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A Hydrogen Polyphosphide Salt of the First Homoleptic Strontium Ammine Complex: Synthesis and Structure Analysis of $[Sr(NH_3)_8]HP_{11}\cdot NH_3$

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Introduction

Structural studies of the discrete polyanions of the p-block elements known as Zintl anions[1] often have involved the use of large, noncoordinating cations for stabilization and crystallization purposes. Most prominent have been cryptand-encapsulated alkali metal cations,[2] but quaternary ammonium and phosphonium ions have also played an important role, especially for chalcogenide-containing species.[3] Recently, the ammine complexes of alkali and alkaline earth metal cations as well as of certain lanthanide cations have been found to serve as voluminous counterions in exactly the same manner. Up to now, known species include $Li(NH_3)_4^+$ in $[Li(NH_3)_4]_3P_{11}\cdot 5NH_3$,[4] $Ba(NH_3)_9^{2+}$ in $BaCsP_{11}\cdot 11NH_3$,[5] and $Yb(NH_3)_8^{3+}$ and $La(NH_3)_9^{3+}$ in $[Yb(NH_3)_8][Cu(S_4)_2]\cdot NH_3$, $[Yb(NH_3)_8][Ag(S_4)_2]\cdot 2NH_3$, and $[La(NH_3)_9][Cu(S_4)_2]$.[6] Each of these studies represents the first crystallographic characterization of the respective homoleptic cationic ammine complex, although the fact that salts of the "hard" cations of the first two groups as well as of the lanthanides form ammonia-rich ammoniates in perfect analogy to hydrates has been known for a long time.[7] The reason for the late investigation of these complexes is their low stability, especially when compared to the well-known ammine complexes of the transition metal cations. The alkali metal species decompose well below 273 K, while the di- and trivalent complexes of the alkaline earth metal cations and the lanthanides seem to be more stable; a crystallographic data set of $[La(NH_3)_9][Cu(S_4)_2]$ was collected at room temperature.[6] Further thermal instability often arises from additional free ammonia of crystallization present in the compounds obtained from liquid ammonia. Nevertheless, if appropriate handling of the reaction products is ensured, the ammine complexes of "hard" cations offer an attractive alternative to cryptand-encapsulated alkali metal cations and quaternary ammonium cations with respect to synthesis and characterization of Zintl anion compounds. These ammine complexes form in and from a solvent which is very suitable for Zintl anion chemistry,[8] are very stable to a reducing environment, and make di- and even trivalent counterions available, which may be an important advantage when highly charged anions are concerned. Furthermore, their ability to shrink by losing ammonia at very moderate temperatures obviously introduces a new "soft-chemistry" route to binary and ternary compounds.

We were interested in using a divalent voluminous counterion for the preparation of the recently discovered hydrogen polyphosphide HP_{11}^{2-}.[9] In this note, we report the synthesis and crystal structure of the new compound $[Sr(NH_3)_8]HP_{11}\cdot NH_3$.

Experimental Section

$[Sr(NH_3)_8]HP_{11}\cdot NH_3$ was synthesized from Cs_3P_{11} in liquid ammonia using an ion exchange resin loaded with Sr^{2+} cations and additional resin in the original proton-containing form. All manipulations were carried out under dry argon in all-glass reaction and handling vessels that were dried in vacuo. Ammonia (Bayer AG, purity 2.8) was made anhydrous by distilling it first from sodium and then from potassium and was stored as a potassium−ammonia solution at 195 K. Cs_3P_{11} was synthesized from the elements (stoichiometric mixture) in a sealed glass ampule according to the procedure given in the literature.[10] *Caution*! The reaction is highly exothermic, and serious explosions occur upon improper handling! Red phosphorus was obtained from Hoechst (electronic grade), cesium was prepared by reduction of CsCl (Fluka, p.a.) with calcium[11] and purified by double distillation in vacuo. The ion exchange resin Amberlyst 15 (Fluka) was loaded with strontium cations by exhaustive washing on a column with an aqueous solution of $Sr(NO_3)_2$ (Merck, p.a.) and conditioned for the use in liquid ammonia according to the literature procedure.[12]

Into an H-shaped reaction vessel fitted with a glass frit (porosity 3) separating the two sides were placed in the same side ca. 0.3 g (ca. 4×10^{-4} mol) of Cs_3P_{11} and 2 g of Sr^{2+}-loaded resin (corresponding to ca. 3.6×10^{-3} mol of Sr^{2+} on the exchange resin; the maximal equivalent capacity of the resin is 4.6×10^{-3} mol g^{-1}) as well as 0.1 g of H^+-containing resin. About 40 mL of NH_3 was frozen into the vessel at 77 K. The vessel was allowed to warm slowly to 238 K. After 5 days, the deep red solution was separated from the resin beads by decanting through the glass frit into the other side of the reaction vessel. The red crystalline product which had formed on the resin was redissolved and transferred by repeated washings with fresh liquid NH_3. During the subsequent evaporation of the solvent, a red crystalline product accumulated, which decomposed to a glasslike black solid when the solvent was removed. This decomposition product is X-ray amorphous and contains varying amounts of nitrogen depending on the duration of pumping. If placed in a sealed glass ampule at 473 K, the decomposition product starts to expel phosphorus, which crystallizes as white phosphorus in the opposite end of the ampule.

Structure Determination. Small amounts of the crystalline product were transferred directly from the liquid ammonia into perfluoroether oil (RS 3000 and RS 216, Riedel de Haen) which was cooled to 220 K by a stream of cold nitrogen. Single crystals were selected with the help of a microscope and picked upon the tip of a capillary mounted on a goniometer head. They were immediately submerged in liquid nitrogen and transferred to the diffractometer.[13] Crystal data and structure refinement: $H_{28}N_9P_{11}Sr$, $M = 582.6$, red blocks, orthorhombic, space group $Pna2_1$ (No. 33), $a = 18.824(5)$ Å, $b = 13.604(2)$ Å, $c = 9.657(2)$ Å, $V = 2473.0(9)$ Å^3, $Z = 4$, $D_c = 1.565$ g cm^{-3}, μ(Mo Kα) $= 2.90$ mm^{-1}, $F(000) = 1176$ electrons; number of measured reflections 5396, number of independent reflections 2849 ($R_{int} = 0.08$), number of observed reflections with $I > 2\sigma(I)$ 2392, number of parameters 207, number of restraints 7. The lattice parameters were determined

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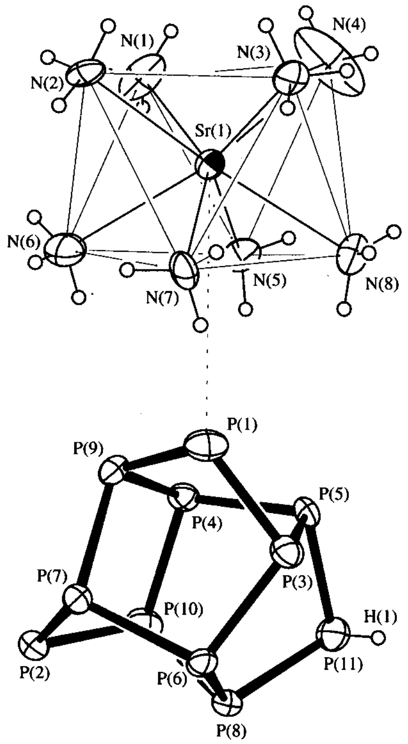

Figure 1. ORTEP plot of the asymmetric unit of $[Sr(NH_3)_8]HP_{11}\cdot NH_3$ excluding the additional solvent molecule (50% probability ellipsoids; hydrogen atoms assigned circles with an arbitrary radius). Selected interatomic distances (Å) and angles (deg): Sr(1)−N(1) 2.701(11), Sr(1)-N(8) 2.708(9), Sr(1)-N(7) 2.727(10), Sr(1)-N(2) 2.738(8), Sr(1)-N(5) 2.741(8), Sr(1)-N(3) 2.757(9), Sr(1)-N(4) 2.761(14), Sr(1)-N(6) 2.784(11), Sr(1)-P(1) 4.462(4), P(1)-P(3) 2.160(5), P(1)-P(9) 2.164(5), P(2)-P(7) 2.151(5), P(2)-P(10) 2.170(5), P(3)-P(5) 2.192(5) 2.192(5), P(3)-P(6) 2.224(4), P(4)-P(5) 2.212(5), P(4)-P(9) 2.246(5), P(4)-P(10) 2.259(5), P(5)-P(11) 2.220(5), P(6)-P(8) 2.230(4), P(6)-P(7) 2.243(4), P(7)-P(9) 2.193(4), P(8)-P(11) 2.186(5), P(8)-P(10) 2.190(4), P(11)-H(1) 1.23(12), N(1)-N(4) 3.22(2), N(1)-N(2) 3.36(2), N(1)-N(5) 3.36(2), N(1)-N(6) 3.36(2), N(2)-N(3) 3.326(13), N(2)-N(6) 3.40(2), N(2)-N(7) 3.558(13), N(3)-N(4) 3.16(2), N(3)-N(8) 3.362(14), N(3)-N(7) 3.421(14), N(4)-N(8) 3.42(2), N(4)-N(5) 3.67(2), N(5)-N(8) 3.185(12), N(5)-N(6) 3.29(2), N(6)-N(7) 3.38(2), N(7)-N(8) 3.186(14); P(3)-P(1)-P(9) 96.82(2), P(7)-P(2)-P(10)96.1(2), P(8)-P(11)-P(5)99.1(2).

by a CAD4 indexing program and refined by a least-squares routine with the angular settings of 25 reflections ($12° < \theta < 18°$). Diffraction data were collected with an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å) at 123(2) K to $\theta_{max} = 23°$ by using $\omega/2\theta$ BPB scans. Three intensity control reflections were measured every hour, showing no decay. Intensity data were corrected for Lorentz and polarization effects and for absorption effects (ψ scans, nine reflections). The structure was solved by direct methods (SHELXS-86[14]) and refined on F^2 using all 2849 independent reflections (SHELXL-93[15]). All the hydrogen atoms were located by difference Fourier synthesis; the hydrogen atoms of the ammonia molecules attached to Sr were fixed to the nitrogen atoms in a riding mode and not refined. The hydrogen atoms of the free ammonia molecule were restrained to equal H−H and N−H distances and refined isotropically. The final R_{w2} value was 0.150 [corresponding to a conventional R value of 0.052 by using only reflections with $I > 2\sigma(I)$]. The largest peak and hole in the final difference Fourier map were 0.99 (in the vicinity of Sr) and −0.64 e Å^{-3}, respectively.

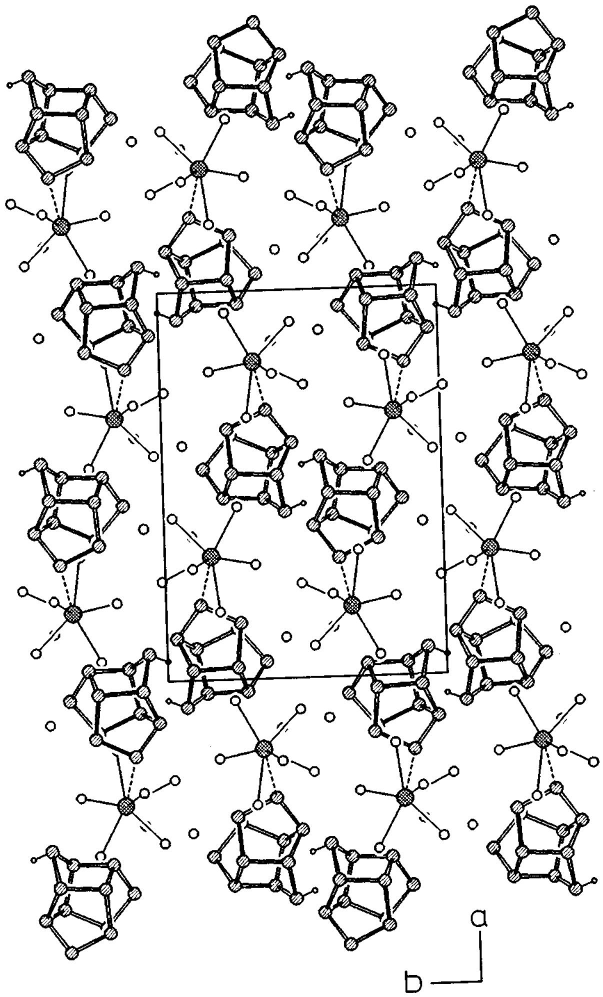

Figure 2. Projection of the structure of $[Sr(NH_3)_8]HP_{11}\cdot NH_3$ onto the *ab* plane.

Results and Discussion

For the directed synthesis of the highly reactive hydrogen polyphosphide HP_{11}^{2-} from P_{11}^{3-}, both a "soft" protonation at low temperatures and the trapping of the product by crystallization as a salt with large noncoordinating counterions have proven to be necessary.[9] In the reaction reported now, these conditions are met by introducing both the protons and Sr^{2+}, which subsequently forms the ammine complex $Sr(NH_3)_8^{2+}$, by means of an ion exchange resin. Thus, the diffusion of the protons from the resin into the solution provides the necessary control for the protonation of P_{11}^{3-}, which is crucial, as the simple addition of NH_4^+ to the reaction mixture results in impure products due to decomposition side reactions. The reaction design using exchange resins both avoids this problem and leads to a convenient one-step process, which yields crystalline $[Sr(NH_3)_8]HP_{11}\cdot NH_3$ exclusively.

The crystal structure of $[Sr(NH_3)_8]HP_{11}\cdot NH_3$ is built from ionic $Sr(NH_3)_8^{2+}$ and HP_{11}^{2-} units with one additional molecule of NH_3 of solvation per formula unit. The strontium cation environment in the ammine complex is best described as a square antiprism (Figure 1). The deviations from ideal square antiprismatic coordination are small, the angle between the two squares is 43°, and the mean deviation of the nitrogen atoms from the best plane of the squares is 0.08 Å. The Sr−N distances range from 2.701 to 2.784 Å. We believe this complex to be the first crystallographically characterized homoleptic ammine complex of the strontium cation; a search of the 1996 version of the Inorganic Crystal Structure Database[16] did not

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even yield a single example for a crystal structure with a $Sr^{2+}-NH_3$ contact. The square antiprismatic structure of the complex, however, corresponds well with both crystal structures of the recently reported ammine complex of trivalent ytterbium $Yb(NH_3)_8^{3+}$ [6] and is also in accordance with the ammine complexes found in the isotypic series $[M(NH_3)_8](PH_2)_2$ (M = Ca, Eu, Yb).[17] With organic amine ligands, an 8-fold nitrogen environment of Sr^{2+} is only known for the tetrakis(ethylenediamine) complex $[Sr(en)_4]^{2+}$.[18]

The hydrogen polyphosphide anion HP_{11}^{2-} derives from the trishomocubane-shaped undecaphosphane P_{11}^{3-} [19] by adding a proton to one of the three two-bonded, formally negatively charged phosphorus atoms. This results in a substantial distortion of the polyphosphorus cage, as the protonated phosphorus atom has significantly larger bond lengths to neighboring atoms than the remaining two-bonded sites as well as a larger bond angle (P(11)−P(5) 2.220(5) Å and P(11)−P(8) 2.186(5) Å *versus* P(1)−P(3) 2.160(5) Å, P(1)−P(9) 2.164(5) Å, P(2)−P(7) 2.151(5) Å, and P(2)−P(10) 2.170(5) Å; P(5)−P(11)−P(8) 99.1(2)° *versus* P(3)−P(1)−P(9) 96.8(2)° and P(7)−P(2)−P(10) 96.1(2)°). These results agree well with the two crystal structures of HP_{11}^{2-} having quaternary ammonium counterions obtained previously.[9] However, in contrast to the earlier structure determinations, which were hampered by site symmetry problems and poor crystal quality, respectively, the hydrogen atom could now be unequivocally localized and isotropically refined.

A curious feature of the crystal structure is the orientation of the ammine complex and the hydrogen polyphosphide toward each other. The two structural units are positioned in such a way that one of the two-bonded phosphorus atoms points through one of the squares of the antiprism toward strontium; a line from P(1) to Sr (indicated by dashes in Figure 1) passes precisely through the center of this square. The corresponding distance of 4.462(4) Å is significantly shorter than all the other Sr−P distances in the structure (>5 Å) but much larger than the sum of the relevant radii of 3.16 Å (1.40 Å for 8-fold-coordinated Sr^{2+} [20] and 1.76 Å for P in ion complexes between polyphosphides and group 1 and 2 cations (our structural data)). Additionally, no distortion of the square in question is observed, which would be expected if P(1) played a significant role in the coordination of the strontium ion. Nevertheless, we believe that this arrangement is not accidental, but reflects rather weak but noticeable Sr−P interactions and consequently a certain amount of ion pairing in the structure. This interpretation is supported by the fact that the (neutral!) formula unit $Sr(NH_3)_8$-HP_{11} displays a crystal packing (Figure 2) much more reminiscent of molecular structures than the kind of roughly NaCl- or CsCl-like structure one would expect for a purely ionic packing of the rather round $Sr(NH_3)_8^{2+}$ and HP_{11}^{2-} units.

$[Sr(NH_3)_8]HP_{11}\cdot NH_3$ demonstrates that ammine complexes of group 2 elements can be useful voluminous counterions for the isolation of highly reactive Zintl anions and are able to substitute quaternary ammonium ions in the stabilization of hydrogen polyphosphides. These complexes represent a facile way of introducing divalent cations into Zintl ion chemistry and are easily accessible via ion exchange in liquid ammonia. Additionally, the synthesis reported here using ion exchange resin also for the protonation of phosphides represents another, highly rational route to hydrogen polyphosphides.

Supporting Information Available: X-ray crystallographic files, in CIF format, are available on the Internet only. Access information is given on any current masthead page.

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