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Layers built from caesium cations and heptaphosphanortricyclane† anions: synthesis and crystal structure of $[\mathrm{NEt_3Me}][\mathrm{Cs_2P_7}]\cdot\mathrm{NH_3}$ and $[\mathrm{NEt_4}][\mathrm{Cs_2P_7}]\cdot4\mathrm{NH_3}$

Nikolaus Korber* and Jörg Daniels

Institut für Anorganische Chemie der Universität Bonn, Gerhard-Domagk-Strasse 1, D-53121 Bonn, Germany

Exchange of one caesium cation of $\mathrm{Cs_3P_7}$ for $\mathrm{NEt_3Me^+}$ or $\mathrm{NEt_4^+}$ in liquid ammonia gave $[\mathrm{NEt_3Me}][\mathrm{Cs_2P_7}]\cdot\mathrm{NH_3}$ **1** and $[\mathrm{NEt_4}][\mathrm{Cs_2P_7}]\cdot4\mathrm{NH_3}$ **2**, respectively. The crystal structure of the compounds have been determined. They show the existence of corrugated $^2_\infty[\mathrm{Cs_2P_7}]^-$ layers stacked along the crystallographic *a* axis in both compounds. The layers are topologically equivalent in **1** and **2**. While the layers are repeated in the same orientation in **1**, stacking mode AAA, they have two different orientations in **2**, stacking mode ABAB, where B is related to A by a mirror plane. The space between the layers contains ammonia of solvation completing the co-ordination of caesium, and the tetraalkylammonium cations.

The wealth of homoatomic polyphosphorus structural elements in both metal polyphosphides and polyphosphanes has been the subject of recent reviews.[1–3] One of the most intriguing aspects of polyphosphorus chemistry is the similarity between molecular compounds like (organo-substituted)phosphanes and the solid-state phosphides; for example, the heptaphosphane(3) $\mathrm{P_7H_3}$[2] contains the same heptaphosphanortricyclane cage as $\mathrm{Ba_3P_{14}}$[4] or $\mathrm{Cs_3P_7}$.[5] Consequently, most attention given to solid polyphosphides by the chemical community has focused on these 'molecular' aspects of the phosphorus dumbbells, chains, cages and layers embedded in metal cation matrices. Thanks to von Schnering a second important aspect of polyphosphide chemistry has been recognised: its similarity to certain elements of co-ordination chemistry. According to von Schnering and Hönle,[1] 'the crystalline [polyphosphide] phases can already be seen as complexes, because definite assignments exist between the co-ordination of the metal atoms and the donor functions of the anions'. This is a matter of course for the phosphides of the transition metals, but still not universally accepted for the numerous binary polyphosphides of the alkali and alkaline-earth metals, which could also be seen as simple salts with polyatomic anions. Taking up von Schnering's interpretation, these phases should rather be regarded as complex three-dimensional networks formed by ion–ion and ion–dipole metal–phosphorus interactions between the homoatomic polyphosphorus structural elements and the metal cations. These interactions are, of course, neither very strong nor of high directionality, especially in phases of the alkali metals. Nevertheless, the existence of a number of molecular alkali metal–polyphosphide ion complexes which form upon dissolution of the binary phases provides some experimental support for von Schnering's interpretation. The solid-state structures of ion complexes like $[\mathrm{Rb(en)}]_3[\mathrm{P_7}]$ (en = ethane-1,2-diamine)[1] and $[\mathrm{Li(tmen)}]_3[\mathrm{P_7}]$ (tmen = $\mathrm{Me_2NCH_2CH_2NMe_2}$)[6] show isolated neutral alkali-metal heptaphosphides $\mathrm{M^I{}_3P_7}$ with the cations residing over the trapezoidal sides of the nortricyclane cage; the co-ordination of the cations is completed by the solvent molecules.

Very recently, structural intermediates with respect to dimensionality were found between the zero-dimensional ion complexes and the three-dimensional networks of the binary alkali-metal polyphosphides. One-dimensional $^1_\infty[\mathrm{RbP_7}]^{2-}$ chains and two-dimensional $^2_\infty[\mathrm{Cs_2P_{11}}]^-$ layers exist in $[\mathrm{NMe_4}]_2[\mathrm{RbP_7}]\cdot\mathrm{NH_3}$ and $[\mathrm{NEt_4}][\mathrm{Cs_2P_{11}}]$, which were synthesised by partial exchange of the alkali-metal cations for tetraalkylammonium cations in $\mathrm{Rb_3P_7}$ and $\mathrm{Cs_3P_{11}}$ in liquid ammonia.[7] Since these compounds are so far the sole examples for this type of 'low-dimensional alkali-metal polyphosphides', we set out to prepare some analogous compounds. We were especially interested to see whether the anionic alkali metal–polyphosphide 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.

Results

Slow interdiffusion of a suspension of $\mathrm{Cs_3P_7}$ with solutions of equimolar amounts of $[\mathrm{NEt_3Me}]\mathrm{Br}$ or $[\mathrm{NEt_4}]\mathrm{I}$ in liquid ammonia yielded transparent, pale yellow crystalline plates in the former and large, orange crystals like octahedra in the latter case. The crystals became opaque immediately upon removal of the solvent, regardless of whether this was done by filtration or by slow distillation at 233 K and reduced pressure. After removal of the solvent, both products were unstable at room temperature; even under strictly inert conditions they decomposed visibly to dark orange powders within a few minutes. Like nearly all polyphosphides with isolated cage anions,[1] the products were also highly reactive towards air and moisture. These properties rendered their characterisation much more difficult than that of $[\mathrm{NMe_4}]_2[\mathrm{RbP_7}]\cdot\mathrm{NH_3}$ and $[\mathrm{NEt_4}][\mathrm{Cs_2P_{11}}]$,[7] which were prepared by an analogous route, but could be handled under dry argon for some time without damage to the crystals or decomposition.

We were able to obtain a crystal structure analysis for both compounds by employing a technique which ensures temperatures below 223 K for all steps of the selection and preparation of the crystals.[8] The results confirmed the presence of ammonia of solvation in both products, as was strongly indicated by their behaviour upon the removal of the solvent. Equations (1) and (2) express the formation of the compounds (at −40 °C).

$$\mathrm{Cs_3P_7} + [\mathrm{NEt_3Me}]\mathrm{Br} + \mathrm{NH_3} \longrightarrow [\mathrm{NEt_3Me}][\mathrm{Cs_2P_7}]\cdot\mathrm{NH_3} + \mathrm{CsBr} \quad (1)$$

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† Heptaphosphatricyclo$[2.2.1.0^{2,6}]$heptane.

$$Cs_3P_7 + [NEt_4]I + 4NH_3 \longrightarrow [NEt_4][Cs_2P_7]\cdot 4NH_3 + CsI \quad (2)$$

Views of the structures of compounds **1** and **2** along their crystallographic *c* axes show corrugated $_\infty^2[Cs_2P_7]^-$ layers stacked along the *a* axes in both (Fig. 1). The caesium cations are co-ordinated almost exclusively by P atoms in **1**, and only one ammonia molecule of solvation is necessary to complete the co-ordination sphere of one of the two crystallographically inequivalent cations. In **2**, both the crystallographically inequivalent Cs are co-ordinated by two ammonia molecules each in addition to the P_7 cages. The layers are separated by the respective tetraalkylammonium cations. Fig. 2 provides a view of the $_\infty^2[Cs_2P_7]^-$ layers lying in the *bc* face of the unit cells of both compounds. Striking similarities are immediately apparent, which are also reflected by the similarity of the corresponding unit-cell parameters: b = 12.265(9), c = 16.59(1) Å in **1** and b = 13.023(2), c = 17.069(6) Å in **2**; the monoclinic angle β = 90.69(9)° in **1** is also close to the 90° angle in orthorhombic **2**. In fact, the $_\infty^2[Cs_2P_7]^-$ layers shown in Fig. 2 are generated by the same symmetry elements in both structures: **1** crystallises in space group $P12_1/c\,1$ (no. 14) with a 2_1 screw axis running parallel to *b* through $c = \frac{1}{4}$ and $c = \frac{3}{4}$, and a glide plane normal to the projection plane parallel to *c* cutting through $b = \frac{1}{4}$ and $b = \frac{3}{4}$ with a glide vector of $c/2$. The effects of the corresponding symmetry operations on the P_7 cage can easily be recognised in Fig. 2. The same symmetry elements are present in the $_\infty^2[Cs_2P_7]^-$ layer in the structure of **2**, which crystallises in the orthorhombic space group $P2_1/b2_1/c2_1/a$ (no. 61). Only the screw axis parallel to *b* and the glide plane parallel to *c* take effect in the generation of the layer from **2** depicted in Fig. 2, because the additional symmetry elements of the space group become effective only in connection with parts of the structure residing above or below this layer. The projections normal to the crystallographic *b* axis shown in Fig. 3 illustrate the different

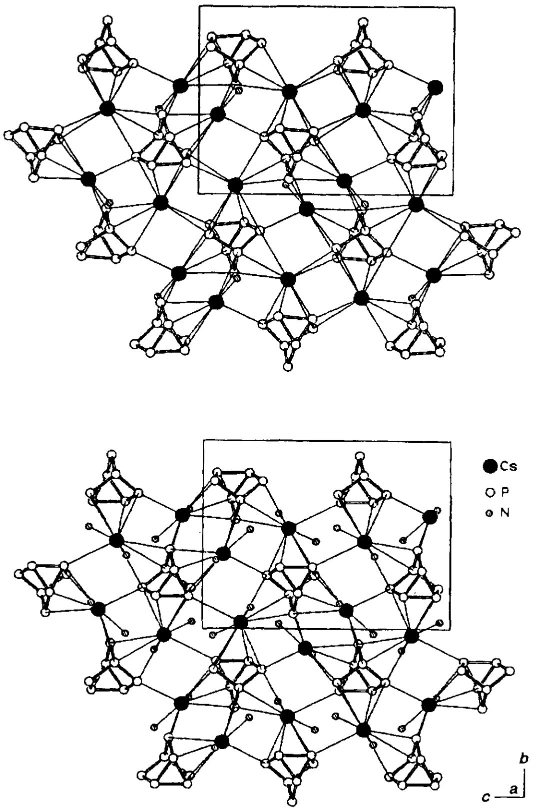

Fig. 2 View on the $_\infty^2[Cs_2P_7]^-$ layers in the *bc* faces of the unit cells of compounds **1** (top) and **2** (bottom)

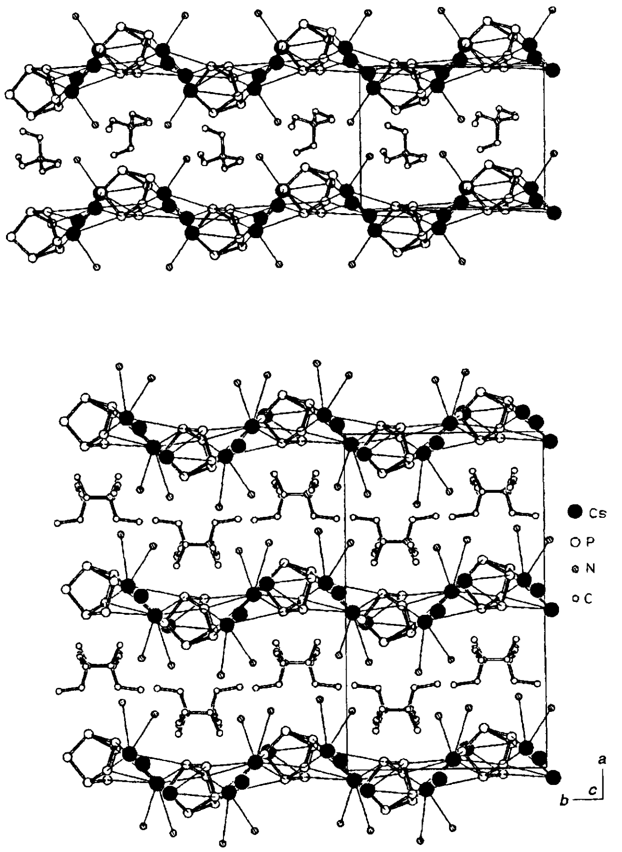

Fig. 1 Structures of compounds **1** (top) and **2** (bottom) projected on the *ab* plane

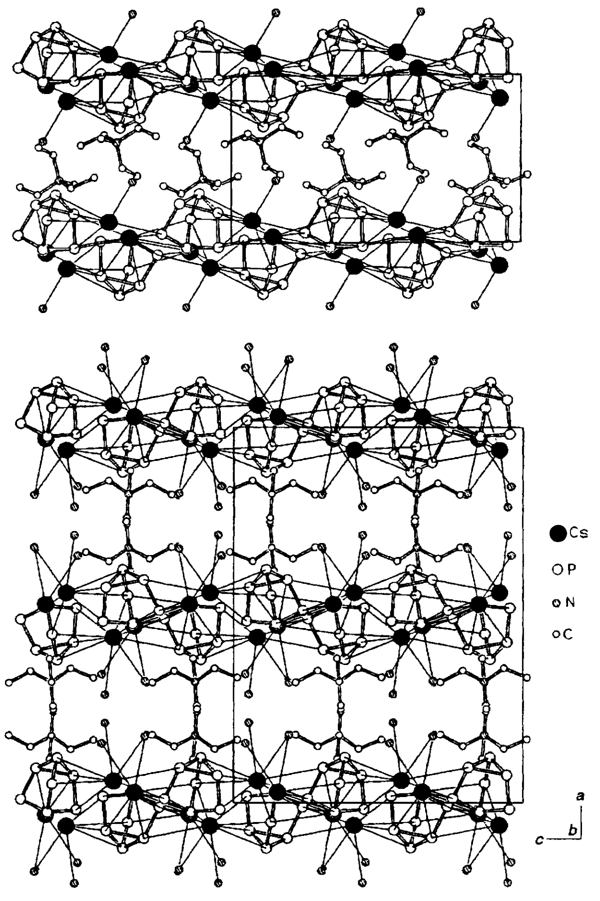

Fig. 3 Structures of compounds **1** (top) and **2** (bottom) projected on the *ac* plane

stacking modes of **1** and **2** which result from the additional symmetry elements in the structure of **2**. While the same layer is always repeated in **1**, corresponding to a stacking mode . . . AAA . . ., it is repeated every second layer in **2**, corresponding to a stacking mode . . . ABAB . . ., with B being a mirror image of A. Consequently, the unit-cell parameter *a* is approximately doubled for **2** [a = 22.378(4)] in comparison to **1** [a = 9.75(1) Å].

Fig. 4 allows a detailed inspection of the co-ordination spheres of the two crystallographically independent caesium cations in compound **1**. Atom Cs(1) has close contacts to nine P atoms from three P_7^{3-} cages, the corresponding Cs(1)–P distances range from 3.537 to 3.807 Å. The next closest distance after these initial nine is more than 15% larger [Cs(1) • • • P(1) 4.394 Å]. Atom Cs(2) is co-ordinated by seven P atoms from three P_7^{3-} cages and by one N atom of an ammonia molecule of solvation. The Cs–N(2) distance is 3.121 Å and the Cs–P distances range from 3.452 to 3.796 Å. The next closest Cs–P distance is 4.311 Å [Cs(2) • • • P(5)]. Both of the caesium cations reside over trapezoidal sides of the cage in an η^4-like co-ordination, which is very similar to the ion-pairing situation found in $[Rb(en)]_3[P_7]$.[1] There is, however, no significant distinction between the distances from the caesium cations to the P atoms of these cage sides and the distances to the P atoms of the other co-ordinating cages. Therefore, the interpretation of the Cs_2P_7 partial structure as a two-dimensional infinite $^2_\infty[Cs_2P_7]^-$ layer is clearly more appropriate. The Cs–P distances show a marked preference for the two-fold-linked P atoms as co-ordinating atoms; these are formally negatively charged and seem to have superior donor properties towards the caesium cations.

The endocyclic bond lengths and angles of the nortricyclane cage in compound **1** reveal small but significant deviations from ideal $3m$-C_{3v} symmetry. This distortion can be related to Cs-to-P interactions: the single P–P bond of the triangular P_3 base of the cage which is not bridged by a caesium ion is significantly shorter [P(5)–P(7) 2.262 Å] than its counterparts [P(5)–P(6) 2.283 and P(6)–P(7) 2.278 Å]. Another effect of the fact that only two of the three trapezoidal sides of the cage are capped by caesium cations is a smaller P(2)–P(1)–P(4) angle (100.6°) as compared to P(2)–P(1)–P(3) (102.1) and P(4)–P(1)–P(3) (102.9°). The height *h* of the cage, which has been used as a measure of the ionic character for the nortricyclane cage,[1] is 2.978 Å. The relative height *Q*, which was introduced in order to compare nortricyclane cages formed by different elements[1] is 1.309 with $Q = h/d_{m(\Delta)}$, $d_{m(\Delta)}$ = 2.274 Å being the average bond length in the P_3 base of the cage.

In Fig. 5 an ORTEP plot of the co-ordination spheres of the two crystallographically independent caesium cations in compound **2** is shown from the same viewing angle as for **1** in Fig. 4 in order to facilitate comparison of the two structures. The centres of gravity of the cage anions are farther apart in **2** (shortest distance 7.89 Å) than in **1** (shortest distance 7.70 Å) which leads to Cs–P distances in **2** that are generally larger than in **1**. Owing to the equivalent symmetry operations within the layers, Cs(1) is co-ordinated by the same P atoms in **2** as in **1**; the corresponding distances, however, range from 3.701 to 4.287 Å. The cut-off after the first co-ordination sphere is much less pronounced in **2**, the value for Cs(1)–P(1) (4.555 Å) being only 6% larger than 4.287 Å. The less tight co-ordination of Cs(1) by P atoms leaves room for two ammonia molecules of solvation co-ordinating to Cs(1) from below the layer (in Fig. 5). The Cs–N distances are short [Cs(1)–N(2) 3.53 and Cs(1)–N(5) 3.62 Å], but not nearly as short as the Cs(2)–N(2) distance in **1**. The phosphorus co-ordination sphere of Cs(2) in **2** is equivalent to that in **1** as well, with larger Cs–P distances except for Cs(2)–P(4^{I}), which is somewhat shorter in **2** than in **1** (3.533 *vs.* 3.599 Å). The N atoms of two ammonia molecules of solvation complete the co-ordination of Cs(2) from above the layer (in Fig. 5). Their distances to Cs(2) [Cs(2)–N(3) 3.62(1) and Cs(2)–N(4) 3.53(1) Å] are larger than the single Cs–N contact in **1** as well. Despite the generally larger Cs–P distances in **2** as compared to **1**, the distortion of the nortricyclane cage in **2** is equal to that in **1** within standard deviations. This is seen best by inspecting the bond lengths within the P_3 base of the cage: P(5)–P(7) 2.261 *vs.* P(5)–P(6) 2.282 and P(6)–P(7) 2.288 Å. The height of the cage is h = 2.996 Å, the relative height Q = 1.316.

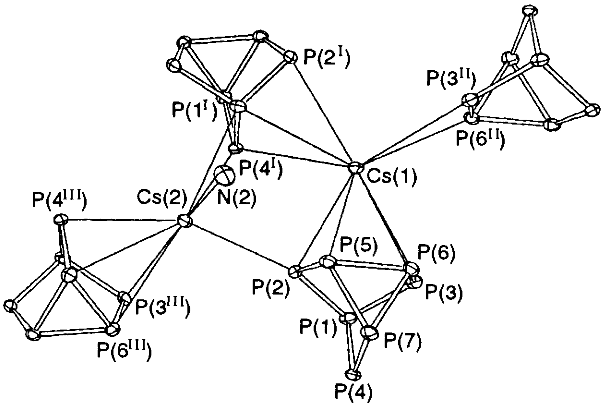

Fig. 4 An ORTEP[9] plot of the co-ordination of Cs(1) and Cs(2) in compound **1** (50% probability ellipsoids). Selected interatomic distances (Å): Cs(1)–P(2) 3.537(3), Cs(1)–P(3) 3.634(3), Cs(1)–P(2^{I}) 3.679(3), Cs(1)–P(4^{I}) 3.730(3), Cs(1)–P(5) 3.742(3), Cs(1)–P(6^{II}) 3.750(3), Cs(1)–P(1^{I}) 3.780(3), Cs(1)–P(6) 3.805(3), Cs(1)–P(3^{II}) 3.807(3), Cs(2)–N(2) 3.121(7), Cs(2)–P(2) 3.452(3), Cs(2)–P(4^{III}) 3.579(3), Cs(2)–P(3^{III}) 3.598(3), Cs(2)–P(4^{I}) 3.599(4), Cs(2)–P(1^{I}) 3.720(3), Cs(2)–P(7^{III}) 3.760(3), Cs(2)–P(6^{III}) 3.796(3), P(2)–P(5) 2.121(3), P(2)–P(1) 2.165(3), P(1)–P(4) 2.175(3), P(1)–P(3) 2.180(3), P(5)–P(7) 2.262(3), P(5)–P(6) 2.283(3), P(7)–P(4) 2.116(3), P(7)–P(6) 2.278(3) and P(6)–P(3) 2.126(3). Symmetry operations used to generate equivalent atoms: I $-x + 2, y + \frac{1}{2}, -z + \frac{3}{2}$; II $-x + 2, -y, -z + 1$; III $x, -y - \frac{1}{2}, z + \frac{1}{2}$

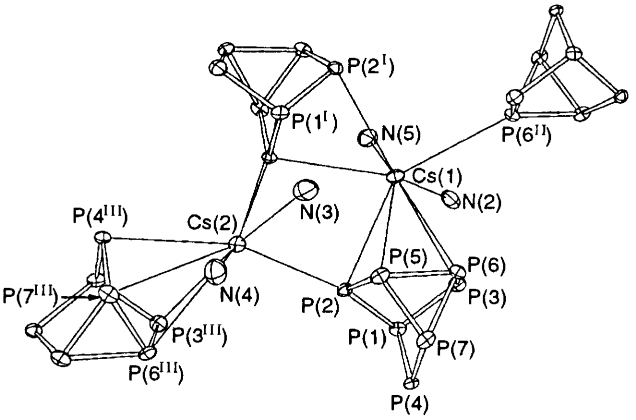

Fig. 5 An ORTEP plot of the co-ordination of Cs(1) and Cs(2) in compound **2** (50% probability ellipsoids). Selected interatomic distances (Å): Cs(1)–N(2) 3.534(13), Cs(1)–N(5) 3.62(2), Cs(1)–P(2) 3.701(3), Cs(1)–P(2^{I}) 3.725(3), Cs(1)–P(4^{I}) 3.738(3), Cs(1)–P(3) 3.752(3), Cs(1)–P(5) 3.889(3), Cs(1)–P(6) 3.902(3), Cs(1)–P(1^{I}) 4.063(3), Cs(1)–P(6^{II}) 4.137(3), Cs(1)–P(3^{II}) 4.287(3), Cs(2)–N(4^{III}) 3.526(12), Cs(2)–P(4^{I}) 3.533(3), Cs(2)–P(2) 3.538(3), Cs(2)–N(3^{III}) 3.619(13), Cs(2)–P(4^{III}) 3.666(3), Cs(2)–P(3^{III}) 3.673(3), Cs(2)–P(7^{III}) 3.784(3), Cs(2)–P(6^{III}) 3.799(3), Cs(2)–P(1^{I}) 3.978(3), P(3)–P(6) 2.120(4), P(3)–P(1) 2.179(4), P(2)–P(5) 2.125(4), P(2)–P(1) 2.176(4), P(4)–P(7) 2.115(4), P(4)–P(1) 2.180(4), P(6)–P(5) 2.282(5), P(6)–P(7) 2.288(4) and P(5)–P(7) 2.261(4). Symmetry operations used to generate equivalent atoms: I $-x, y + \frac{1}{2}, -z + \frac{3}{2}$; II $-x, -y, -z + 2$; III $x, -y - \frac{1}{2}, z - \frac{1}{2}$

Discussion

Our results suggest that there may be a positive answer to the question posed in ref. 7 and in the Introduction whether the novel low-dimensional alkali metal–polyphosphide substructures have an intrinsic tendency to form. Compounds **1** and **2** are only the third and fourth examples of this new type of compound which results from partial exchange of the metal cations in alkali-metal polyphosphides with tetraalkylammonium cations. The fact that the $^2_\infty[Cs_2P_7]^-$ layers in both new compounds have the same topology provides support for the assumption that an optimum arrangement exists at least for each two-dimensional alkali metal–polyphosphide substructure, which is adopted in the solid state even if differently sized tetraalkylammonium counter cations are present. For the sake of this argumentation it is particularly important to note that **1** and **2** are by no means isostructural, but crystallise in different space groups with completely differently arranged tetraalkylammonium cations, and that even the positioning of one $^2_\infty[Cs_2P_7]^-$ layer towards the next is dissimilar in the two structures, resulting in two different stacking modes. The ability of this type of compound to incorporate ammonia molecules of solvation seems to add flexibility, helping to accommodate the different tetraalkylammonium cations. Of course, only two compounds containing the same layer represent a very limited data set, and no further conclusions should be drawn until more data are available. Nevertheless, the fact that the $^2_\infty[Cs_2P_7]^-$ layer found in the present study survives the change of the tetraalkylammonium cation, the space group and the number of ammonia molecules of solvation without fundamental rearrangement provides further experimental support to von Schnering's thesis that definite correlations exist between the co-ordination of the metal cations and the donor functions of the polyphosphide anions, even for alkali-metal compounds.[1]

Another deficit of the present study with respect to the question discussed above is the limited scope concerning the tetraalkylammonium cations. The ions NEt_4^+ and NEt_3Me^+ differ by a single methylene group, which constitutes only a minor change in form and size of the quaternary cation. This is compensated to some extent by the completely dissimilar arrangement of these cations in the interlayer gaps (Figs. 1 and 3). Larger changes of the quaternary cations with respect to size while maintaining the integrity of the $^2_\infty[Cs_2P_7]^-$ layers are probably very difficult, because electroneutrality dictates a fixed P_7-to-cation ratio. Thus, an analogously composed compound with a very large quaternary cation like PPh_4^+ is likely to contain isolated $[Cs_2P_7]^-$ ion complexes, instead. The trend towards larger distances among the centres of gravity of the cage anions can be observed even for the small increase in quaternary cation size in going from **1** to **2**.

The slight distortion of the P_7^{3-} cage anions from ideal $3m$-C_{3v} symmetry, which can be related to the co-ordination of the cage by the metal cations, is in full agreement with previous findings for the compound $[NMe_4]_2[RbP_7]{\cdot}NH_3$, which contains $^1_\infty[RbP_7]^{2-}$ chains.[7] In this compound the bonds which are not bridged by rubidium cations are significantly shorter than their counterparts. Owing to the different composition, only one side of the nortricyclane cage is capped by rubidium cations, which causes an even larger difference in length between the capped bond (2.299 Å) and the other bonds within the triangular base of the cage (2.277 and 2.274 Å). Other effects on endocyclic bond lengths and angles caused by co-ordination are also more pronounced for the rubidium compound as compared to **1** and **2**; the differences tend to be levelled out in these structures because the P_7^{3-} cages are much more evenly surrounded by metal cations. Nevertheless, there is now a clear trend indicating that P–P bonds in polyphosphides which are bridged by alkali-metal cations are longer than any counterparts not involved in co-ordination.

The marked preference of the caesium cations for two-fold-linked P atoms as co-ordinating atoms, which is reflected by the fact that all of the shortest Cs–P distances involve such atoms, comes as a surprise, however. A similar phenomenon has not been observed for $[NMe_4]_2[RbP_7]{\cdot}NH_3$ or $[NEt_4][Cs_2P_{11}]$; in the latter compound none of the shortest Cs–P distances involved two-fold-linked P atoms.[7] This indiscriminate behaviour towards both types of P atoms belonging to the cage anions is consistent with the situation found in the binary alkali-metal hepta- and undeca-phosphides and in sharp contrast to the structures of molecular $M^I{}_3P_7$ compounds like $[Rb(en)]_3[P_7]$.[1] These findings made us believe that the metal-to-polyphosphide bonding situation in the novel low-dimensional alkali metal–polyphosphide substructures is more similar to the three-dimensionally extended binary phases than to the zero-dimensional ion complexes. However, the present findings indicate more incremental changes from one bonding situation to the other, with the compounds **1** and **2** being located between $[NMe_4]_2[RbP_7]{\cdot}NH_3$ or $[NEt_4][Cs_2P_{11}]$ and the molecular ion complexes which display a very tight ion-pairing interaction between the metal cations and the formally negatively charged two-fold-linked P atoms. These incremental changes seem to be related to the incorporation of solvent molecules which co-ordinate to the alkali-metal cations: in $[NMe_4]_2[RbP_7]{\cdot}NH_3$ and $[NEt_4][Cs_2P_{11}]$ the alkali-metal cations are completely surrounded by P atoms from the cage anions (as in the binary phases), while for **1** and **2** and of course for the molecular ion complexes, solvent molecules are necessary to complete the co-ordination of the metal cations. It is interesting that ammonia molecules of solvation which do not co-ordinate to the metal cations as in $[NMe_4]_2[RbP_7]{\cdot}NH_3$ or in $Cs_3As_7{\cdot}NH_3$[10] are far more difficult to remove than those in **1** or **2**, which tend to lose the ammonia of solvation even at low temperatures.

The elevation *h* of the apical P atom with respect to the P_3 base is a very sensitive parameter which reflects the transfer of electrons to the heptaphosphanortricyclane cage.[1] Neutral P_7 cages in P_7R_3 (R = $M^{IV}Me_3$ or $M^{IV}Ph_3$) have an average *h* of 3.15 Å, while P_7^{3-} in ionic compounds has an average *h* of 3.00 Å due to the electrostatic repulsion between the negatively charged P atoms. On going from Li_3P_7 to Cs_3P_7 an increase in electron transfer is indicated by a small decrease from h = 3.016 to 2.969 Å. The values for *h* observed in **1** (2.978 Å) and **2** (2.996 Å) fit into this concept very well. It is probable that a value of approximately 2.97 Å represents a lower limit due to the covalent forces maintaining bond lengths and angles.

Although the interactions between alkali-metal cations and polyphosphide anions are not very strong and of low directionality (when compared for example to transition-metal complexes), there is now evidence that there exists indeed a co-ordination chemistry between those cations and polyphosphide 'ligands'. This provides further support for von Schnering's view of the binary alkali-metal polyphosphides as three-dimensionally extended complexes. The novel alkali metal–polyphosphide substructures link the binary polyphosphides to the molecular ion complexes, and may be seen as intermediates with respect to structural dimensionality in an imaginary process of increasing separation of the network of the binary phases. There is experimental evidence that an ammoniate $Cs_3P_7{\cdot}3NH_3$ exists which would represent a further intermediate of this process.[11]

Experimental

All manipulations were carried out under dry argon in all-glass reaction and handling vessels which 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. Ethyltrimethylammonium bromide and tetraethylammonium iodide (Aldrich) were dried *in vacuo* at 333 K for 2 d. The compound Cs_3P_7 was synthesised from the elements in a sealed glass ampoule according to the procedure given in the literature.[1] **CAUTION**: these reactions are highly exothermic and serious explosions occur upon improper handling! Red phosphorus was obtained from Hoechst ('electronic grade'), caesium by reduction of the chlorides with calcium[12] and purification by double distillation *in vacuo*. Elemental analyses were performed by the microanalytical laboratory of the institute.

General preparative procedure for [NEt$_3$Me][Cs$_2$P$_7$]·NH$_3$ 1 and [NEt$_4$][Cs$_2$P$_7$]·4NH$_3$ 2

Into a U-shaped reaction vessel fitted with a glass frit (porosity 3) separating the two sides, Cs$_3$P$_7$ (0.250 g, 4.06×10^{-4} mol) and an equimolar amount of the respective tetraalkylammonium halogenide were placed into opposing sides. Ammonia (*ca.* 30 cm^3) was frozen into the vessel at 77 K. The vessel was allowed to warm slowly to 233 K. The reactions were completed after 2 weeks for compound **1** and after 4 weeks for **2** at 233 K. Upon removal of the solvent the compounds apparently lose the ammonia of solvation; the transparent, crystalline products turn into amorphous powders. Speed and temperatures preferably below 273 K are essential in subsequent handling of the products; they were transferred to and stored in sealed glass ampoules under argon at 193 K. The elemental analysis was performed on the product **2** without ammonia of solvation (Found: C, 15.50; H, 3.75; Cs, 41.10; N, 1.95. Calc. for $C_8H_{20}Cs_2NP_7$: C, 15.70; H, 3.30; Cs, 43.35; N, 2.30%). Owing to the extreme sensitivity of **1** after the removal of the solvent, no elemental analysis could be performed.

For the crystal preparation we adapted the technique described by Kottke and Stalke[8] to our needs. Small amounts of the reaction products 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 nitrogen. Single crystals suitable for a structure analysis were selected with the help of a microscope and picked up on the tip of a capillary mounted on a goniometer head. They were then immediately submerged in liquid nitrogen, and transferred to the diffractometer.

Crystallography

Crystal data and structure refinement for compound 1. $C_7H_{21}Cs_2N_2P_7$, $M = 615.87$, yellow plates, monoclinic, space group $P2_1/c$ (no. 14), $a = 9.75(1)$, $b = 12.265(9)$, $c = 16.59(1)$ Å, $\beta = 90.69(9)°$, $U = 1983(3)$ Å^3, $Z = 4$, $D_c = 2.063$ g cm^{-3}, μ(Mo-Kα) = 4.23 mm^{-1}, $F(000) = 1168$. 8168 Reflections measured, 3875 independent ($R_{int} = 0.092$), 3670 observed [$I > 2\sigma(I)$], 177 parameters, six restraints.

The lattice parameters were determined by a CAD4 indexing program and refined by a least-squares routine with the angular settings of 25 reflections ($14 < \theta < 21°$). Data were collected on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å) at 123(2) K to $\theta_{max} = 26°$ by using ω–BPB (background-peak-background) scans. Three intensity control reflections were measured every hour, showing no decay. Intensity data were corrected for Lorentz-polarisation and absorption effects (ψ scans, nine reflections). The structure was solved by direct methods (SHELXS 86[13]) and refined on F^2 using all 3875 independent reflections (SHELXL 93[14]). The hydrogen atoms of the triethylmethylammonium cation were inserted at calculated positions and not refined. Those of the ammonia molecule of solvation were located by Fourier-difference synthesis; all N–H and H···H distances were restrained to be equal. Hydrogen atoms of the ammonia molecule were refined isotropically, all other atoms anisotropically. The final $wR2$ value was 0.174 [corresponds to a conventional R value of 0.064 using only reflections with $I > 2\sigma(I)$]. The largest peak and hole in the final Fourier-difference map were 2.53 (in the vicinity of the Cs$^+$) and −5.01 e Å^{-3} respectively. Final atom coordinates are given in Table 1.

Table 1 Atomic coordinates (× 10^4) for compounds **1** and **2**

Atom	x	y	z
[NEt$_3$Me][Cs$_2$P$_7$]·NH$_3$ **1**			
Cs(1)	9 578(1)	483(1)	6 444(1)
Cs(2)	11 387(1)	−755(1)	9 267(1)
P(2)	10 628(2)	−1 941(1)	7 428(1)
P(1)	9 782(2)	−3 092(1)	6 566(1)
P(5)	12 438(2)	−1 498(1)	6 811(1)
P(7)	13 021(2)	−3 015(1)	6 120(1)
P(6)	11 875(2)	−1 643(1)	5 476(1)
P(4)	11 518(2)	−4 186(1)	6 424(1)
P(3)	9 790(2)	−2 152(1)	5 451(1)
N(1)	6 110(5)	−2 485(5)	4 000(3)
N(2)	13 771(6)	507(5)	8 444(4)
C(1)	4 045(7)	3 734(6)	9 768(4)
C(2)	6 952(6)	−2 417(6)	8 244(4)
C(3)	14 577(6)	−2 546(6)	8 809(4)
C(4)	6 493(6)	−1 593(6)	7 633(4)
C(5)	6 573(6)	−1 465(6)	4 426(4)
C(6)	6 372(7)	−1 541(6)	9 523(4)
C(7)	5 862(7)	1 532(6)	6 704(4)
[NEt$_4$][Cs$_2$P$_7$]·4NH$_3$ **2**			
Cs(1)	289(1)	348(1)	8 460(1)
Cs(2)	−594(1)	−1 012(1)	5 821(1)
P(3)	177(1)	−2 158(2)	9 534(2)
P(2)	−111(1)	−2 162(2)	7 589(2)
P(4)	−513(1)	−4 193(2)	8 682(2)
P(1)	238(1)	−3 151(2)	8 510(2)
P(6)	−732(1)	−1 720(2)	9 433(2)
P(5)	−932(1)	−1 731(2)	8 122(2)
P(7)	1 196(1)	−3 096(2)	8 864(2)
N(1)	−1 780(3)	3 104(6)	8 668(5)
N(2)	1 565(5)	−351(9)	9 556(7)
N(3)	−1 761(5)	−5 274(9)	11 913(7)
N(4)	−2 141(5)	−3 639(10)	10 529(7)
N(5)	1 806(7)	1 155(10)	8 060(8)
C(1)	−2 578(4)	−1 575(8)	8 720(7)
C(2)	−3 219(4)	−3 066(8)	8 675(7)
C(3)	1 425(4)	−3 524(8)	10 661(7)
C(4)	−1 491(5)	3 506(8)	7 918(7)
C(5)	−2 480(5)	−4 573(9)	13 739(8)
C(6)	−1 159(4)	1 441(9)	8 584(6)
C(7)	1 666(6)	−3 297(9)	9 866(7)
C(8)	−1 792(6)	−8 189(10)	12 170(8)

Crystal data and structure refinement for compound 2. $C_8H_{32}Cs_2N_5P_7$, $M = 681.00$, yellow plate, orthorhombic, space group $Pbca$ (no. 61), $a = 22.378(4)$, $b = 13.023(2)$, $c = 17.069(6)$ Å, $U = 4974(2)$ Å^3, $Z = 8$, $D_c = 1.82$ g cm^{-3}, μ(Mo-Kα) = 3.384 mm^{-1}, $F(000) = 2640$. 6854 Reflections measured, 3457 independent ($R_{int} = 0.063$), 2668 observed [$I > 2\sigma(I)$], 240 parameters, 132 restraints.

The lattice parameters were determined as for compound **1** except that ($12 < \theta < 19°$). Diffraction data were collected to $\theta_{max} = 23°$. Three intensity control reflections measured every hour showed a total decay of 2.0%. Intensity data were corrected for linear isotropic decay and Lorentz-polarisation effects. The crystal was lost before ψ scans could be collected; the DIFABS procedure by Walker and Stuart[15] was used for the correction of absorption effects. The structure was refined on F^2 using all 3457 independent reflections as for **1**. The hydrogen atoms of the tetraethylammonium cation were inserted at calculated positions and not refined. Those of the ammonia molecules were located and treated as for those of **1**. The final $wR2$ value was 0.159 [corresponds to a conventional R value of 0.059 using only reflections with $I > 2\sigma(I)$]; the value before DIFABS correction was 0.22. The largest peak and hole in the final Fourier-difference map were 2.49 (in the vicinity of the caesium cation) and −2.15 e Å^{-3} respectively. Final atom coordinates are given in Table 1.

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

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