173. Synthesis and Crystal Structure of Tricaesium Heptaphosphide–Ammonia(1/3) $Cs_3P_7 \cdot 3\ NH_3$

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Recrystallization of Cs_3P_7 from liquid NH_3 yields the triammoniate $Cs_3P_7 \cdot 3\ NH_3$, which loses the weakly bound NH_3 of crystallization below 253 K. A low-temperature crystal-structure analysis shows that $Cs_3P_7 \cdot 3\ NH_3$ consists of a framework of heptaphosphanortricyclane anions P_7^{3-} and Cs^+ cations with NH_3 molecules completing the coordination of the cations. The framework is built from Cs_3P_7 layers connected by only few Cs···P interactions, the interlayer gap being filled by a two-dimensional network of NH_3. The Cs_7P_7 part of the structure completes a family of alkali-metal-polyphosphide substructures which range from $^{1}_{\infty}[RbP_7]^{2-}$ or $^{1}_{\infty}[CsP_{11}]^{2-}$ chains over $^{2}_{\infty}[Cs_2P_n]^-$ layers ($n = 7, 11$) to now $^{3}_{\infty}[Cs_3P_7]$ frameworks.

Introduction. – For a long time, the coordination chemistry of polycyclic phosphide anions like P_7^{3-} and P_{11}^{3-} with alkali-metal cations was restricted to few discrete molecular complexes like $[Li(men)]_3P_7$ [1] (tmen = $Me_2NCH_2CH_2NMe_2$) or to the binary phases themselves, which, like most metal polyphosphides, 'can already be seen as complexes, because definite assignments exist between the coordination of the metal atoms and the donor functions of the anions' (*von Schnering* and *Hönle* in [2]). Recently, a number of compounds with one- or two-dimensionally extended alkali-metal-polyphosphide substructures has been found [3–6], which can be seen as intermediates between the 'zero-dimensional' ion complexes and the three-dimensional network of the binary alkali-metal phosphides. They are synthesized by exchanging one or two of the metal cations of $M^1_3P_n$ (M^1 = Rb, Cs; $n = 7, 11$) in liquid ammonia against non-coordinating cations like tetraalkylammonium ions or ammine complexes of alkaline-earth metal ions [6]. If two of the three original cations are removed, the remaining Rb or Cs cations form chains with the polyphosphide cages, *e.g.* $^{1}_{\infty}[RbP_7]^{2-}$ in $(NMe_4)_2RbP_7 \cdot NH_3)$ [3] or $^{1}_{\infty}[CsP_{11}]^{2-}$ in $[Ba(NH_3)_{8.5}]CsP_{11}$ [6]. Removal of only one alkali-metal cation results in layers like $^{2}_{\infty}[Cs_2P_{11}]^-$ in $(NEt_4)Cs_2P_{11}$ [3] or $^{2}_{\infty}[Cs_2P_7]^-$ in $(NEt_3Me)Cs_2P_7 \cdot NH_3$ and $(NEt_4)Cs_2P_7 \cdot 4\ NH_3$ [4]. In both chains and layers, the alkali-metal cations try to achieve a coordination sphere consisting exclusively of P-atoms; nevertheless, in most compounds of this kind, ammonia molecules of crystallization are needed to complete the eight- or nine-fold coordination of the metal cations. These ammoniates are usually very difficult to characterize, because they tend to decompose rapidly even below room temperature due to loss NH_3. Structurally, the NH_3 molecules of crystallization serve together with the non-coordinating cations to separate the alkali-metal-polyphosphide chains or layers completely from each other. Consequently, it seemed to be likely that, even if no cation were exchanged, an analogous compound would be possible with only NH_3 filling the voids in a three-dimensionally extended alkali-metal-polyphosphide framework, which would be the last structural intermediate before the densely packed binary phases themselves. However, although the existence of ammoniates of the alkali-metal polyphosphides has been suspected for a long time [7], their rapid decomposition prevented any characterization until recently [8]. As the structure analysis of ammoniates of alkali-metal compounds is now greatly faciliated by modern low-temperature X-ray techniques, we have started to look for ammoniates of alkali-metal polyphosphides.

Results and Discussion. – We observed $Cs_3P_7 \cdot 3\ NH_3$ for the first time as a by-product in a metathesis reaction in liquid ammonia which used Cs_3P_7 as a starting material. Subsequent experiments have shown that $Cs_3P_7 \cdot 3\ NH_3$ reproducibly precipitates in the form of transparent, plate-like crystals, when a suspension of the only weakly soluble binary compound in liquid ammonia is stored at 233 K for at least 7 days. If the crystals are removed from the mother liquor into an atmosphere of dry Ar, decomposition yielding a yellow powder takes place immediately even below 253 K. The initial decomposition product is amorphous in the X-ray diffraction experiment. After annealing for 2 days at 473 K, however, the powder lines of α-Cs_3P_7 [9] are reproduced.

A low-temperature X-ray structure analysis of the crystals has confirmed that an ammoniate of the composition $Cs_3P_7 \cdot 3\ NH_3$ was formed. The structure consists of a three-dimensional framework built from Cs^+ cations and heptaphosphanortricyclane P_7^{3-} anions. *Fig. 1* illustrates that the majority of P···Cs interactions is concentrated in Cs_3P_7 slabs parallel to the crystallographic direction [101], with only two P···Cs contacts per formula unit connecting the slabs. The resulting cavities are filled by the NH_3 molecules of crystallization, which coordinate to the Cs^+ ions and form a two-dimensional network with holes for the interlayer P···Cs contacts (*Fig. 2*). The shortest N···N distances within the network range from 3.55 to 3.91 Å, which probably precludes any significant H-bond-

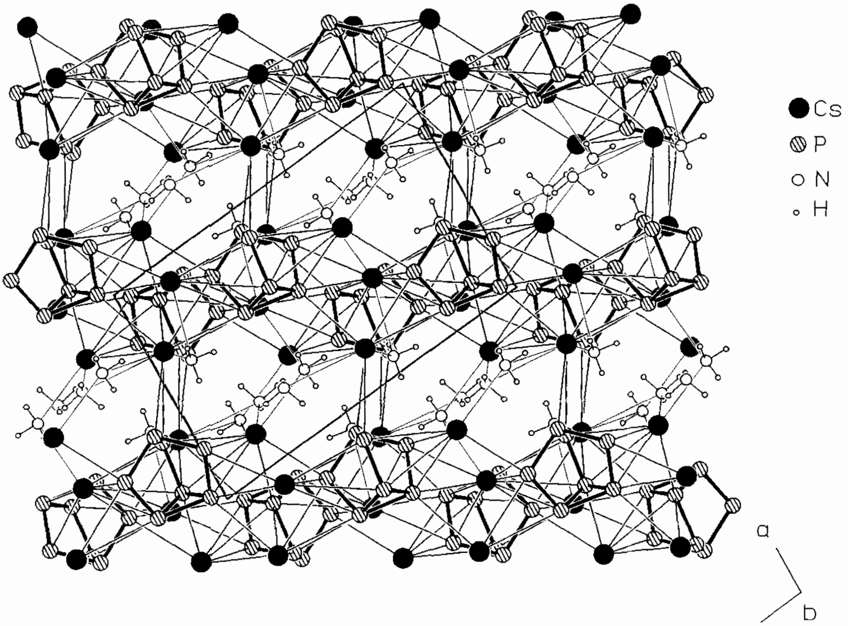

Fig. 1. *View of the crystal structure of* $Cs_3P_7 \cdot 3\ NH_3$ *projected on the* ac *plane*

ing. Instead, the Cs···N ion-dipole interactions seem to be dominant. Each Cs^+ ion has two contacts with NH_3 molecules, which in turn means that each NH_3 molecule serves as a bridging ligand between two of the three crystallographically inequivalent Cs^+ ions. The corresponding Cs···N distances lie between 3.25 and 3.61 Å, which is in good agreement with previously observed values for ammoniates of Cs compounds [4–6].

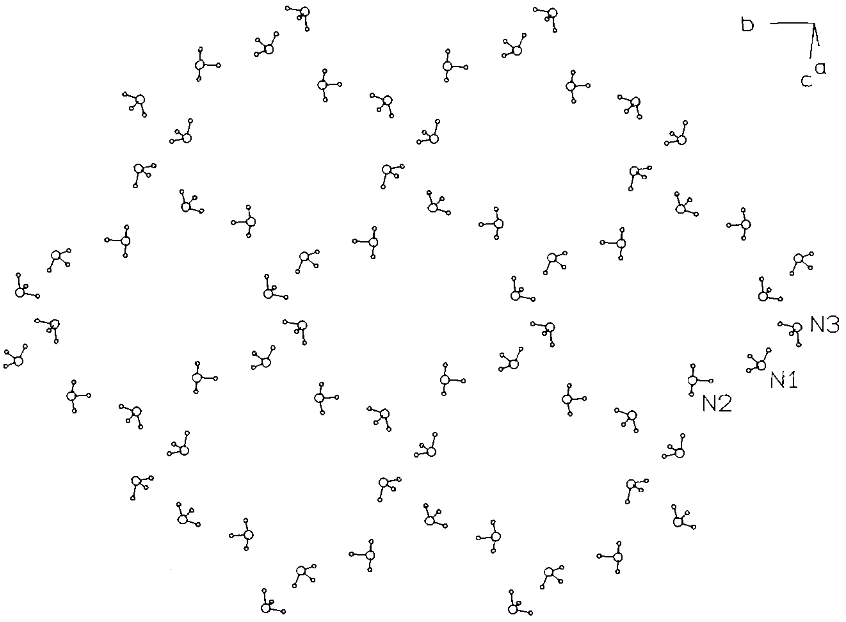

Fig. 2. *The network of NH_3 molecules in the interlayer gap in $Cs_3P_7 \cdot 3\ NH_3$*

Fig. 3, a, depicts the spatial relationship between the P_7^{3-} cage and the cations. The preferred position for metal cations is clearly the trapezoidal side of the cage, where an η^4-like coordination is possible. All three sites are occupied in $Cs_3P_7 \cdot 3\ NH_3$, which is very similar to the arrangement in the molecular complex $[Li(men)]_3P_7$ [1]. In the extended solid-state structure, however, the Cs^+ ions are additionally coordinated by further cages, building the Cs_3P_7 framework this way. This is especially obvious for Cs(2), which resides over the sides of two cages and is additionally coordinated in a side-on manner by P(2) and P(5). Together with the two contacts to N-atoms of ammonia, this leads to a total coordination number of ten for Cs(2); however, several of the corresponding Cs···P distances are at the upper limit of the range of previously observed values (Cs···P distances from 3.5 to 4.1 Å, beyond 4.1 Å there is usually a clear cut-off [3–6]). As can be seen in *Fig. 3, a*, Cs(3) occupies the remaining side of the heptaphosphanortricyclane cage, and has additional close contacts to P(6) and P(4) from two other cages, which results in an eight-fold coordination together with the two N-contacts. The Cs···P distances range from 3.57 to 3.78 Å in this case. Finally, Cs(1) is coordinated by seven P-atoms from four different cage anions (Cs···P distances between 3.55 and 4.08 Å) and thus has a total coordination number of nine. In all three instances, the shortest Cs···P distances involve the formally negatively charged, two-bonded P-atoms of the cage anion. However, the distances to the three-bonded P-atoms are only slightly larger, implying that there is no real functional difference between the two kinds of P-atoms, and that the negative charge is fairly evenly distributed over the seven atoms of the cage. All in all, the heptaphosphanortricyclane anion is surrounded by ten Cs^+ ions (*Fig. 3, a*), which closely resembles the environment of P_7^{3-} in α-Cs_3P_7 [9] with a twelve-fold coordination (*Fig. 3, b*). The main difference lies in the lower coordination of the apical atom P(1) in $Cs_3P_7 \cdot 3\ NH_3$ and in the disappearance of the cation with the interesting η^3-like coordination by the trigonal base of the cage which is present in α-Cs_3P_7. Consequently, as can be seen from *Fig. 1*, the interlayer gaps in $Cs_3P_7 \cdot 3\ NH_3$ are near the top and the bottom of the cage. Since the environment of the cage corresponds fairly well to the ideal C_{3v} symmetry of the P_7^{3-} ion, no significant distortions of the cage are discernible from the intracage bonds or angles.

The existence of a phase like $Cs_3P_7 \cdot 3\ NH_3$ provides the last link in a now continuous chain of alkali-metal-polyphosphide substructures ranging from the densely packed binary phases over frameworks, layers, and chains to isolated molecular complexes. Apart from showing what a rich coordination chemistry is possible between heavy

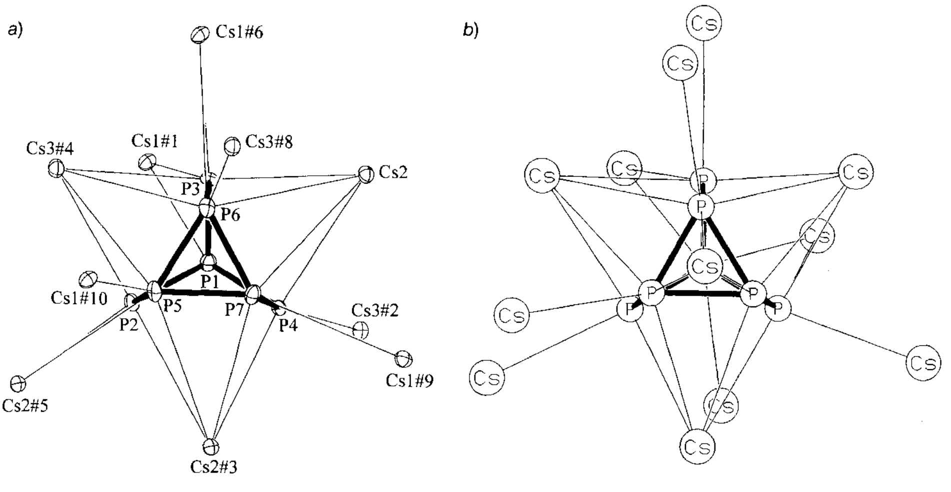

Fig. 3. a) *ORTEP Plot of the coordination of P_7^{3-} by the Cs cations* (50% probability ellipsoids). Selected interatomic distances [Å] and angles [°]: P(1)–Cs(1 # 1) 3.682(4), P(2)–Cs(3 # 4) 3.753(4), P(2)–Cs(2 # 5) 3.774(4), P(2)–Cs(2 # 3) 3.905(4), P(3)–Cs(1 # 6) 3.554(4), P(3)–Cs(2) 3.676(4), P(3)–Cs(3 # 4) 3.703(4), P(3)–Cs(1 # 1) 3.764(4), P(4)–Cs(3 # 2) 3.569(4), P(4)–Cs(1 # 9) 3.648(4), P(4)–Cs(2 # 3) 3.671(4), P(4)–Cs(2) 3.753(4), P(5)–Cs(1 # 10) 3.694(4), P(5)–Cs(3 # 4) 3.760(4), P(5)–Cs(2 # 5) 3.835(4), P(5)–Cs(2 # 3) 4.016(4), P(6)–Cs(3 # 4) 3.739(4), P(6)–Cs(3 # 8) 3.775(4), P(6)–Cs(2) 4.000(4), P(6)–Cs(1 # 6) 4.083(4), P(7)–Cs(1 # 9) 3.788(4), P(7)–Cs(2 # 3) 3.873(4), P(7)–Cs(2) 4.063(4), P(1)–P(3) 2.179(5), P(1)–P(4) 2.182(5), P(1)–P(2) 2.185(5), P(2)–P(5) 2.131(5), P(3)–P(6) 2.133(6), P(4)–P(7) 2.122(5), P(5)–P(7) 2.273(5), P(5)–P(6) 2.288(5); P(3)–P(1)–P(4) 102.0(2), P(3)–P(1)–P(2) 101.6(2), P(4)–P(1)–P(2) 102.7(2), P(5)–P(2)–P(1) 98.2(2), P(6)–P(3)–P(1) 98.9(2), P(7)–P(4)–P(1) 98.2(2), P(2)–P(5)–P(7) 105.4(2), P(2)–P(5)–P(6) 105.4(2), P(3)–P(6)–P(7) 104.9(2), P(3)–P(6)–P(5) 104.3(2), P(4)–P(7)–P(6) 105.8(2), P(4)–P(7)–P(5) 105.7(2), P(7)–P(5)–P(6) 59.6(2), P(7)–P(6)–P(5) 59.9(2), P(6)–P(7)–P(5) 60.6(2). Symmetry operations used to generate equivalent atoms # 1 $-x, -y+1, -z+1$; # 2 $x-1/2, -y+1/2, z+1/2$; # 3 $-x+1/2, y-1/2, -z+1/2$; # 4 $x, y+1, z+1$; # 5 $x+1/2, -y+3/2, z+1/2$; # 6 $x, y+1, z$; # 8 $-1x+1, -y+1, -z$; # 9 $-x+1/2, y+1/2, -z+1/2$; # 10 $-x+1, -y+1, -z+1$. b) *Coordination of P_7^{3-} by the Cs cations in α-C_3P_7* [9].

alkali-metal cations and polyphosphides, they hint at the amount of ion-pairing in solutions of the polyphosphides in liquid ammonia, which is probably the reason for the difficulties encountered in the chemistry with 'naked' polyphosphide anions [10].

Experimental. – All manipulations were carried out under dry Ar in all-glass reaction and handling vessels that were dried *in vacuo*. Ammonia (*Bayer AG*) was made anh. by distilling it first from Na, then from K, and was stored as a K/NH_3 soln. at 195 K. Cs_3P_7 was synthesized from the elements in a sealed glass ampoule according to the procedure given in [9]. Red phosphorus was obtained from *Hoechst* ('electronic grade'), caesium was synthesized by reduction of the chlorides with Ca [11] and purified by double distillation *in vacuo*.

Preparation of $Cs_3P_7 \cdot 3\ NH_3$. *Ca.* 300 mg of Cs_3P_7 were placed into a *Schlenck*-type glass vessel. NH_3 (40 ml) was frozen into the vessel at 77 K. The vessel was then stored at 233 K until a visible amount of the Cs_3P_7 had transformed to transparent $Cs_3P_7 \cdot 3\ NH_3$. The first crystals were visible after 7 d, the charge used for the crystal selection had been stored for 2 months. No complete recrystallization has yet been observed. This technique, however, is superior to the alternative procedure of dissolving Cs_3P_7 in an H-type glass vessel and separating the soln. *via* a glass frit.

For the crystal preparation, we have adapted the technique described by *Kottke* and *Stalke* [12] to our needs. Small amounts of the crystals were transferred directly from the liquid ammonia into perfluoroether (*RS 3000* and *RS 216*, *Riedel de Haen*) which was cooled to 213 K by a stream of cold N_2. A single crystal which was suitable for an X-ray structure analysis was selected with the help of a microscope and picked up on the tip of a capillary mounted on a goniometer head. The crystal was then immediately submerged in liquid N_2, and transferred to the diffractometer.

Crystal Data and Structure Refinement. $H_9Cs_3N_3P_7$, $M = 666.62$, pale-yellow plates, monoclinic, space group $P2_1/n$ (No. 14), $a = 9.277(4)$, $b = 12.676(3)$, $c = 14.259(6)$ Å, $\beta = 97.35(3)°$, $V = 1663(1)$ Å^3, $Z = 4$, $D_c = 2.663$ g cm^{-3}, $\mu(\mathrm{Mo}K_\alpha) = 7.282$ mm^{-1}, $F(000) = 1188$ electr. No. of reflections measured 2439, No. of independent reflections 1252 ($R_{int} = 0.085$), No. of observed reflections with $I > 2\sigma(I)$ 1102, No. of parameters 145, No. of restraints 72. The lattice parameters were determined by a CAD4 indexing program and refined by a least-squares routine with the angular settings of 25 reflections. Diffraction data were collected on an *Enraf-Nonius CAD4* diffractometer with graphite monochromated MoK_α radiation ($\lambda = 0.71073$ Å) at 123(2) K to $\theta_{max.} = 22°$ using $\omega/2\theta$-BPB scans. Three intensity control reflections were measured every hour, showing negligible decay. Intensity data were corrected for *Lorentz* and polarization effects and for absorption effects (psi-scans, 9 reflections). The structure was solved by direct methods (SHELXS-86 [13]) and refined on F^2 using all 1252 independent reflections (SHELXL-93 [14]). The H-atoms were located by difference *Fourier* synthesis; all intramolecular N–H and H–H distances were restrained to be equal. H-Atoms were refined isotropically, all other atoms anisotropically. The final wR_2 value was 0.085 (corresponds to a conventional R value of 0.034 using only reflections with $I > 2\sigma(I)$). The largest peak and hole in the final difference *Fourier* map were 0.74 (in the vicinity of Cs) and −0.69 eÅ^{-3}, respectively.

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