No aromaticity of P_6^{4-} observed *via* solid state ^{31}P-NMR spectroscopy†

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The solid state NMR spectra of the binary alkali hexaphosphides Rb_4P_6 and Cs_4P_6 unambiguously show the P_6^{4-} anion not to be aromatic.

Among the numerous alkali and alkaline earth metal polyphosphides,[1] the extremely air and moisture sensitive alkali metal hexaphosphides M_4P_6 (M = K, Rb, Cs) are rather unusual because some multiple P–P bonding has to be taken into account to explain the electron distribution in the planar, almost perfectly hexagonal P_6^{4-} anions. Given the obvious similarities to the benzene molecule, the anion has been suspected to show aromaticity[2–4] like P_5^{-} [5,6] or the newly discovered P_4^{2-}.[7,8] Specifically, one double bond and four of the ten lone pairs of P_4^{6-} would result in a 10π aromatic system according to Hückels rule.[9–11] Recently, it has also been shown that the hexaphosphides are interesting starting materials for the synthesis of a variety of poly- and hydrogenpolyphosphides in liquid ammonia as they disproportionate readily.[12] Thus, the hexaphosphide anions only seem to be stable and isolable as the binary solids which crystallize in space group *Fmmm* as putatively semi-conducting black solids with green–purple luster.[2] Two crystallographically non-equivalent phosphorus atoms in the asymmetric unit occupy the 8*h* and 16*m* Wyckoff positions which results in D_{2h} point group symmetry for the P_6^{4-} anions with P–P bond lengths between 2.14 and 2.16 Å. The P–M (M = K, Rb, Cs) distances for the first coordination sphere are in the range of 3.35 to 3.46 for M = K, 3.46 to 3.62 Å for M = Rb and 3.57 to 3.78 Å for M = Cs, and all M–M distances are larger than 4 Å.[2,13–15] The compounds may thus be seen as ionic. As we have shown recently, delocalization of electrons in a polyphosphide may not be infered from the P–P distances only,[7,8,12] since the P–P bonds of the triangular base to the formally negative charged phosphorus atoms in P_7^{3-} are also only 2.14 Å long on average and were shown to be essentially single bonds.[12] Also, the P_6^{4-} anion is preparable in some organometallic complexes.[16–22] So far any attempts to observe the P_6^{4-} anion in solution or in a crystal outside its highly coordinated environment of the M_4P_6 phases (Fig. 1) or organometallic complexes have failed. An assignment of a singlet to P_6^{4-} in ^{31}P-NMR spectra of the M_4P_6 species dissolved in en[2] was shown to be in error, and we reassigned this singlet to the lone pair aromatic cyclotetraphosphide anion P_4^{2-}.[7,8,12,23–25] Surprisingly, we recently succeeded in obtaining an ammoniate of the cyclohexaarsenide anion As_6^{4-} from the isotypic binary alkali hexaarsenides M_4As_6 (M = Rb, Cs) in a chair-like conformation. Because this finding indicates the presence of free As_6^{4-} in solution, we also addressed the potential structures of the free P_6^{4-} anion in *ab initio* calculations which showed it not to be planar and not 10π aromatic.[24,25] Since the crystallographically determined symmetry is only an averaged one, we used the solid state NMR experiment to determine the local symmetry of the P_6^{4-} moiety in Rb_4P_6 and Cs_4P_6. More important, no experimental chemical shifts for the difficult to prepare hexaphosphides were available and thus no experimental data for its putative aromaticity were on-hand.

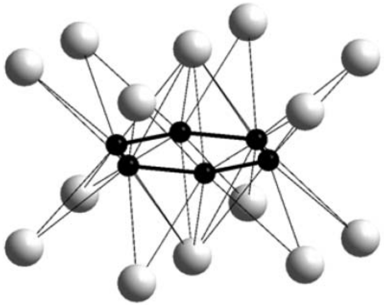

Fig. 1 Coordination of the P_6^{4-} anion in Cs_4P_6.

As can be seen from the ^{31}P-MAS-NMR spectrum of Rb_4P_6 at 13 kHz and 300 K (Fig. 2), there are two signals in a 2 : 1 ratio at −54.9 ppm (chemical shift anisotropy, csa = −548 ppm, η = 0.27, full width at half maximum 0.8 kHz) and −68.1 ppm (csa = −533 ppm, η = 0.25, full width at half maximum 1.0 kHz). This confirms the crystallographic symmetry and clearly shows no low field shifts, which would be expected for aromatic species like the P_5^{-} and the P_4^{2-} anions with 470 ppm (NaP_5 in THF at 25 °C)[5,6] and 349 ppm (−35 °C, Cs_2P_4 in liquid ammonia solution),[7,8] respectively. In the ^{31}P-MAS-NMR spectrum of Cs_4P_6 (Fig. 3), also recorded at 13 kHz and 300 K, there is just one signal at −19.4 ppm (csa = −536 ppm, η = 0.30). However, the signal is very broad with a full width at half maximum of about 1.5 kHz. From this fact and also from the shape of the signal, one might suspect actually two unresolved signals but further measurements at higher spinning frequencies did not improve the resolution of the signals. Nevertheless, a chemical shift of −19.4 ppm does not render this system aromatic, either.

Despite the similarities to the other planar polyphosphide ring anions and despite the obvious difficulty to explain the electronic structure with a single Lewis formula, the concept of aromaticity cannot be used to explain the nature of P_6^{4-} in the binary alkali metal hexaphosphides.

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† Dedicated to Professor Hans Hartl on the occasion of his 65th birthday.

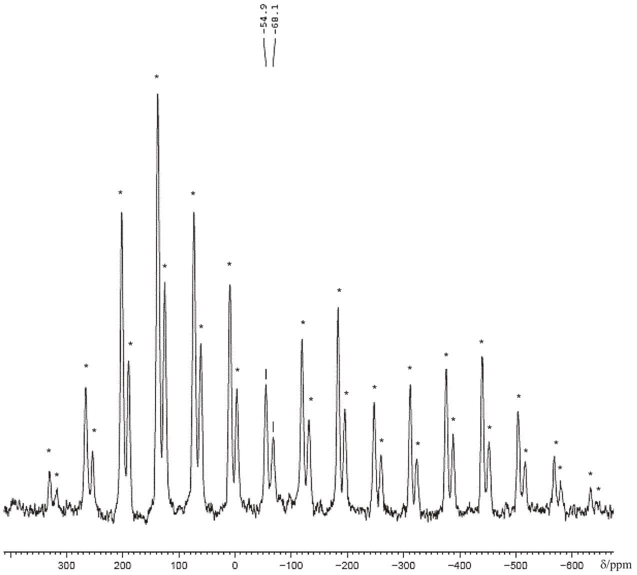

Fig. 2 ^{31}P-MAS-NMR spectrum of Rb_4P_6 at 13 kHz spinning frequency and 300 K. Spinning sidebands are marked by asterisks.

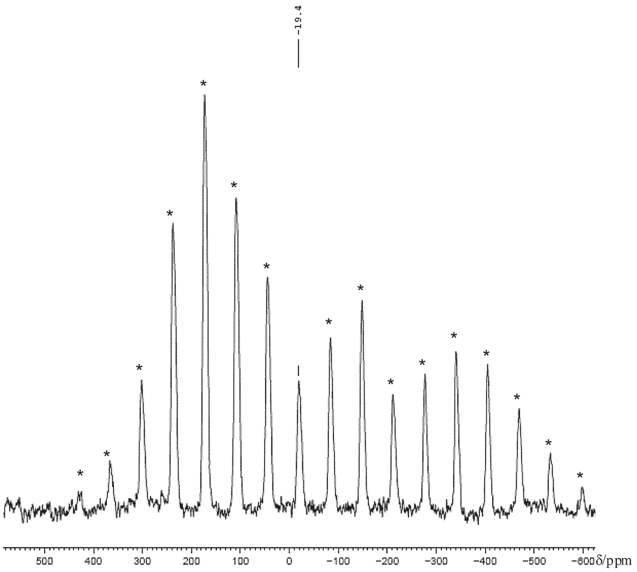

Fig. 3 ^{31}P-MAS-NMR spectrum of Cs_4P_6 at 13 kHz spinning frequency and 300 K. Spinning sidebands are marked by asterisks.

The alkali hexaphosphides M_4P_6 (M = Rb, Cs) were prepared according to procedures described in the literature from electrograde phosphorus (99.9999%, Hoechst) and distilled rubidium or caesium, respectively.[2,14,15] No other crystalline phases were detected *via* X-ray powder diffraction in glass capillaries with 0.5 mm diameter (Stoe Stadi P, germanium-monochromatized CuK$_\alpha$ radiation with $\lambda = 1.540598$ Å at room temperature). Due to heavy absorption of the X-ray beam in the case of the caesium compound, it was diluted with dried glass powder in the ratio of 1 : 10 for the powder diffraction experiment only. In the course of the solid state NMR experiment, no indications for amorphous phosphorus-containing impurities were encountered.

The ^{31}P-MAS-NMR experiments were carried out on a BRUKER Avance DSX spectrometer equipped with a commercial 4 mm MAS-NMR triple-resonance probe. The magnetic field strength was 11.75 T corresponding to a ^{31}P resonance frequency of 202.54 MHz. All spectra were acquired using a single pulse excitation. A commercially available pneumatic control unit was used to limit MAS frequency variations to a 2 Hz interval for the duration of the experiment. Samples were spun at 13 kHz. The chemical shift values given refer to 85% phosphoric acid as the external chemical shift reference. The chemical shift values refer to a deshielding scale. The repetition rate of the experiments is 64 s. 16 Transients per ^{31}P spectrum were accumulated. Simulations of the chemical shift parameters were done by minimizing the squared difference between experiment and simulation using the SIMPSON MINUIT routines and the same chemical shift conventions as in SIMPSON.[26,27]

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