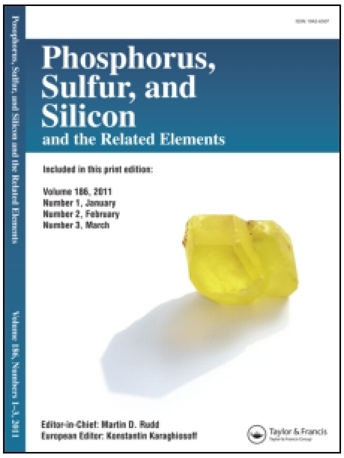

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GENERATING ZINTL ANIONS: HOMOATOMIC POLYANIONS OF GROUP 15 ELEMENTS BY OXIDATIVE COUPLING OF SMALLER ANIONS OR DIRECT REDUCTION OF THE ELEMENTS IN LIQUID AMMONIA

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The new polyphosphorus Zintl anion P_{22}^{4-} has been synthesised by combining two P_{11}^{3-} anions by oxidation with Br_2I^- in liquid ammonia. The single crystal structure analysis shows that P_{22}^{4-} consists of two trishomocubane-like cages connected by a single bond. While the former method makes use of pre-formed Zintl anions extracted from solids, the second route presented involves direct reduction of the elements with the expanded metal $Li(NH_3)_4$. Reaction of $Li(NH_3)_4$ with P, As, and Sb yields $[Li(NH_3)_4]_4P_{14}$, $[Li(NH_3)_4]_3As_7 \cdot NH_3$ and $[Li(NH_3)_4]_3[Li_2(NH_3)_2Sb_5] \cdot 2\ NH_3$. The Sb compound contains the new Zintl anion cyclo-Sb_5^{5-} , which is stabilised in the ion complex $(Li_2(NH_3)_2Sb_5)^{3-}$.

Keywords: Zintl ions; homoatomic polyanions; expanded metals;

INTRODUCTION

Compounds of the group 15 elements P, As and Sb with electropositive metals may contain a variety of covalently bound, anionic substructures, which cover the whole spectrum between threeanionic substructures, which cover the whole spectrum between three-dimensionally extended structures and isolated polyanions. Especially well investigated and catalogued are polyphosphides [1]. From a synthetic chemist's point of view, the isolated polyanions are particularly attractive, since they may be excised from the solids and used for solution reactions. For these species, the term Zintl anions is widely used [2], in recognition of Zintl's pioneering work on homoatomic polyanions of main group elements in solution [3]. Over the years, synthetic work with group 15 Zintl anions has almost exclusively dealt with the well-known P_7^{3-} and As_7^{3-} ions with nortricyclane-like cage structure; the reactions reported include protonation, alkylation and metalation [4] as well as several reactions with transition metal compounds [5].

In our efforts to explore further the synthetic potential of homoatomic Zintl anions of group 15 elements, we have concentrated so far on reactions in anhydrous liquid ammonia, the use of which had been discontinued for some time in favour of organic solvents like en or tmeda. Solids like $M^I_3E_7$ and $M^I_3E_{11}$ (M^I = Na-Cs, E = P, As) containing the cage anions E_7^{3-} and E_{11}^{3-} dissolve congruently to yield stable solutions, which have subsequently been used for cation exchange [6] and protonation [7] reactions with tetraalkylammonium salts. The former resulted in new compounds both with "naked" P_{11}^{3-} and various alkali metal-polyphosphide substructures like $^{1}_{\infty}[RbP_7]^{2-}$ chains or $^{2}_{\infty}[Cs_2P_n]^-$ layers (n = 7, 11), the latter in the first stable hydrogen polyphosphides $H_2P_7^-$ and HP_{11}^{2-}.

RESULTS AND DISCUSSION

Oxidative Coupling of Polyphosphides

Polyphosphide cage anions such as P_7^{3-} or the trishomocubane-like P_{11}^{3-} have two-fold-linked, formally negatively charged P atoms, which should be suitable reaction sites for the formation of new bonds between cages by removing two electrons. Oxidation of polyphosphides, however, usually leads directly to amorphous red phosphorus. We have now found that by controlled mild oxidation at lower temperatures (–70 °C) using Br_2I^-, directed and nearly quantitative oxidative coupling of two P_{11}^{3-} ion can be achieved (Fig. 1). The polyhalogenide Br_2I^- is added *via* its $NEtMe_3^+$ salt, which

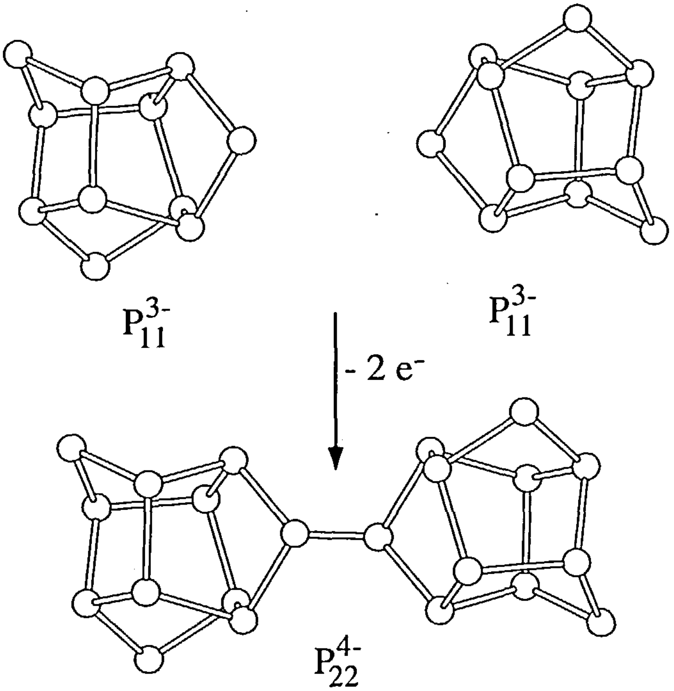

FIGURE 1 Directed oxidative coupling of two P_{11}^{3-}

conveniently provides a large non-coordinating counter ion for the crystallisation of the new polyphosphide anion P_{22}^{4-}. $(NEtMe_3)_4P_{22} \cdot 2 NH_3$ crystallises in the space group *Pbca* with the anion situated on an inversion centre. The P-P bond connecting the two cages is 2.23 Å long, which corresponds exactly to the medium single bond length between two three-fold-linked P atoms [1]. P_{22}^{4-} has a structural analogy in As_{22}^{4-}, which formed from Rb_3As_7 and $Fe_2(CO)_9$ by an unknown route and was isolated as a (Rb·crypt) salt [10].

Direct reduction of P, As and Sb in liquid ammonia

Another route to group 15 Zintl anions involves direct reduction of the elements with alkali metals in liquid ammonia, which is how Zintl originally discovered these species [3]. The solids precipitating from these solutions are thermally very unstable ammoniates. Since we have developed methods to characterise ammoniates which start to decompose at –30 °C (e.g. $Li_3P_{11} \cdot 17 NH_3$ [8] or $BaCsP_{11} \cdot 11 NH_3$ [9]), we have now been able to identify the primary crystalline products of the reaction of Li with excess red P, As or Sb. A special advantage of Li is that it subsequently forms the relatively stable ammine complex $Li(NH_3)_4^+$ which is isoelectronic to NMe_4^+. Indeed, the reactions of Li in very concentrated solutions in liquid ammonia are better perceived as melt reactions with the expanded metal $Li(NH_3)_4$ [11] (FP –184 °C).

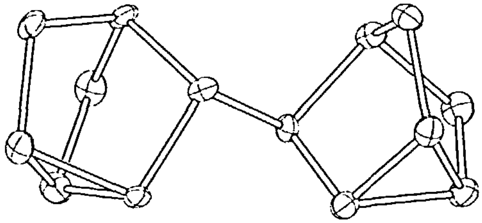

FIGURE 2 P_{14}^{4-} in the structure of $[Li(NH_3)_4]_4P_{14}$

The reaction of $Li(NH_3)_4$ and red phosphorus yields $[Li(NH_3)_4]_4P_{14}$ containing the anion P_{14}^{4-} which consists of two nortricyclane-like cages connected by a single bond (Fig. 2). In the crystal structure (Fig. 3), these polyanions are separated by the $Li(NH_3)_4^+$ complexes which serve as large, non-coordinating counter cations in exactly the same manner as tetraalkylammonium ions or cryptates. The reaction of $Li(NH_3)_4$ and As yields $[Li(NH_3)_4]_3As_7 \cdot NH_3$ with the well-known As_7^{3-} cage (Fig. 4), while the same reaction with Sb results in

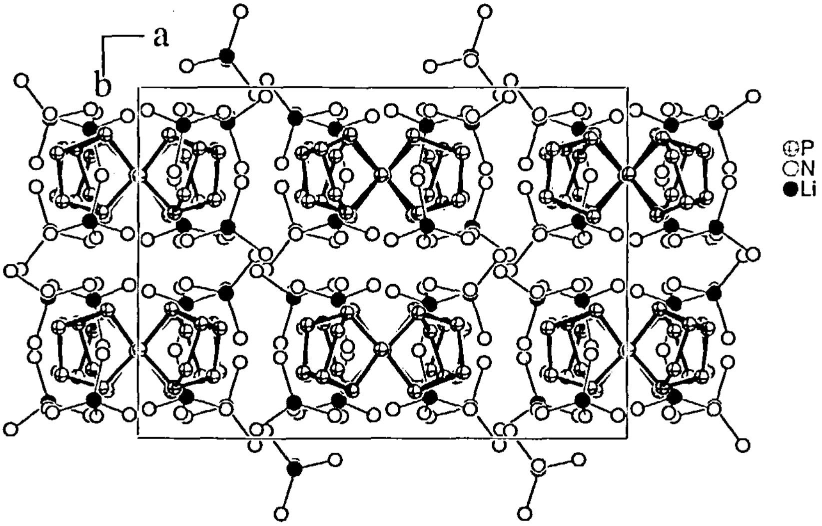

FIGURE 3 View of the crystal structure of $[Li(NH_3)_4]_4P_{14}$

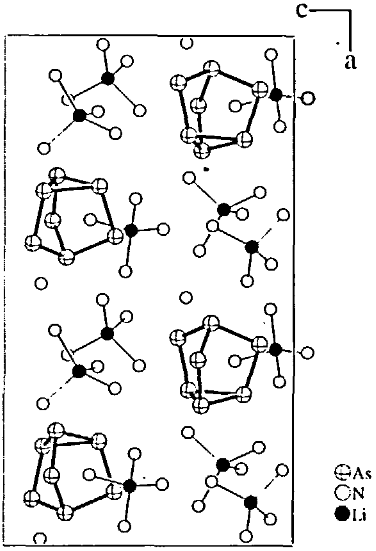

FIGURE 4
$[Li(NH_3)_4]_3As_7 \cdot NH_3$

$[Li(NH_3)_4]_3[Li_2(NH_3)_2Sb_5] \cdot 2\ NH_3$ containing the novel Zintl anion cyclo-Sb_5^{5-} [12]. This unprecedented, highly charged ring in envelope conformation is stabilised in the ion complex $(Li_2(NH_3)_2Sb_5)^{3-}$ (Fig. 5) which again crystallises with $Li(NH_3)_4^+$ counter ions. This ion complex demonstrates the versatility of the expanded metal $Li(NH_3)_4$ as a reducing agent: it subsequently forms large cations, but it is also able to partly expel the weakly bound ammonia, and coordinate Li directly to highly charged anions which would otherwise be unstable in such an environment. This indicates that a number of other homoatomic polyanions with high charge-per-atom ratio like As_5^{3-} or Sb_3^{3-}, which were detected by Zintl in liquid ammonia solutions long ago [3], could be stabilised in ammoniates in a similar manner.

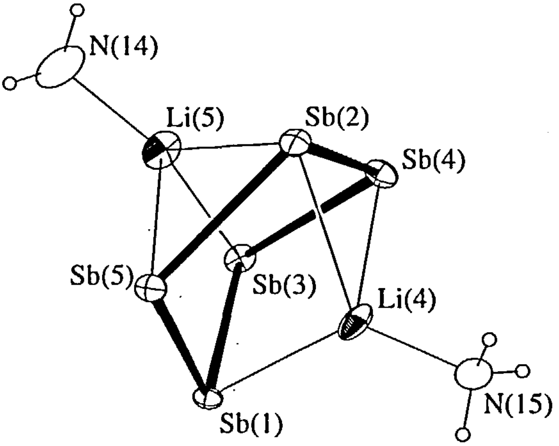

FIGURE 5 Cyclo-Sb_5^{5-} in the ion complex $(Li_2(NH_3)_2Sb_5)^{3-}$

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