₃], [Ni(cod)₂], [Pt(PPh₃)₃] or [Au(PPh₃)₉]. It is significant that these reactions involve only a simple ligand exchange reaction, and do not cause a substantial rearrangement of the binary inter-metalloid cluster core.²⁷

The extension of this protocol to clusters containing group 15 elements has not been explored in detail, but there is a readily accessible family of starting materials available in the form of the crown-like [M@As₈]³⁻ clusters, the first example of which, [Nb@As₈]³⁻, was reported in 1986.²⁸ Since then, the family has been extended to include [Mo@As₈]³⁻,²⁹ and [Cr@As₈]³⁻,²⁹ as well as the Sb analogues, [Mo@Sb₈]³⁻ and [Nb@Sb₈]³⁻.²⁸,²⁹ A broad survey of the electronic structure of the [M@P₈]³⁻ family, encompassing M = Cr, Mo, Mn, Tc, Re, Ti, Zr, Hf and Pn = As, Sb; n = 1, 2, 3, has also been reported using density functional theory.²¹ The four As atoms on either side of the crown in the [M@As₈]³⁻ unit form a region of high electron density, which has the potential to coordinate large alkali metals such as Rb, K, and hence form chain structures such as [RbNbAs₈]²⁻ and [KCrAs₈]²⁻. In addition, the high oxidation state transition metal ion can serve as a 2-electron acceptor to form d₅ complexes with Lewis basic reagents.¹⁶,²² In a very recent study we showed that the reaction of [M@As₈]³⁻, M = Nb, Ta, with a source of low-valent Cu can lead to the formation of an extended [As₈]₁₀⁻ ligand, where a tri-cyclo As₇ unit is connected to a conserved As₈ crown via a bridging As atom. Although mechanistic details are hard to elucidate, this reaction necessarily involves extensive cleavage and rearrangement of As₈ bonds. In this paper we extend these studies to report the reactions of [K([2.2.2]crypt)][Nb@As₈] or [K([2.2.2]crypt)][K-Ta@As₈] with an organometallic source of Zn(n), ZnMes₂. In both cases the reactions generate 12-vertex cage type ternary intermetalloid clusters, [K([2.2.2]crypt)][Nb@As₈(ZnMes)₄]·2·tol·(1) and [K([2.2.2]crypt)][Ta@As₈(ZnMes)₄]·en·(2) where the As₈⁻ crown has been split into two As₄⁻ units, bridged by [ZnMes] fragments. The products are characterised by X-ray crystallography and mass spectrometry, and the electronic structures and formation pathways are explored using density functional theory.

Results and discussion

At elevated temperatures, ethylenediamine (en) solutions of [K([2.2.2]crypt)][Nb@As₈] or [K([2.2.2]crypt)][K-Ta@As₈] react with a toluene (tol) solution of ZnMes₂ (Mes = 1,3,5-trimethylbenzene) to form [K([2.2.2]crypt)][Nb@As₈(ZnMes)₄]·2·tol·(1) or [K([2.2.2]crypt)][Ta@As₈(ZnMes)₄]·en·(2), in ca. 30% and 25% yield, respectively. In the case of [K([2.2.2]crypt)][K-Ta@As₈], one further equivalent of [2.2.2]crypt was added to the reaction to sequester the non-encrypted K⁺ ion. Diffusion of the reaction solution afforded dark-green block-like crystals of 1 and red-brown strip-like crystals of 2, both of which proved suitable for single-crystal X-ray diffraction study. Under similar reaction conditions, [K([2.2.2]crypt)][Ta@As₈(CdMes)₄] could also be isolated by replacing ZnMes₂ with CdMes₂ as starting reagent, but we have not yet been able to isolate crystals of sufficient quality to allow full structural characterization. Both 1 and 2 crystallise in the monoclinic space group P2₁/n with a single [M@As₈(ZnMes)₄]³⁻ (M = Nb, Ta) anion and solvent molecules (en, tol) as well as three [K([2.2.2]crypt)]⁺ cations in the corresponding unit cell. Fig. 1 shows the molecular structure of the cluster anion in 1: full crystallographic details are given in ESI (Table S1†). For better visualization, different labels are used to distinguish the anionic cluster and the molecular compounds, and 1a-2a represent the anionic clusters in compounds 1–2, respectively.

The two anionic clusters [Nb@As₈(ZnMes)₄]³⁻ (1a) and [Ta@As₈(ZnMes)₄]³⁻ (2a) are isosstructural and adopt almost perfect S₄ point symmetry. They contain two tetrameric zig-zag As₄⁻ oligomers linked by four [ZnMes] groups in a µ₄:µ₃:µ₄:µ₁ coordination mode. The As–As bond lengths in 1a and 2a lie in the range 2.377–2.539 Å, values which are typical of As–As single bonds in polyarsenide Zintl clusters such as As₇⁻ and As₁₁⁻.²⁴ The As–Zn distances (2.497(6)–2.693(6) Å for 1a, 2.500(9)–2.690(8) Å for 2a, respectively) are relatively widely dispersed because the As₈⁻ units contain As centres that are formally mono- and di-anionic (in the centre and the termini of the As₄⁻ units), respectively.²⁵ For comparison, As–Zn bond lengths in [ZnAs₈]³⁻ and [ZnAs₁₁]⁴⁻ are at the shorter end of this range (2.488–2.536 Å,²⁶ and 2.481–2.573 Å,²⁷ respectively). The M–Zn (M = Nb, Ta) distances (2.778(9)–2.796(9) Å for 1a, 2.782(7)–2.795(8) Å for 2a) are considerably longer than those in organometallic complexes such as [[C₃H₅]₂NH₂H₂ZnC₅H₅] (2.541 Å)²⁸ and [[CH₃C₅H₄]₂TaH(HZnC₅H₄)₂] (2.589 Å)²⁹ that are known to contain Nb/Ta–Zn bonds, precluding any direct metal–metal bonding in these clusters.

The overall stoichiometry of the reaction, [M@As₈]³⁻ + 4 ‘ZnMes’ → [M@As₈(ZnMes)₄]³⁻, suggests a possible mechanism in which a transient [Zn(n)]Mes fragments which cause the reductive cleavage of the As₈⁻ crown to form the two separate As₄⁻ fragments present in the product. Power and co-workers have reported a stable dimer of Zn(i)Ar (Ar = C₆H₃-2,6-
1518.3754 \) \text{([TaAs}_8\text{ZnMes})_2 \}) \text{−} \text{product suggests a stepwise pathway, and indeed we}

retain the 1 : 8 ratio of M to As, a clear indication of the robust

nature of the \([\text{M}@\text{As}_8]\) unit, even under quite harsh reaction

conditions.

It is striking that all of the major peaks in the ESI-MS

patterns for peak \([	ext{[K(2.2.2-crypt)]_2{TaAs}_8(ZnMes)_4}]^- \) \text{−} \text{at}

\(m/z = 2348.8193\) and \(\text{[TaAs}_8\text{ZnMes})_2 \}) \text{−} \text{at}

\(m/z = 1518.3754\). The experimental mass distributions are

depicted in black, and the theoretical masses of the isolobal

isotope distribution are shown in red.

\([\text{CuMes(PPh}_3)_2] \) \text{−} \text{produced by the reduction of ArZnCl with Na}

in ethanol,\(^{38}\) but there is no equivalent reducing agent present

in these reactions, and the precise mechanism by which the

low-valent Zn entities are formed remains uncertain. Reductive

elimination of Mes\(_2\) from ZnMes\(_2\) is one possibility, and there is

literature precedent for similar reactions,\(^{31}\) but we have not

been able to confirm the presence of Mes\(_2\) in solution. The need

for four equivalents of ZnMes to cleave two As–As bonds in the

product suggests a stepwise pathway, and indeed we find

evidence to support this in the negative-ion mass spectrum of 2

(Fig. 2), which shows prominent peaks for the parent ion at \(m/z =

1518.3754\) \text{([TaAs}_8\text{ZnMes})_4 \}) \text{−} \text{and at}

\(m/z = 2348.8193\) \text{([K(2.2.2-crypt)]_2{TaAs}_8(ZnMes)_4})^- \text{−}

but also for the cluster with only two ZnMes units, \([\text{TaAs}_8(ZnMes)_2] \}) \text{−} \text{at}

\(m/z = 1148.3488\). It is striking that all of the major peaks in the ESI-MS

retain the 1 : 8 ratio of M to As, a clear indication of the robust

nature of the \([\text{M}@\text{As}_8]\) unit, even under quite harsh reaction

conditions.

The DFT-computed potential energy profile (ADF2021,\(^{33}\) PBE
functional,\(^{33}\) triple-zeta polarised basis set – full details given in

the ESI\(^{\dagger}\)) for the reaction of \([\text{TaAs}_8]^3-\) with ZnMes shown in

Fig. 3. The energy profile \(E_{\text{rel}} = -3.71 \text{ eV}\) for the reaction from 

\([\text{TaAs}_8]^3-\) to \(2[\text{TaAs}_8(ZnMes)_2]^3-\) is the greater accessibility of transient monovalent “ZnMes”

compared to zerovalent Cu.

**Comparison to other 12-vertex clusters**

A complementary perspective on the bonding in these clusters comes from noting their formal relationship to the \([\text{M}@\text{Ge}_8\text{As}_4]\)\(^{31}\) \text{−} (\text{M = V, Ta}) clusters reported recently by Dehnen

and co-workers (Fig. 4).\(^{34}\) The \([\text{ZnMes}]^2\) \text{−} fragment is isolobal

with Ge\(^{-}\) and also with As\(^{-}\), and so the 60-electron, 12-vertex

cages can be formulated as \([\text{Ge}_8\text{As}_4]^8\) \text{−} \text{in} \([\text{TaAs}_8]\) \text{−} and

as \([\text{As}_8(ZnMes)_4]^8\) \text{−} \text{in} \([\text{TaAs}_8(ZnMes)_2] \}) \text{−} \text{and \([\text{TaAs}_8(ZnMes)_2] \}) \text{−} \text{are also compared in}

Fig. 4. The contribution of Ta 5d orbitals to the occupied

manifold is minor in both cases, suggesting that the Ta\(^{\text{v}}\)

oxidation state is a reasonable first approximation for the

electronic structure. In the \([\text{TaAs}_8]\) \text{−} \text{case, there is}

substantial mixing between the Ge and As 4s/4p manifolds in

both the occupied and virtual space, and the peaks that lie

\(\sim 1.0 \text{ eV above and below the Fermi level have Ge and As}\)

and products: \(2[\text{TaAs}_8(ZnMes)_2]^3-\) \text{−} \text{to}

\([\text{TaAs}_8]^3-\) + \(\text{[TaAs}_8(ZnMes)_4]^3-\), \(\Delta E = -2.08 \text{ eV}\), so is unlikely to be

amenable to isolation.

The cluster products obtained from the reaction with

ZnMes\(_2\) make a striking contrast to the corresponding reactions of \([\text{M}@\text{As}_8]\)\(^{31}\) with \([\text{CuMes(PPh}_3)_2] \) \text{−} described in our

previous paper,\(^{21}\) where two As\(^{10-}\) units merged to form a single

contiguous As\(_{16}\) \text{−} ligand. The mechanistic details of the

reactions with Cu are far from clear, not least because, unlike

the reactions described here, the Nb/Ta : As ratio is differen-

t in reagents and products. Nevertheless, reductive cleavage of the

As\(_8\) crown into As\(_4\) fragments is clearly not involved, and the key

difference between the two metal reagents, ZnMes\(_2\) here and

[\text{CuMes(PPh}_3)_2] \text{−} \text{in the previous work, appears, therefore, to}

be the greater accessibility of transient monovalent “ZnMes”

compared to zerovalent Cu.
Figure 4 Structures and projected densities of states for the 12-vertex cluster anions {Ta@[As8(ZnMes)4]}3− (a) and {Ta@[Ge8(As)4]}3− (b), with thermal ellipsoids at the 50% probability level. The molecular structures of {Ta@[Ge8(As)4]}3− is disordered, and the calculated minimum structure is presented here. The organic −Mes ligands are omitted in {Ta@[As8(ZnMes)4]}3−. The projected DOS is summed over all atoms of a given type.

In summary, we have established that the [Nb@As8]3− and [Ta@As8]3− anions can be used as synthetic precursors to ternary As-rich clusters where the M : As ratio of 1 : 8 is conserved. Their reactions with ZnMes2 yield cluster compounds of the general formula [M@[As8(ZnMes)4]]3− (M = Nb, Ta), where two As–As bonds of the original crown-like As8− unit are cleaved to form two As6− fragments. The presence of clusters with two, rather than four, [ZnMes] units in the ESI-MS spectra suggests a step-wise pathway where [ZnMes] units are added sequentially with progressive fragmentation of the As8− ring. The reaction of [M@[As8]] units with low-valent transition metal organometallics described in this paper presents new possibilities for the construction of ternary arsenic-rich nanoclusters with tightly controlled stoichiometries.

Data availability

Detailed experimental procedures, crystallographic supplementation, electrospray ionization mass spectrometry (ESI-MS) analysis, energy-dispersive X-ray (EDX) spectroscopic analysis, and quantum-chemical studies can be found in the ESI.†

Author contributions

Z. M. S. conceived the project and designed the experiments. W. Q. Z. performed the synthesis and the single-crystal X-ray diffraction as well as analysed the data. H. W. T. M. and J. E. M. performed the quantum chemical calculations and analysed the data. All authors co-wrote the manuscript.

Conflicts of interest

There are no conflicts to declare.

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Notes and references