

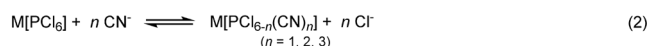
Tetracyanido(difluorido)phosphates $M^+[PF_2(CN)_4]^{-**}$

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Abstract: The systematic study of the reaction of $M[PF_6]$ salts and Me_3SiCN led to a synthetic method for the synthesis and isolation of a series of salts containing the unprecedented $[PF_2(CN)_4]^-$ ion in good yields. The reaction temperature, pressure, and stoichiometry were optimized. The crystal structures of $M[PF_2(CN)_4]$ ($M=[nBu_4N]^+$, Ag^+ , K^+ , Li^+ , $H_5O_2^+$) were determined. X-ray crystallography showed the exclusive formation of the cis isomer in accord with ^{31}P and ^{19}F solution NMR spectroscopy data. Starting with the $K[PF_2(CN)_4]$ the room temperature ionic liquid EMIm- $[PF_2(CN)_4]$ was prepared exhibiting a rather low viscosity.

In the quest for new materials with improved properties, salts containing robust weakly coordinating anions are of general interest. Such anions can be used in ionic liquids (ILs),^[1–6] in electrolytes,^[2,7–12] for the stabilization of unusual cations,^[10,11,13] or transient species.^[3] One major activity in designing new robust anions focusses on the synthesis of cyanide-based anions and their utilization in ILs.^[4,14–26] Salts bearing the tetracyanidoborate anion, $[B(CN)_4]^-$, were first obtained by Willner et al. in the reaction of $[Bu_4N]X$, BX_3 ($X=Br, Cl$) and KCN in toluene.^[27] A more efficient synthesis for tetracyanidoborates on a larger scale starting from the readily available reagents $K[BF_4]$, $LiCl$, and KCN was published by the same group in 2003^[23] along with studies of the thermal behavior of the mixed cyanidofluoridoborates, $K[BF_n(CN)_{4-n}]$ ($n=1–3$). ILs containing the $[B(CN)_4]^-$ ion are used in electrochemical applications (e.g. solar cells and batteries).^[28] Owing to the laborious synthesis, making use of huge amounts of lithium chloride in a sinter process producing large amounts of waste, there was a need for alternatives to cyanidoborate derivatives (e.g. cyanido-(fluorido)phosphates) or more efficient routes to tetracyanidoborates. As early as 1930, it was attempted to prepare

phosphorus(V) cyanides (e.g. $P(CN)_5$) in the reaction of $P(CN)_3$ with $(CN)_2$ by Gall and Schüppen.^[29] They proposed the in situ generation of $P(CN)_5$, which, however, decomposed rapidly at standard conditions [Scheme 1, Eq. (1)]. In



Scheme 1. Synthesis of $P^V(CN)_5$ and cyanido(chlorido)phosphates.

a series of publications, the preparation of salts bearing cyanido(chlorido)phosphate ions of the type $[PCl_{6-n}(CN)_n]^-$ ($n=1–3$) were described, but none of these salts was fully characterized.^[30,31] The hitherto published syntheses started from PCl_6^- salts (or from PCl_6^- salts in situ generated from PCl_5 and MCl ; $M=R_4N^+$, $R=nBu, Et$) utilizing cyanido-chlorido exchange agents, such as $AgCN$ or KCN [Scheme 1, Eq. (2)].

In 1980 Chevrier et al. reported solution ^{19}F NMR spectroscopy data of the $[PF_5CN]^-$ ion. Shortly thereafter, Dillon et al. published ^{31}P NMR data of reaction mixtures containing $[PF_{6-n}(CN)_n]^-$ ($1 \leq n \leq 4$) und $[PF_3Cl_{3-n}(CN)_n]^-$ ($1 \leq n \leq 3$).^[32,33] These reaction mixtures had been generated by treating PF_5 with $[Et_4N]CN$ and $[PCl_4(CN)_2]^-$ with AgF , respectively. Only recently, BMIm $[PF_3(CN)_3]$ was obtained by the reaction of BMIm $[PCl_3(CN)_3]$ and $Ag[BF_4]$ after 4 days of reaction time (BMIm = 1-butyl-3-methylimidazolium).^[34] To our knowledge salts bearing simple CN-functionalized phosphates of the type $[PF_2(CN)_4]^-$ have not been isolated and fully characterized to date. Herein, we describe facile large-scale syntheses of a series of salts bearing the $[PF_2(CN)_4]^-$ ion, which can easily be transformed into room temperature ILs by salt metathesis reaction.

$[nBu_4N][PF_2(CN)_4]$ (**1**) could easily be obtained in the reaction of $[nBu_4N][PF_6]$ with an excess of Me_3SiCN under autogenous pressure in a steel autoclave at high temperatures [180–210 °C, Equation (3)].^[35] As summarized in Table S8 (see the Supporting Information), the best conditions to isolated almost pure **1** in 40 % yield were 10 equivalents of Me_3SiCN at 200 °C for 16–18 h. When the excess of Me_3SiCN was decreased to 8 equivalents the yield of isolated product dropped to 33 % (and more impurities, such as $[PF_{6-n}(CN)_n]^-$ species, appeared), whereas raising the excess to above 10 equivalents did not lead to a higher yield. But it should be noted that an increase of the excess of Me_3SiCN up to 20 equivalents already gave small quantities of $[PF(CN)_5]^-$, which was detected by $^{19}F/^{31}P$ NMR spectroscopy (Supporting Information). Increasing the reaction temperature above 200 °C led to the polymerization of Me_3SiCN and decomposition of the product as indicated by the formation of

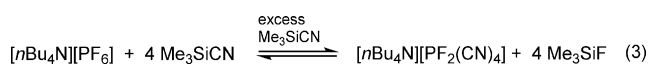
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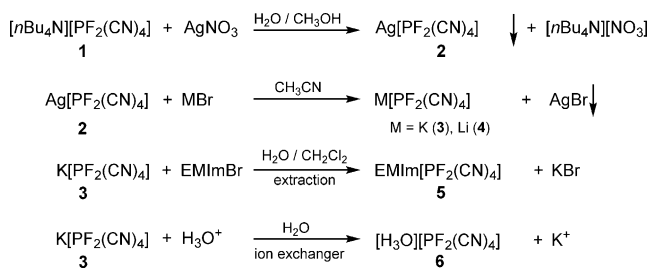
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a highly viscous black oil. The analogous reaction using $K[PF_6]$ instead of $[nBu_4N][PF_6]$ yielded only a mixture of different $K[PF_{6-n}(CN)_n]$ ($n = 0, 1, 2$, and 3) species. All these optimizing experiments were carried out with rather small amounts of PF_6^- salt (450 mg, 1.16 mmol); a scale-up was carried out with the 20-fold amount (9.52 g, 24.57 mmol). In this scale-up experiment the temperature and pressure were monitored as a function of the time. The temperature was almost constant after heating up to 200 °C within 30 min (199–205 °C), no hot spots could be detected. The pressure steadily increased during heating phase finally reaching a maximum pressure of 13 bar, which decreased in the course of the reaction to 10 bar. The work-up was accomplished by the decomposition of remaining free cyanide by H_2O_2 and subsequent extraction with acetonitrile. The solid brown raw product was recrystallized from ethanol to obtain 5.93 g (58 %, 14.27 mmol) of **1** as a light beige crystalline substance (m.p.: 64–66 °C). As shown by X-ray structure elucidation and $^{19}F/^{31}P$ NMR experiments, the *cis* isomer is exclusively formed in the course of the reaction. Compound **1** is thermally stable up to 315 °C, dissolves in acetonitrile, THF, and ethanol but is almost insoluble in water and hexane. With diethyl ether and toluene, the formation of a two-phase system is observed at room temperature.



With **1** as the starting material, subsequent cation-exchange reactions (Scheme 2) gave in good yields (80–90 %) monocationic salts of the *cis*- $[PF_2(CN)_4]^-$ anion with



Scheme 2. Cation-exchange reactions of $[PF_2(CN)_4]^-$ salts (*cis* isomer).

Ag^+ (**2**), K^+ (**3**), Li^+ (**4**), H_3O^+ (**6**)/ $H_5O_2^+$ (**6**- H_2O), and $EMIm^+$ (**5**). Selected properties of salts **1–6** are summarized in Table 1. All the salts are thermally stable up to well over 100 °C (117–334 °C). The white silver salt **2** is almost insoluble in Et_2O , $MeOH$, and acetone but dissolves well in CH_3CN . Colorless crystals of potassium salt **3** and lithium salt **4** easily dissolve in water (the lithium salt is extremely hygroscopic) and organic solvents, such as CH_3CN and $EtOH$, but are almost insoluble in Et_2O . 1-Ethyl-3-methylimidazolium ($EMIm$) salt **5** is a room temperature IL (m.p.: –32 °C) with a fairly low viscosity of 21 mPas (cf. $EMIm[B(CN)_4]$: 21 mPas)^[28] making this IL a rather interesting compound for application, for example, as an electrolyte for dye-

Table 1: Properties of $M[PF_2(CN)_4]$ salts along with selected structural parameters.

M	<i>n</i> Bu ₄ N	Ag	K	Li	H ₃ O ^[c]	EMIm
m.p. [°C]	64–66	–	229	–	–	–32
<i>T</i> _{dec.} [°C]	316	184	250	334	117	201
<i>v</i> _{CN} ^[d]	2202	2235	2212 br	2226 br	2229	2202
	2193	2219	–	–	2218	2195
C–N ^[a] [Å]	1.18(1)	1.135(8)	1.142(1)	1.142(3)	1.135(5)	–
C–N ^[a] [Å]	1.16(2)	1.134(8)	1.142(1)	1.142(3)	1.133(5)	–
C–N ^[b] [Å]	1.129(6)	1.140(5)	1.142(1)	1.142(3)	1.139(5)	–
C–N ^[b] [Å]	1.152(5)	1.140(5)	1.142(1)	1.142(3)	1.133(5)	–
P–F [Å]	1.591(2)	1.586(3)	1.6032(6)	1.5880(9)	1.583(3)	–
P–F [Å]	1.603(2)	1.586(3)	1.6032(6)	1.5880(9)	1.588(2)	–

[a] With a *trans* CN group. [b] With a *trans* F atom. [c] Upon drying in vacuum, one water molecule can be removed from **6**- H_2O at room temperature yielding the H_3O^+ salt. [d] CN stretching modes from IR/ATR spectra (wavenumbers in cm^{-1}).

sensitized solar cells. IL **5** is immiscible with water, Et_2O , toluene, or *n*-hexane forming a two-phase system. However, **5** mixes well with CH_2Cl_2 , acetone, CH_3CN , THF, or alcohols.

The solution (CD_3CN) ^{19}F NMR data of all the $[PF_2(CN)_4]^-$ salts show a doublet at $\delta = -6.1$ ppm with a coupling constant $^1J(^{19}F-^{31}P) = 730$ Hz. In the ^{31}P NMR spectrum a triplet at $\delta = -263.7$ ppm with $^1J(^{31}P-^{19}F) = 730$ Hz is observed. A comprehensive summary of all the experimentally determined and computed NMR data of $[PF_{6-n}(CN)_n]^-$ ($n = 0–6$) species can be found in the Supporting Information (Table S10). The computed IR spectrum of the $[PF_2(CN)_4]^-$ ion has four different CN stretching modes, two in-phase ($\nu_{CN,ip}$) and two out-of-phase ($\nu_{CN,op}$) modes in the expected region 2235–2193 cm^{-1} of which only two can be observed in the IR/Raman spectra. The smallest wavenumbers of $\nu_{CN,ip}$ and $\nu_{CN,op}$, respectively, are found for the *n*Bu₄N⁺ and $EMIm^+$ salts with values (Table 1), that differ little, clearly indicating very weak cation–anion interactions. As previously shown, coordination of Lewis acidic centers to a CN species causes a significant band shift to higher wavenumbers.^[36] Since the highest wavenumber ($\Delta\nu_{CN} = 33$ cm^{-1} with respect to **1**) is observed for the silver salt **2**, the strongest interaction with CN groups can be assumed. The shift to higher wavenumbers also correlates with a slightly smaller (averaged) C–N distance (Table 1, see below), which decreases along the series $Ag^+ \approx H_5O_2^+ < Li^+ \approx K^+ < nBu_4N^+$. The structures of $M[PF_2(CN)_4]$ ($M = nBu_4N$, Ag, Li, K, H_5O_2) were determined. Selected molecular parameters are listed in Table 1.

All structure determinations unequivocally confirm the presence of almost C_{2v} symmetrical *cis*- $[PF_2(CN)_4]^-$ anions (Figure 1) featuring a hexacoordinate phosphorus atom surrounded by four cyanido and two fluoro ligands with bond angles close to 90 and 180°. Interestingly, two shorter (1.83–1.85 Å for the *trans* cyanido groups) and two slightly longer P–C bond lengths (1.85–1.87 Å, cf. $\Sigma r_{cov}(P-C) = 1.86$ Å,^[37] for the *cis* cyanido ligands) are always determined. The P–F bond lengths are found in the typical range (1.586–1.603 Å) of P–F single bonds ($[Me_4N][PF_6]$: 1.568–1.592 Å).^[38] $[nBu_4N][PF_2(CN)_4]$ crystallizes in the triclinic

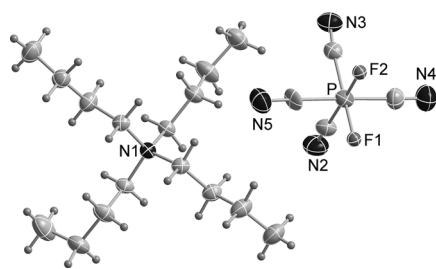


Figure 1. ORTEP drawing of the molecular structure of the ion pair in $[n\text{Bu}_4\text{N}][\text{PF}_2(\text{CN})_4]$. Thermal ellipsoids set at 50% probability at 173 K.

space group $P\bar{1}$ with two formula units per cell. The structure consists of separated ions with no significant cation⋯anion contacts as expected for a weakly coordinating cation.

Since the $[\text{PF}_2(\text{CN})_4]^-$ ion is capable of coordinating either by all six ligands (2F^- and 4CN^-) or only four ligands to Lewis acidic centers, it was of interest to crystallize the metal salts (Ag, Li, K) as well as an oxonium salt. Interestingly, the Ag and Li salts crystallized isotypically in the space group $Pbcm$ featuring exclusively cyanide complexation with tetrahedral coordination around the metal ions (Figure 2), while

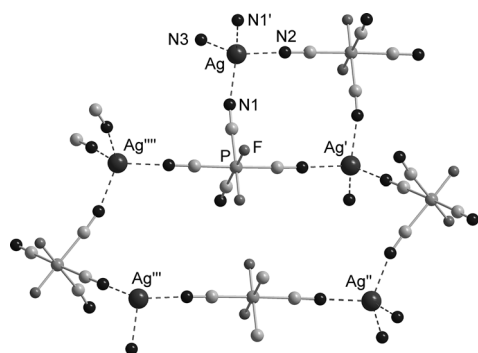


Figure 2. 12-membered and 24-membered rings as main structural motifs in $\text{Ag}[\text{PF}_2(\text{CN})_4]$. The same motifs are found in $\text{Li}[\text{PF}_2(\text{CN})_4]$.

the potassium salt crystallized in the space group $Pnna$ exhibiting both cyanide as well as fluoride coordination leading to hexacoordinate K^+ ions (Figure S1). Both tetrahedrally coordinated Ag^+ and Li^+ ions are surrounded by four different $[\text{PF}_2(\text{CN})_4]^-$ ions and vice versa the $[\text{PF}_2(\text{CN})_4]^-$ ion is surrounded by four metal ions utilizing all four CN groups for coordination while the fluoro ligands remain uncoordinated (Figure 2). The $\text{M}(\text{CN})_4$ ($\text{M} = \text{Ag}, \text{Li}$) tetrahedra are slightly distorted to C_1 symmetry with Ag–N separations in the range 2.260–2.281 Å (2.286(2) Å in $\text{Ag}[\text{Al}(\text{O}-\text{C}_6\text{H}_4-\text{CN})_4]$)^[26] and Li–N separations of 2.033–2.057 Å (cf. 2.054(1) Å in $\text{Li}[\text{Al}(\text{O}-\text{C}_6\text{H}_4-\text{CN})_4]$)^[26] respectively. Either two or four of these tetrahedra are always linked in such a way that either a slightly puckered 12-membered ring, composed of two M^+ ions four CN linkers and two P atoms (transannular Ag⋯Ag distance of 6.906(6) Å; Li⋯Li 7.898(4) Å), or a puckered 24-membered ring is formed (Figure 2). These connected 12- and 24-membered rings represent the main structural motifs within a 3D network (Figure 3 left). A closer

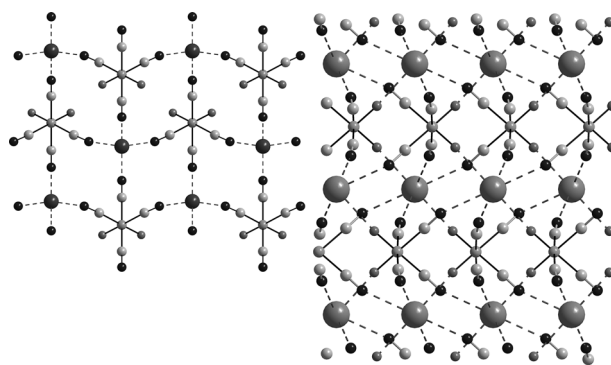


Figure 3. View at the unit cell of $\text{Ag}[\text{PF}_2(\text{CN})_4]$ along the a axis (left) and along c axis (right) for $\text{K}[\text{PF}_2(\text{CN})_4]$.

look at the 3D networks revealed a highly interpenetrated structure for both metal salts which does not have large free channels or pores. For $\text{M}[\text{PF}_2(\text{CN})_4]$ ($\text{M} = \text{Ag}, \text{Li}$) two independent infinite frameworks (Figure S2) were observed.

$[\text{H}_5\text{O}_2][\text{PF}_2(\text{CN})_4]$ salt was crystallized from water at pH 6 displaying the typical Zundel $[\text{H}_5\text{O}_2]^+$ ion in which two water molecules are linked by one proton through strong hydrogen bonds ($\text{O1}\cdots\text{O2}$ 2.385(7) Å). As depicted in Figure 4, each

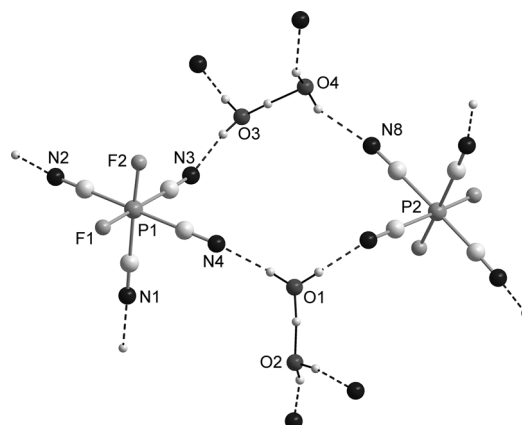


Figure 4. 18-membered rings as main structural motif in $[\text{H}_5\text{O}_2]^-$ $[\text{PF}_2(\text{CN})_4]$.

Zundel ion $[\text{H}_5\text{O}_2]^+$ coordinates by four $\text{O}-\text{H}\cdots\text{NC}$ hydrogen bonds to four different $[\text{PF}_2(\text{CN})_4]^-$ ions ($\text{O}\cdots\text{N}$ distances between 2.74–2.78 Å), and each $[\text{PF}_2(\text{CN})_4]^-$ ion is surrounded by four Zundel ions leading to a twofold interpenetrated 2D network. Only very weak $\text{F}\cdots\text{H}$ interactions can be assumed since all the $\text{F}\cdots\text{O}$ distances are larger than 3 Å. The main structural motif is composed of a 18-membered ring which includes two $[\text{H}_5\text{O}_2][\text{PF}_2(\text{CN})_4]$ ion pairs (Figure 4).

At the M06-2X/aug-cc-pvDZ level of theory, two isomers are found for the $[\text{PF}_2(\text{CN})_4]^-$ ion (*cis*- C_{2v} and *trans*- D_{4h}) with the *cis* isomer energetically slightly favored by 2.71 kcal mol^{−1} (ΔG^{298}) in agreement with the experimental results. Experimentally we could show, that salts bearing the *cis*- $[\text{PF}_2(\text{CN})_4]^-$ ion can be prepared from PF_6^- and Me_3SiCN .

In agreement with these results the gas-phase Gibbs energies for the consecutive substitution reactions [Eq. (4)] are all



exergonic, decreasing for $n=0-4$ (ΔG^{298} : -9.12 , -6.83 , -3.07 , -2.47 , -0.09 kcal mol $^{-1}$), but endergonic for $n=5$ (2.48 kcal mol $^{-1}$, Tables S11, S12).

In conclusion, we present herein for the first time a facile, high-yield synthesis and isolation of salts bearing the water stable $[\text{PF}_2(\text{CN})_4]^-$ ion. The $[\text{PF}_2(\text{CN})_4]^-$ ion could be utilized for the synthesis of low-viscosity ILs, and as building block for the design of coordination polymers, when Lewis acidic metals were used as counterions. Hence, we expect that salts, containing the $[\text{PF}_2(\text{CN})_4]^-$ ion, might be applied as electrolytes, new coordination building blocks for the design of coordination polymers, and for studies of fundamental physical properties (e.g. magnetic properties) with transition-metal ions as counterions.

Experimental Section

Caution! Cyanide compounds are potentially poisonous! Appropriate safety precautions (cyanide detector) should be applied. Experimental details can be found in the Supporting Information.

Keywords: cyanides · inorganic synthesis · ionic liquids · phosphates · structure elucidation

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