Alkali Metal Polyphosphides in Low Dimensions: Synthesis and Structure of $[(CH_3)_4N]_2RbP_7(NH_3)$ and $[(C_2H_5)_4N]Cs_2P_{11}$

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Partial exchange of the alkali metal ions for tetraalkylammonium cations of Rb_3P_7 and Cs_3P_{11} in liquid ammonia results in the formation of $[(CH_3)_4N]_2RbP_7(NH_3)$ (**1**) and $[(C_2H_5)_4N]Cs_2P_{11}$ (**2**). The crystal structures reveal the existence of one-dimensional $^1_\infty[RbP_7]^{2-}$ chains in the former and two-dimensional $^2_\infty[Cs_2P_{11}]^-$ layers in the latter compound. The nortricyclane cage in **1** is distorted by one-sided coordination to the Rb ions in a manner that can be related to the valence tautomerism of the free P_7^{3-} anion.

Binary metal polyphosphides have been studied extensively over the last two decades, revealing an unexpected wealth of composition and structures[1]. Much less work has been done on the use of these compounds as starting materials for chemical reactions, utilizing their polyphosphorus structural elements as building blocks in new compounds. Prime candidates for reactions are the polyphosphides with isolated Zintl anions such as $M^I_3P_7$ and $M^I_3P_{11}$ (M^I = Na$-$Cs), which offer the possibility of getting polyphosphorus synthons without having to break any phosphorus-phosphorus bonds. Most of the chemistry reported up to now has concentrated on the derivatisation of heptaphosphanotricyclane P_7^{3-}, including protonation, alkylation, and metalation reactions[2−5]. Recently, various reactions of P_7^{3-} with transition metal compounds were investigated[6−8], which have resulted in several new compounds mainly of the $[\eta^4\text{-}P_7M(CO)_3]^{3-}$ type (M = Mo, W) with norbornane-like P_7 fragments. K_3P_7 was used as a starting material in these reactions, requiring activation by cryptand [2.2.2] or 18-crown-6 to facilitate dissolution of the polyphosphide and to break the K^+/P_7^{3-} ion pairing in solution.

An alternative route to "naked" polyphosphide anions would be the use of polyphosphides in which the alkali metal ions have been exchanged for quaternary ammonium or phosphonium cations. Surprisingly, only one polyphosphide of this kind was reported in the literature, the in many ways remarkable hexadecaphosphide $(PPh_4)_2P_{16}$ which forms by an unknown mechanism upon the addition of PPh_4Br to a suspension of Na_3P_7 in THF[9]. The main reason for this scarcity may have been disclosed by Eichhorn et al., who, in a very recent publication, describe the use of tetraalkylammonium salts as alkylating agents for the polyphosphide Zintl anions in $P_7M(CO)_3]^{3-}$-type complexes and for P_7^{3-} itself[8]. Obviously, the twofold-linked phosphorus atoms of the Zintl anions are very effective nucleophilic reaction sites which affect the dealkylation of the usually unreactive tetraalkylammonium cations even at room temperature. In this context, the earlier findings by Haushalter et al. concerning the low stability of $[(CH_3)_4N]_4Sn_9$ may also be relevant[10]. In spite of these warning signals we decided to attempt the preparation of solid polyphosphides of the nortricyclane type P_7^{3-} and the trishomocubane ("ufosane") type P_{11}^{3-} in which some or all of the metal ions are exchanged for tetraalkylammonium cations.

Results

Liquid ammonia was chosen as a solvent because it seemed reasonable to take precautions against low thermal stability of the reaction products. Slow interdiffusion of solutions of $[(CH_3)_4N]I$ and Rb_3P_7 and of $[(C_2H_5)_4N]I$ and Cs_3P_{11} at −40°C yielded crystalline products which were honey-coloured in the first case and bright red in the latter case. Both have a low solubility in liquid ammonia as they could be treated repeatedly with boiling ammonia at 240 K to remove the alkali metal iodides and excess starting material. Subsequent elemental analysis revealed that no complete cation exchange had taken place: the P_7 compound retains one and the P_{11} compound retains two alkali metal ions per formula unit. If we take the results of the crystal structure analysis into account the equations (1) and (2) apply.

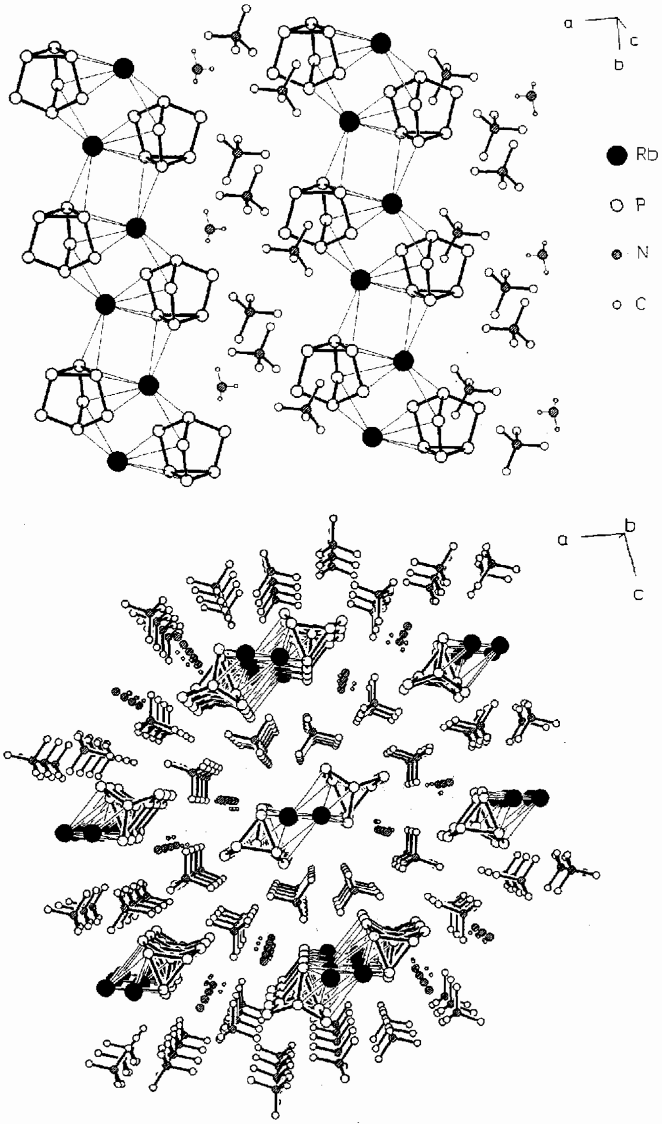
$$Rb_3P_7 + 2\,[(CH_3)_4N]I + NH_3 \rightarrow \underset{\mathbf{1}}{[(CH_3)_4N]_2RbP_7(NH_3)} + 2\,RbI\ (233\ K) \qquad (1)$$

$$Cs_3P_{11} + [(C_2H_5)_4N]I \rightarrow \underset{\mathbf{2}}{[(C_2H_5)_4N]Cs_2P_{11}} + CsI\ (233\ K) \qquad (2)$$

Both compounds are highly reactive towards air and moisture, even more so than the binary polyphosphides used as starting materials. Both are thermally unstable at room temperature: the intensity control reflections of a 0.11 × 0.24 × 0.37 mm^3 crystal of **1** showed a decay of over 70% after 14 h at 295(2) K; a crystal of **2** of similar size showed a decay of 45% after 21 hours at the same temperature. No loss of ammonia could be induced by applying a vacuum of 10^{-3} mbar to a sample of **1** at −40 °C; this behaviour is very similar to that of $\mathrm{Cs_3As_7 \cdot NH_3}$[11]. Recently, we found that only ammonia molecules which coordinate an alkali metal ion like $\mathrm{Rb^+}$ or $\mathrm{Cs^+}$ are easily removed in compounds of this type[12].

A low-temperature single-crystal structure analysis showed that **1** is composed of discrete heptaphosphanortricyclane cage anions $\mathrm{P_7^{3-}}$, rubidium and tetramethylammonium cations, and neutral ammonia molecules. The rubidium ions are coordinated by $\mathrm{P_7^{3-}}$ in such a fashion that infinite $^1_\infty[\mathrm{RbP_7}]^{2-}$ chains are formed running parallel to the crystallographic *b* axis (Figure 1). The $^1_\infty[\mathrm{RbP_7}]^{2-}$ chains are separated by $\mathrm{(CH_3)_4N^+}$ ions and $\mathrm{NH_3}$ molecules. The single rubidium ion in the asymmetric unit has close contact to eight phosphorus atoms from three different cage anions (Figure 2); the corresponding P−Rb distances range from 3.484 to 3.680 Å. The next closest distance to phosphorus is significantly larger (4.323 Å). No significant distinction can be made between close contacts to twofold-linked P atoms (which are formally negatively charged) and threefold-linked P atoms; the distance between Rb and the threefold-linked P7#1 (3.513 Å) is practically the same as those between Rb and the twofold-linked P1 and P5 (3.514 and 3.484 Å).

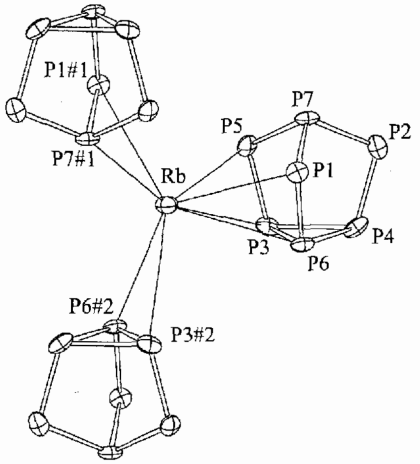
Figure 1. Top: View of the structure of **1** perpendicular to the *a*−*c* plane; bottom: view along the *b* axis



The $\mathrm{P_7^{3-}}$ cage is slightly but significantly distorted from $3m$-C_{3v} threefold symmetry. The P−P bonds to those two phosphorus atoms P2 and P4 which do not coordinate to rubidium are shorter than the corresponding bonds between coordinating atoms: P2−P7 2.169 vs. P5−P7 2.186, P1−P7 2.188 Å and P4−P3 2.274, P4−P6 2.277 vs. P3−P6 2.299 Å. There is no significant difference between the angles P1−P7−P2, P2−P7−P5, and P1−P7−P5, however. The height *h* of the cage, which was used as a measure of the ionic character of the nortricyclane cage[1], is 2.973 Å. The relative height *Q*, which was introduced in order to compare nortricyclane cages formed by different elements[1], is 1.302 with $Q = h/\bar{d}_\Delta$, $\bar{d}_\Delta$ = 2.283 Å being the average bond length in the $\mathrm{P_3}$ base of the cage.

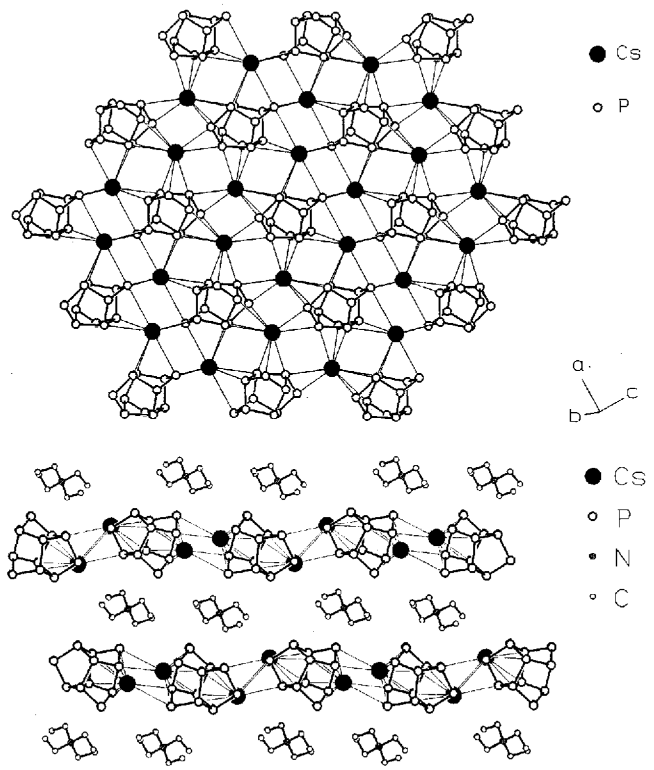
The single-crystal structure analysis of **2** shows that it is also composed of discrete ionic units. In this case, the caes-

Figure 2. ORTEP plot of the coordination of Rb in **1** (50% probability ellipsoids). − Selected interatomic distances [Å] and angles [°]: Rb−P(5) 3.484(1), Rb−P(7)#1 3.513(1), Rb−P(1) 3.514(1), Rb−P(1)#1 3.567(1), Rb−P(6)#2 3.582(1), Rb−P(3) 3.611(1), Rb−P(6) 3.646(1), Rb−P(3)#2 3.680(1), P(1)−P(6) 2.120(1), P(1)−P(7) 2.188(1), P(2)−P(4) 2.122(1), P(2)−P(7) 2.169(1), P(3)−P(5) 2.122(1), P(3)−P(4) 2.274(1), P(3)−P(6) 2.299(1), P(4)−P(6) 2.277(1), P(5)−P(7) 2.186(1), P(1)−P(2) 3.410(1), P(1)−P(5) 3.408(1), P(2)−P(5) 3.377(1); P(6)−P(1)−P(7) 98.38(3), P(4)−P(2)−P(7) 98.34(3), P(5)−P(3)−P(4) 105.09(3), P(5)−P(3)−P(6) 105.27(3), P(4)−P(3)−P(6) 59.73(3), P(2)−P(4)−P(3) 105.01(3), P(2)−P(4)−P(6) 105.63(3), P(3)−P(4)−P(6) 60.68(3), P(3)−P(5)−P(7) 98.31(3), P(1)−P(6)−P(4) 105.39(3), P(1)−P(6)−P(3) 104.85(3), P(4)−P(6)−P(3) 59.59(3), P(2)−P(7)−P(5) 101.64(3), P(2)−P(7)−P(1) 103.05(3), P(5)−P(7)−P(1) 102.05(3). − Symmetry operations used to generate equivalent atoms: #1 − *x*, −*y*, −*z*; #2 − *x*, −*y* + 1, −*z*



ium ions are coordinated by trishomocubane ("ufosane") cages in such a way that planar $^2_\infty[Cs_2P_{11}]^-$ layers result which are separated by layers of $(C_2H_5)_4N^+$ cations (Figure 3). Both of the caesium ions in the asymmetric unit have eight close contacts to phosphorus atoms from three (symmetry-equivalent) P_{11}^{3-} cages each (Figure 4). The corresponding Cs−P distances range from 3.590 to 3.988 Å for Cs1 and from 3.594 to 3.831 for Cs2. The cutoff after these eight shortest distances is much less pronounced than in **1**, the next-nearest Cs−P distances being 4.244 Å for Cs1 and 4.079 for Cs2. No clear distinction is possible between close contacts to twofold-linked and to threefold-linked P atoms.

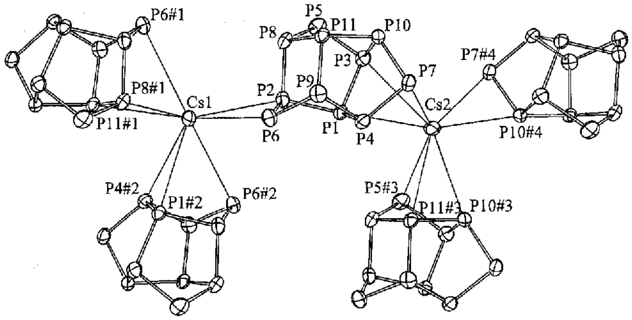
Figure 3. Top: View of the $^2_\infty[Cs_2P_{11}]^-$ layer in **2**; bottom: view of the structure of **2** parallel to the $^2_\infty[Cs_2P_{11}]^-$ layers



The P_{11}^{3-} "ufosane" cage ideally has 32-D_3 symmetry. No significant deviation from this symmetry is discernible in the structure of **2**. Consequently, all the observed bond lengths in the cage can be reduced to three symmetry-inequivalent bond lengths. The bonds emanating from the P atoms which lie on the threefold axis (P1 and P11) are present six times and have an average value of d_m = 2.243 Å, the bonds from the twofold-linked P atoms (P5, P6, and P7) are also sixfold (d_m = 2.153 Å) and the three bonds connecting the pairs of the remaining threefold-linked P atoms (P4 and P9, P2 and P8, P3 and P10) have an average value of d_m = 2.205 Å. The height h of the cage, which in this case is the distance between the two apical P atoms, is 3.763 Å.

Discussion

Figure 4. ORTEP plot of the coordination of Cs1 and Cs2 in **2** (50% probability ellipsoids). − Selected interatomic distances [Å] and angles [°]: Cs(1)−P(2) 3.590(2), Cs(1)−P(8)#1 3.629(2), Cs(1)−P(4)#2 3.641(2), Cs(1)−P(6) 3.709(2), Cs(1)−P(11)#1 3.710(2), Cs(1)−P(6)#2 3.760(2), Cs(1)−P(1)#2 3.922(2), Cs(1)−P(6)#1 3.980(2), Cs(2)−P(10)#3 3.594(2), Cs(2)−P(10)#4 3.599(2), Cs(2)−P(1) 3.626(2), Cs(2)−P(5)#3 3.679(2), Cs(2)−P(3) 3.733(2), Cs(2)−P(7)#4 3.744(2), Cs(2)−P(11)#3 3.775(2), Cs(2)−P(7) 3.831(2), P(1)−P(2) 2.230(2), P(1)−P(4) 2.242(2), P(1)−P(3) 2.266(2), P(7)−P(10) 2.148(2), P(7)−P(4) 2.153(2), P(5)−P(8) 2.146(2), P(5)−P(3) 2.154(2), P(8)−P(2) 2.202(2), P(8)−P(11) 2.244(2), P(3)−P(10) 2.202(2), P(2)−P(6) 2.157(2), P(9)−P(6) 2.157(2), P(9)−P(4) 2.211(2), P(9)−P(11) 2.247(2), P(10)−P(11) 2.232(2); P(2)−P(1)−P(4) 102.05(8), P(2)−P(1)−P(3) 101.40(8), P(4)−P(1)−P(3) 102.55(8), P(10)−P(7)−P(4) 95.45(8), P(8)−P(5)−P(3) 95.75(8), P(5)−P(8)−P(2) 101.06(9), P(5)−P(8)−P(11) 105.53(8), P(2)−P(8)−P(11) 100.83(8), P(5)−P(3)−P(10) 101.24(8), P(5)−P(3)−P(1) 105.96(9), P(10)−P(3)−P(1) 99.47(8), P(6)−P(2)−P(8) 100.03(9), P(6)−P(2)−P(1) 105.77(8), P(8)−P(2)−P(1) 101.25(8), P(6)−P(9)−P(4) 100.04(8), P(6)−P(9)−P(11) 105.08(8), P(4)−P(9)−P(11) 100.07(8), P(7)−P(4)−P(9) 101.18(9), P(7)−P(4)−P(1) 105.24(8), P(9)−P(4)−P(1) 101.39(8), P(7)−P(10)−P(3) 101.73(8), P(7)−P(10)−P(11) 106.37(8), P(3)−P(10)−P(11) 100.93(8), P(10)−P(11)−P(8) 102.27(8), P(10)−P(11)−P(9) 102.16(8), P(8)−P(11)−P(9) 102.21(8), P(9)−P(6)−P(2) 96.52(8). − Symmetry operations used to generate equivalent atoms: #1 $-x, -y+1, -z$; #2 $-x+1, -y+1, -z$; #3 $x+1, y, z$; #4 $-x+1, -y+2, -z-1$



Our results show that it is possible to prepare solid polyphosphides in which the metal ions are partially exchanged for tetraalkylammonium cations, although the products are thermally unstable at room temperature. Total exchange of the cations resulting in quasi-binary compounds is much more difficult and has been achieved only in the case of the compounds $[(C_2H_5)_4N]_3P_{11}$ and $[(CH_3)_3(C_2H_5)N]_3P_{11}$ so far[13]. The pronounced tendency of polyphosphide anions to form ion complexes in solution was demonstrated by the solid-state structures of compounds like $[Rb(en)]_3P_7$[1] and $[Li(tmeda)]_3P_7$[15], which are isolated neutral $M^I_3P_7$ molecules surrounded by neutral ligands completing the coordination of the alkali metal ions. An important difference of these compounds as compared to **1** and **2** is that whereas in the ion complexes the cations predominantly interact with the twofold-linked phosphorus atoms which are formally negatively charged, in **1** and **2** no preference for either twofold-linked or threefold-linked phosphorus is apparent. In this respect **1** and **2** are very similar to the binary alkali metal heptaphosphides and undecaphosphides, which form three-dimensional networks making use of ion-ion and ion-dipole interactions between alkali metal ions and phosphorus atoms without any marked preference for the formally negatively charged phosphorus atoms[1]. Compounds **1** and **2** can be seen as having one-dimensional and two-dimensional alkali metal metal polyphosphide substructures, in which the bonding situation is similar to that of the binary compounds. As in the binary compounds, **1** and **2** succeed in completing the coordination of the alkali metal ions with polyphosphides only, without having to incorporate solvent molecules (we have so far prepared several analogous compounds where this is not the case[12]).

With respect to the structural dimensionality of alkali metal polyphosphides **1** and **2** are filling the gap between the discrete "zero-dimensional" ion complexes mentioned above and the three-dimensional networks formed in the binary compounds. Upon close inspection, one can even detect a trend towards ion-pairing and stronger interaction between alkali metal ion and twofold-linked P atoms from **2** to **1**: in **1**, two of the three shortest Rb–P distances involve twofold-linked P atoms, whereas in **2** none of the three closest neighbours for either Cs1 or Cs2 are the formally negatively charged atoms. In **1**, the rubidium ion resides over one of the sides of the nortricyclane cage, thus being in contact with four P atoms. This arrangement resembles an ion-pairing situation (Figure 2); the Rb ion is, however, just as closely coordinated by atoms of the two neighbouring cages. In comparison, no indication of ion-pairing can be found in **2**.

Nearly all of the endocyclic bond lengths and angles of P_7^{3-} in **1** agree well with the values established previously[1], the only exception is the P3–P6 bond (2.299 Å) in the three-membered P_3 ring which is longer than the largest value reported before (2.287 in α-Cs_3P_7[16]), and is one of the longest P–P bonds found in polyphosphides so far. This bond is strongly influenced by the Rb-to-P interactions (Figure 3): (1) It belongs to the side of the P_7^{3-} cage which faces the rubidium ion and (2) it is bridged by another rubidium ion. It is interesting to note that the breaking of this bond together with the closing of a P1–P5 bond would correspond with the well-known valence tautomerism (bridge head P7 becomes P4) found by Baudler[2], and also the idea of the metal support of this process would be in accordance[1]. The simple cleavage of the P3–P6 bond would result in a diradicalic P_7^{3-} unit with a topology between norbornane and norbornadiene. This fragment is well-known from the transition metal compounds $[\eta^4\text{-}P_7M(CO)_3]^{3-}$ (M = Mo, W)[8]. The transition from a nortricyclane topology to a norbornadiene topology following the coordination to a metal centre was reported for $[\eta^4\text{-}As_7Cr(CO)_3]^{3-}$, which forms from $[Cr(CO)_3(\eta^6\text{-mesitylene})]$ and As_7^{3-}[17]. The interactions of a polyphosphide anion with an alkali metal cation are much weaker than those with a transition metal, of course; nevertheless, the observed lengthening of the P3–P6 bond which is in side-on coordination to two rubidium ions indicates a weaking of this bond. This weakening might be interpreted as a very small first step towards the formation of an η^4-bonded P_7 fragment which forms from P_7^{3-} in the vicinity of a more strongly polarising cation. It should be interesting to see whether more strongly distorted nortricyclane cages form in the case of similar compounds which contain cations like Ba^{2+} or La^{3+}.

The elevation *h* of the apical P atom with respect to the P_3 base is a very sensitive parameter to indicate the transfer of electrons to the heptaphosphanortricyclane cage[1]. Neutral P_7 cages in P_7R_3 [R = $M^{IV}(CH_3)_3$, $M^{IV}(ph)_3$] have an average h = 3.15 Å (Q = 1.42), while P_7^{3-} in ionic compounds has an average h = 3.00 Å (Q = 1.33) due to the electrostatic repulsion between the negatively charged P atoms. Going from Li_3P_7 to Cs_3P_7, an increase of the electron transfer is indicated by a small decrease from h = 3.016 Å to h = 2.969 Å. In compound **1**, *h* is rather small (2.973 Å), which is in accord with our initial purpose of producing "naked" polyphosphide anions. It is, however, not as small as would be expected for a compound in which all of the alkali metal ions have been exchanged and where consequently no back donation of electrons is possible. The value for *h* in **1** is very close to that in $[Rb(en)_3]P_7$ (2.971 Å[1]), indicating that even the proximity of only one rubidium ion is enough to relieve the P_7^{3-} cage of some of its excess charge. It may also be true that this value is the lower limit generated by the covalent forces maintaining bond lengths and bond angles.

A similar dependence of the height *h* on the electron transfer was proposed for the trishomocubane ("ufosane") cage, where *h* is the distance between the two P atoms which lie on the C_3 axis. The effect should be less pronounced due to the larger distance between the formally negatively charged P atoms[1]. As the structure determination of **2** is only the second one of an ionic P_{11} cage compound since the study of Na_3P_{11}[18], the hypothesis was now tested for the first time. Since **2** contains both caesium and tetraethylammonium ions, a larger transfer of electrons and a smaller height *h* was expected. The observed height *h* in **2** (3.763 Å) as compared with that of Na_3P_{11} (3.786 Å[1]) confirmed our assumptions.

The endocyclic bond lengths and angles of the "ufosane" cage of **2** agree well with the values observed in the case of Na_3P_{11}[18]. The bonds connecting the twofold-linked P to their neighbours are somewhat shorter for **2** (2.153 Å as compared to 2.17 Å), which may be another effect of a larger charge transfer.

Of course, any interpretation of the structures of **1** and **2** as low-dimensional, negatively charged alkali metal polyphosphides has to bear in mind that the interactions between the polyphosphide anions and the alkali metal cations are rather weak and of low directionality. The metal-phosphide substructures form only because the interactions betweeen polyphosphide anions and the tetraalkylammonium cations are much weaker still. Nevertheless, it would be interesting to see whether these substructures have an intrinsic tendency to form, i.e. whether they exist with different tetraalkylammonium cations, or whether their formation is governed to a large extent by packing effects instead.

Experimental

All manipulations were carried out under dry argon in all-glass reaction and handling vessels that were dried in vacuo. Ammonia (Bayer AG) was made anhydrous by distilling it first from sodium, then from potassium, and was stored as a potassium-ammonia solution at 195 K. Tetramethylammonium iodide and tetraethylammonium iodide (Aldrich) were dried in vacuo at 333 K for 2 d. Rb_3P_7 and Cs_3P_{11} were synthesised from the elements in sealed glass ampules according to the procedure given in the literature[1]. **CAUTION!** These reactions are highly exothermic and serious explosions **will** happen upon improper handling! Red phosphorus was obtained from Hoechst ("electronic grade"), rubidium and caesium were synthesised by reduction of the chlorides with calcium[19] and purified by double distillation in vacuo. – Elemental analyses: Microanalytical laboratory of the institute.

General Procedure for the Preparation of $[(CH_3)_4N]_2RbP_7(NH_3)$ (**1**) *and $[(C_2H_5)_4N]Cs_2P_{11}$* (**2**): Into an U-shaped reaction vessel fitted with a glass frit (porosity 3) separating the two sides, 0.300 g (6.34×10^{-4} mol) of Rb_3P_7 and 0.256 g (1.27×10^{-3} mol) of $[(CH_3)_4N]I$ or 0.300 g (4.06×10^{-4} mol) of Cs_3P_{11} and 0.104 g (4.06×10^{-4} mol) of $[(C_2H_5)_4N]I$ were placed into opposite sides, respectively. Ca. 30 ml of ammonia was frozen into the vessel at 77 K. The vessel was allowed to warm slowly to 233 K. The reactions were completed after two weeks for **1** and after three days for **2** (due to the higher solubility of Cs_3P_{11} in liquid ammonia) at 233 K. The crystalline products were transferred to an H-shaped vessel with a glass frit (porosity 3) and washed six times with boiling ammonia. The products were stored in sealed glas ampules under argon at 233 K. **1**: $C_8H_{27}N_3P_7Rb$ (467.6): calcd. C 20.55, H 5.82, N 8.99, Rb 18.28; found C 20.42, H 5.80, N 8.91, Rb 18.31. – **2**: $C_8H_{20}Cs_2NP_{11}$ (736.7): calcd. C 13.04, H 2.74, Cs 36.08, N 1.90; found C 13.11, H 2.75, Cs 36.13, N 1.94. – Suitable single crystals for the X-ray structure analyses were selected under a stream of cooled nitrogen and wedged into Lindemann glass capillaries.

Crystal Data and Structure Refinement for **1**[14]: $C_8H_{27}N_3P_7Rb$, $M = 467.59$, yellow needles, crystal size $0.42 \times 0.20 \times 0.19$ mm^3, monoclinic, space group $P2_1/c$ (Nr. 14), $a = 13.002(1)$, $b = 8.509(1)$, $c = 18.625(2)$ Å, $\beta = 100.33(1)°$, $V = 2027.2(3)$ Å^3, $Z = 4$, $D_c = 1.532$ gcm^{-3}, $\mu(\text{Mo-}K_\alpha) = 2.99$ mm^{-1}, $F(000) = 952$ electr. No. of measured reflections 7150, no. of independent reflections 3575 ($R_{int} = 0.0225$), no. of observed reflections with $I > 2\sigma(I)$ 3170, no. of parameters 281. The lattice parameters were determined by a STOE-STADI4 indexing programme and refined by a least-squares routine with the angular settings of 56 reflections (20° $< \theta <$ 28°). Diffraction data were collected with a STOE-STADI4 diffractometer with graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å) at 190(2) K to $\theta_{max} = 25°$ by using a learned profile routine. Three intensity control reflections were measured every hour, showing a total decay of 1.2%. Intensity data were corrected for linear isotropic decay, Lorentz and polarisation effects and for absorption effects (psi-scans, 16 reflections). The structure was solved by direct methods (SHELXS-86[20]) and refined on F^2 using all 3575 independent reflections (SHELXL-93[21]). Hydrogen atoms were located by difference Fourier synthesis and refined isotropically, all other atoms anisotropically. The final wR_2 value was 0.0743 [corresponding to a conventional R value of 0.0330 by using only reflections with $I > 2\sigma(I)$]. The largest peak and hole in the final difference Fourier map were 0.67 and -0.45 eÅ^{-3} respectively.

Crystal Data and Structure Refinement for **2**[14]: $C_8H_{20}Cs_2NP_{11}$, $M = 736.74$, red needle, crystal size $0.40 \times 0.06 \times 0.03$ mm^3, triclinic, space group $P\bar{1}$ (Nr. 2), $a = 7.734(2)$, $b = 10.990(3)$, $c = 15.486(5)$ Å, $\alpha = 73.71(2)$, $\beta = 87.28(2)$, $\gamma = 79.43(2)°$, $V = 1242.0(6)$ Å^3, $Z = 2$, $D_c = 1.970$ gcm^{-3}, $\mu(\text{Mo-}K_\alpha) = 3.64$ mm^{-1}, $F(000) = 700$. No. of measured reflections 8727, no. of independent reflections 3891 ($R_{int} = 0.0274$), no. of observed reflections with $I > 2\sigma(I)$ 3573, no. of parameters 204. The lattice parameters were determined by a CAD4 indexing programme and refined by a least-squares routine with the angular settings of 25 reflections (15° $< \theta <$ 22°). Diffraction data were collected with an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å) at 223(2) K to $\theta_{max} = 24°$ by using ω-BPB scans. Three intensity control reflections were measured every hour, showing a total decay of 2.0%. Intensity data were corrected for linear isotropic decay, Lorentz and polarisation effects and for absorption effects (psi scans, 9 reflections). The structure was solved by direct methods (SHELXS-86[20]) and refined on F^2 by using all 3891 independent reflections (SHELXL-93[21]). All atoms except hydrogen atoms were refined aniostropically, with the hydrogen atoms at calculated positions riding on the carbon atoms. The final wR_2 value was 0.1000 [corresponding to a conventional R value of 0.0377 by using only reflections with $I > 2\sigma(I)$]. The largest peak and hole in the final difference Fourier map were 2.29 (in the vicinity of cesium) and -0.45 eÅ^{-3}, respectively.

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