

An isolated *cyclo*-tetraarsendiide: low temperature synthesis and crystal structure of bis-pentaamminesodium tetraarsendiide–ammonia (1/3)

[Na(NH₃)₅]₂As₄·3NH₃

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Received (in Cambridge, UK) 2nd October 2001, Accepted 23rd November 2001

First published as an Advance Article on the web 11th December 2001

Reduction of an excess of arsenic with a solution of sodium in liquid ammonia yields the thermally unstable title compound [Na(NH₃)₅]₂As₄·3NH₃, which contains isolated square-planar As₄²⁻ ions with a mean As–As bond length of 2.345 Å.

Among the various methods to produce molecular homoatomic polyanions of main group elements, the reduction with solutions of alkali metals in liquid ammonia has to be the first which was systematically explored.¹ This early work culminated in the ingenious work of Zintl and coworkers, who identified various polyanions like Sn₉⁴⁻ and As₇³⁻ in these solutions by potentiometric titrations and dissolution experiments.² Subsequent investigations of these so-called ‘Zintl anions’ abandoned the solvent ammonia for ethylenediamine³ and introduced cryptands as alkali metal cation ligands to facilitate experiments at room temperature and crystal structure determinations.⁴ Recently, the introduction of experimental techniques which make possible the low temperature preparation and crystal structure analysis of solvent-rich ammoniates has shown that the original method may lead to new homoatomic polyanions like *cyclo*-Sb₅⁵⁻,⁵ which could not be identified by the previous investigations, as well as known species like Sn₉⁴⁻.⁶ An important structural feature in the ammoniates containing these anions is the existence of homoleptic ammine complexes of alkali metal cations like Li(NH₃)₄⁺, which mimic the role of cryptates as voluminous counter ions.

We now report on the reaction of sodium with an excess of arsenic in liquid ammonia. While the products of the analogous reductions with lithium and caesium could be identified early on to be [Li(NH₃)₄]₃As₇·NH₃⁷ and Cs₃As₇·6NH₃,⁸ the sodium containing polyarsenide had remained elusive due to its lower thermal stability. The reason for this may be that [Li(NH₃)₄]₃As₇·NH₃ contains the relatively stable tetraammine lithium complex and Cs₃As₇·6NH₃ consists of a network built from Cs⁺–As₇³⁻ contacts, both of which are favourable structural elements in ammoniates. Sodium cations, however, form less stable ammine complexes and, due to hard–soft acid–base (HSAB)⁹ considerations, have a lower tendency to coordinate to polyarsenide anions.

With an improved technique for crystal handling, the title compound [Na(NH₃)₅]₂As₄·3NH₃ was now identified to be the main product of the reaction mentioned above. It forms exclusively if a molar ratio Na : As of 1 : 2 is used as a starting mixture (typical reaction: 0.1717 g (7.469 × 10⁻³ mol) Na, 1.1207 g (0.0150 mol) As in 30 mL NH₃). [Na(NH₃)₅]₂As₄·3NH₃ forms yellow crystals which decompose above 253 K when losing contact with the mother liquor. Its crystal structure† consists of pentaamminesodium complexes, As₄²⁻ rings and ammonia molecules of solvation (Fig. 1). The [Na(NH₃)₅]⁺ complexes are distorted trigonal bipyramids similar to those observed in [Na(NH₃)₅][Na(NH₃)₃(P₃H₃)],¹⁰ The tetraarsendiide ions display a nearly ideal square-planar geometry; they are situated on the crystallographic two-fold axis in such a fashion that As(1) and As(3) occupy special positions on this axis (Wyckoff symbol 4e). Thus, only two crystallographically independent As–As bond lengths (2.3444(8) and

2.3457(8) Å) and three independent bond angles (90.49(4), 89.54(2) and 90.43(4)°) are observed. The crystallographic point group symmetry of the As₄²⁻ anion is C_{2v}.

As₄²⁻ is one of the few examples of homoatomic group 15 polyanions with a formal bond order higher than one; however, the As–As bonds are not significantly shorter than single bonds in other polyarsenides (*i.e.* the As₇³⁻ cage has bond lengths between 2.33 and 2.51 Å,^{7,11} with the shorter bonds connecting to two-bonded As atoms). To our knowledge, this is the first structural report on an isolated As₄²⁻ ion, which had before mainly been observed as a ligand in various transition metal complexes; a representative example is [Nb(η⁵-Cp*)(CO)₂(η⁴-As₄)] with a medium As–As bond length of 2.38 Å.¹² In densely packed solid state structures, a square-planar As₄ ring occurs in the well-known skutterudite structure CoAs₃ (As–As bond length 2.463 Å¹³). However, if CoAs₃ is to be described by an ionic formula, the material properties suggest (Co³⁺)₄(As₄⁴⁻)₃ rather than the presence of As₄²⁻ ions.¹⁴

The tetraarsendiide anion adds to a series of analogous E₄²⁻ ions of the heavier group 15 elements: the isostructural compounds [K(2,2,2)]₂Sb₄¹⁵ and [K(2,2,2)]₂Bi₄¹⁶ reported by Corbett and co-workers both contain isolated square-planar anions of nearly ideal D_{4h} symmetry. An interesting continuation of this series would be P₄²⁻, the existence of which as an isolated anion has not been proven yet; however, *cyclo*-P₅⁻, which is the respective cyclopentadienide derivative rather than

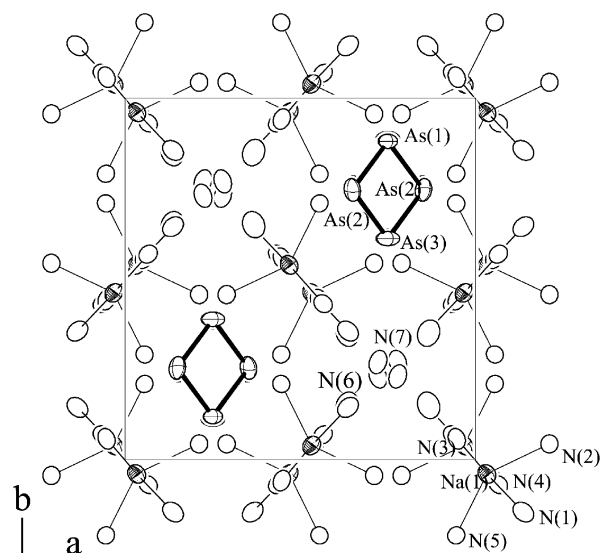


Fig. 1 Projection of the crystal structure of [Na(NH₃)₅]₂As₄·3NH₃ on the *ab* plane. Selected interatomic distances [Å] and angles [°]: As(1)–As(2) 2.3444(8), As(1)–As(3) 2.3444(8), As(2)–As(3) 2.3457(8), As(3)–As(2) 2.3457(8), Na(1)–N(2) 2.443(4), Na(1)–N(5) 2.459(4), Na(1)–N(3) 2.490(5), Na(1)–N(4) 2.495(4), Na(1)–N(1) 2.591(4); As(2)–As(1)–As(2) 90.49(4), As(1)–As(2)–As(3) 89.54(2), As(2)–As(3)–As(2) 90.43(4), N(2)–Na(1)–N(5) 129.59(16), N(2)–Na(1)–N(3) 111.52(15), N(5)–Na(1)–N(3) 118.41(15), N(2)–Na(1)–N(4) 89.64(14), N(5)–Na(1)–N(4) 91.77(14), N(3)–Na(1)–N(4) 95.88(15), N(2)–Na(1)–N(1) 89.35(14), N(5)–Na(1)–N(1) 90.29(14), N(3)–Na(1)–N(1) 82.79(15), N(4)–Na(1)–N(1) 177.91(15).

the cyclobutadiene derivative, has been reported to exist in solutions.¹⁷

Notes and references

† *Crystal data and structure refinement for* [Na(NH₃)₅]₂As₄·3NH₃: *M* = 567.06, monoclinic, space group *I*2/*a* (No. 15), *a* = 12.042(1), *b* = 12.287(1), *c* = 16.122(1) Å, β = 98.59(1)°, *V* = 2358.7(3) Å³, *Z* = 4, μ(Mo-Kα) = 5.66 mm⁻¹, no. of reflections measured 16220, no. of independent reflections 2211 (*R*_{int} = 0.068), *T* = 123(2) K, crystals selected at *T* = 213 K. The H-atoms of the NH₃ molecules coordinating to Li⁺ were located by local ring difference Fourier synthesis and fixed in a riding mode. The H-atoms of N(6) were located by difference Fourier synthesis and refined with fixed displacement parameters. The NH₃ molecule designated by N(7) is situated close to an inversion centre and was refined using split positions, no H-atoms were located in this case. The final *wR*₂ value was 0.072 [corresponds to a conventional *R* value of 0.033 using only reflections with *I* > 2σ(*I*)]. CCDC reference number 174984. See <http://www.rsc.org/suppdata/cc/b1/b108879c/> for crystallographic data in CIF or other electronic format.

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