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Cyanidosilicates – Synthesis and Structure

Jörg Harloff,[a] Dirk Michalik,[a,b] Simon Nier,[a] Axel Schulz,*[a,b] Philip Stoer,[a] and Alexander Villinger[a]

Abstract: Starting from fluoridosilicate precursors in neat cyanotrimethylsilane, $Me_3Si\text{-}CN$, a series of different ammonium salts $[R_3NMe]^+$ ($R = Et$, $^n Pr$, $^n Bu$) with the novel $[SiF(CN)_5]^{2-}$ and $[Si(CN)_6]^{2-}$ dianions were synthesized in facile, temperature controlled F^- / CN^- exchange reactions. Utilizing decomposable, non-innocent cations such as $[R_3NH]^+$, it was possible to generate metal salts of the type $M_2[Si(CN)_6]$ ($M^+ = Li^+, K^+$) via neutralization reactions with the corresponding metal hydroxides. The ionic liquid $[BMIm]_2[Si(CN)_6]$ (m. p. = 72 °C, BMIm = 1-butyl-3-methylimidazolium) was obtained by salt metathesis reaction. All synthesized salts could be isolated in good yields and were fully characterized.

Little is known about neutral binary Si-CN compounds (e.g. Si-CN and $Si(CN)_2$),[1–7] which were studied in an argon matrix or observed in the envelope of a star,[1,3,8] although cyanide-containing silanes such as the cyanotrimethylsilane ($Me_3Si–CN$) are well-known in organic chemistry for their versatile use as cyanosilylation reagent in combination with Lewis acids or bases.[9–14] The higher substituted dicyanodimethylsiliane can be used as protective reagent,[15–17] whereas the tricyanomethylsilane has not been isolated yet, but was assumed to be formed in situ in a reaction of $MeSiCl_3$ with KCN.[18] So far, binary $Si(CN)_4$ has not been synthesized, only a few geometry calculations were published.[19,20] It has been shown that $Me_3Si\text{-}CN$ is a particularly valuable reagent for fluorido / cyanido exchange reactions, which serves, for example, for the synthesis of cyanidoborates ($[B(CN)_{4-n}F_n]^-$,[21–23] n = 0 - 3) as well as phosphates ($[P(CN)_{6-n}F_n]^-$, n = 1 - 5).[24] These reactions are thermodynamically favored due to the formation of fluorotrimethylsilane ($Me_3Si\text{-}F$) that exhibits a strong Si-F bond with an high bond dissociation energy (576 ± 17 kJ mol^{-1}).[25] In addition, the equilibrium of the exchange reaction can be influenced by either using $Me_3Si\text{-}CN$ in large excess or by distilling off $Me_3Si\text{-}F$ under standard conditions (b.p. 16.0 °C). It was also shown that Lewis acids such as $GaCl_3$ can significantly accelerate F^- / CN^- exchange reactions and also allow working at lower temperatures.[22,23] Only less is known about pentacoordinated silicate monoanions, which contain cyanido ligands.[26–35] The first observation dates back to 1980, when Brownstein spectroscopically detected the $[SiF_4(CN)]^-$ anion by means of ^{19}F NMR spectroscopy ($\delta = -130$ ppm).[34] Later, Dixon and co-workers were able to synthesize and isolate $[^n Bu_4N][Me_3Si(CN)_2]$ from a solution of $[^n Bu_4N]CN$ and $Me_3Si\text{-}CN$.[32] Interestingly, $[Me_3SiF(CN)]^-$ ions were discussed as strong nucleophilic cyanide source for S_N2 reactions,[35] while $[Me_3Si(CN)_2]^-$ and $[Me_3Si(CN)Cl]^-$ were reported to be the active species in the enantioselective cyanosilylation reactions of aldehydes and ketones.[26,28,30,33] Astonishingly, no salts bearing the hexacoordinated cyanidosilicate dianions, $[Si(CN)_6]^{2-}$, are known, although the analogous hexapseudohalogenido silicates of the azide,[36] (iso)cyanate,[37,38] and thiocyanate[39] were isolated. Moreover, Fehlhammer et al. reported vibrational data on a suggested $[Si\{NCCr(CO)_5\}_6]^{2-}$ ion featuring an $Si(NC)_6$ core. Following our interest in pseudohalogen chemistry,[40] in particular the cyanide / halogenide exchange reactions,[41,42] we want to report on the successful synthesis of salts containing the $[SiF(CN)_5]^{2-}$ and $[Si(CN)_6]^{2-}$ dianions and close this gap in main group chemistry.

In a first series of experiments, we tried to synthesize the $[Si(CN)_6]^{2-}$ dianion by treating an acetonitrile solution of $SiCl_4$ with two equivalents of [WCC]CN and four equivalents of AgCN as depicted in Scheme 1 (WCC = weakly coordinating cation).[43] All attempts failed with respect to complete hexa-substitution, even upon using a large excess of both cyanido sources, since only partial CN^- / Cl^- exchange was observed as monitored by ^{13}C and ^{29}Si NMR studies. For example, we were able to isolate a silicate with the composition $[Ph_4P]_2[SiCl_{0.78}(CN)_{5.22}] \cdot 4\ CH_3CN$ or when a large excess of AgCN was used, a silver salt containing a $[AgCl(CN)]^-$ ion was obtained (see ESI, Figure S13). By this method we always obtained chloride / cyanide mixtures with a maximum of five cyanido ligands (Figure 1 left). Therefore, we had to change our synthesis strategy and switched to hexafluoridosilicates[44–46] as starting materials.

$$2\,[WCC]CN + 4\,AgCN + SiCl_4 \xrightarrow{\quad /\!/ \quad} [WCC]_2[Si(CN)_6] + 4\,AgCl$$

$$2\,[WCC]CN + 4\,AgCN + SiCl_4 \xrightarrow[\Delta]{CH_3CN} [WCC]_2[SiCl_{4-n}(CN)_{2+n}] \cdots n = 0\text{-}3$$

$$+\ [WCC][Cl\text{-}Ag\text{-}CN] + AgCl$$

Scheme 1. Reaction of [WCC]CN and AgCN with $SiCl_4$ ($[WCC]^+ = [Ph_4P]^+$, $[^n Pr_3NMe]^+$).

First of all, we had to find a suitable synthesis strategy for the production of alkyl-substituted hexafluoridosilicates of the type $[R_4N]_2[SiF_6]$ or $[R_3NH]_2[SiF_6]$. As shown in Scheme 2, two different synthesis pathways (**A** and **B**) were followed: On the one hand, the amines NR_3 (R = ethyl, *n*-propyl) were directly reacted with aqueous hexafluorosilicic acid, H_2SiF_6, which led to the formation of the corresponding $[R_3NH]_2[SiF_6]$ salts in good yields (ca. 70% route **A**). On the other hand, ammonium-methyl carbonates, ionic liquids with a decomposable anion,[47–52] were treated with aqueous H_2SiF_6, which resulted in the formation of tetra-alkylated ammonium salts $[R_3NMe]_2[SiF_6]$ (R = ethyl, *n*-propyl, and *n*-butyl)

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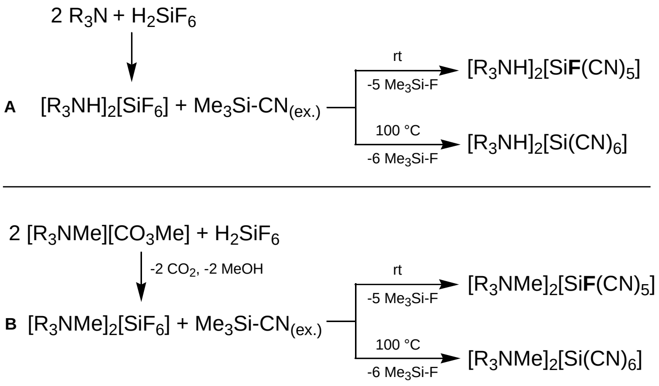
in very good yields (90%). We would like to point out that we always observed (according to ^{19}F NMR experiments) highly dynamic mixtures of $[SiF_6]^{2-}$, $[SiF_5]^-$ and F^- in solution (Figure S30), regardless of whether synthesis route **A** or **B** was chosen. Therefore, only corresponding mixtures were isolated in the solid.



Scheme 2. Synthesis of $[R_3NH]_2[SiF_6]$ and $[R_3NMe]_2[SiF_6]$ as well as their conversion to $[R_3NH]_2[SiF(CN)_5]$ / $[R_3NH]_2[Si(CN)_6]$ and $[R_3NMe]_2[SiF(CN)_5]$ / $[R_3NMe]_2[Si(CN)_6]$ (R = ethyl, *n*-propyl, and *n*-butyl). For reasons of clarity, the $[SiF_5]^-$ impurities in the starting materials were omitted (see ESI).

With hexafluoridosilicates in hand, we were now able to work with cyanotrimethylsilane, Me$_3$Si-CN, as cyanation reagent that was always used in a 20-fold excess compared to the $[SiF_6]^{2-}$ salt. Interestingly, when the reactions were carried out at 25 °C for 2h, we always obtained salts containing the $[SiF(CN)_5]^{2-}$ ion (besides traces of hexacyanidosilicate $[Si(CN)_6]^{2-}$) in moderate yields (50 - 60%). However, when the temperature was increased to 100 °C, the reaction led to the formation of $[Si(CN)_6]^{2-}$ salts in very good yields (60 - 90%) with a reaction time of 2h. With small amounts of GaCl$_3$ as Lewis acid catalyst added to the reaction mixture, the reaction time can be shortened.[22,23] In addition, significantly fewer traces of $[SiF(CN)_5]^{2-}$ ions were detected. The progress of these stepwise cyanation reactions was readily monitored by ^{19}F NMR experiments in CH$_3$CN (Figure S83). For example, after one minute small amounts of Me$_3$Si-F ($\delta[^{19}F] = -157$), $[SiF(CN)_5]^{2-}$ (–75), $[SiF_2(CN)_4]^{2-}$ (–89), $[SiF_3(CN)_3]^{2-}$ (–109) as well as large amounts of $[SiF_6]^{2-}$ (–127 ppm, see also Table S14) were detected. With increasing reaction time, the amount of Me$_3$Si-F and $[SiF(CN)_5]^{2-}$ increases significantly. By means of ^{13}C and ^{29}Si(IG) NMR experiments, the formation of $[Si(CN)_6]^{2-}$ ($\delta[^{13}C] = 140.0$ s; $\delta[^{29}Si] = -307$ s) was proven compared to $[SiF(CN)_5]^{2-}$ ($\delta[^{13}C] = 141.6$ d, 140.3 d; $\delta[^{29}Si] = -273$ d). Interestingly, when no solvent was used, the conversion to $[SiF(CN)_5]^{2-}$ at ambient temperature was complete after 1h, which was not the case, when a solvent such as CH$_3$CN was used. For this reason, all reactions were carried out without solvent and hence the reaction medium can be regarded as a mixture with the characteristics of an ionic liquid. Work-up included removing of all volatiles such as Me$_3$Si-X (X = F, CN) and re-crystallization from acetonitrile that led usually to the formation of crystals suitable for structure elucidation (see ESI Tables S1 - S13 and ORTEP-Figures S1 - S15). As depicted in Figure 1, the formation of $[SiF(CN)_5]^{2-}$ and $[Si(CN)_6]^{2-}$ salts was unequivocally proven by single crystal X-ray diffraction.

Starting from $[R_3NMe]_2[Si(CN)_6]$ salts, we next attempted to produce metal-cyanidosilicate salts by salt metathesis reaction. For example, AgNO$_3$ was reacted with $[^nBu_3NMe]_2[Si(CN)_6]$ in CH$_3$CN. This reaction failed because insoluble silver cyanide or Ag-CN-complex salts were always formed immediately, for example $\{[Ag(PPh_3)_3]_2(CN)\}[Ag(CN)_2] \cdot 3\ CH_3CN$, which could be clearly proven by single crystal structure analysis (Table S8, Figure S11). The great advantage of $[R_3NH]_2[Si(CN)_6]$ over $[R_3NMe]_2[Si(CN)_6]$ salts is that the former have a decomposable, non-innocent cation.[23,24] Therefore, these salts are particularly suitable for the synthesis of metal salts by reacting them with corresponding metal bases as illustrated in Scheme 3 (eq. 1). By this procedure, $M_2[Si(CN)_6]$ (M = Li, K) could be obtained in good to very good yields (68 - 90%) and fully characterized (Figures 2 - 3). $[BMIm]_2[Si(CN)_6]$ was synthesized in a salt metathesis reaction with $K_2[Si(CN)_6]$ utilizing a biphasic system of water and dichloromethane (yield 91%, eq. 2, Scheme 3).[53]

$$[R_3NH]_2[Si(CN)_6] + 2\ MOH \xrightarrow[H_2O]{25\ °C} M_2[Si(CN)_6] + 2\ R_3N + H_2O \quad \textbf{(1)}$$

$$K_2[Si(CN)_6] + 2\ [BMIm]Br \xrightarrow[H_2O/CH_2Cl_2]{25\ °C} [BMIm]_2[Si(CN)_6] + 2\ KBr \quad \textbf{(2)}$$

$$[^nPr_3NH]_2[Si(CN)_6] \xrightarrow{\Delta} 2\ HCN + 2\ ^nPr_3N + Si(CN)_4 \quad \textbf{(3)}$$

Scheme 3. Eq. 1: synthesis of $M_2[Si(CN)_6]$ (M = Li, K), eq. 2: synthesis of $[BMIm]_2[Si(CN)_6]$ and eq. 3: decomposition of $[R_3NH]_2[Si(CN)_6]$ upon thermal treatment.

Table 1. Selected spectroscopic data (T_{dec} in °C, υ_{CN} in cm^{-1}) along with data from ESI-TOF experiments (cat/an = cation/anion of the considered species).

species	T_{dec}	υ_{CN}[a]	NI-ESI[b]	PI-ESI[b]
$[^nPr_3NMe]_2[SiF(CN)$ yield = 50 %	175	2172 (2177)	$[Si(CN)_4F]$ $[Si(CN)_5]^-$	[d]
$[^nPr_3NMe]_2[SiF(CN)$ yield = 56 %	170	2170 (2173)	$[Si(CN)_4F]$ $[Si(CN)_5]^-$	$\{cat_3an_1\}^+$
$[^nBu_3NMe]_2[Si(CN)_6]$ yield = 66 %	200	2164 (2173)	$[Si(CN)_5]^-$	$\{cat_3an_1\}^+$
$[Et_3NH]_2[Si(CN)_6]$ yield = 91 %	140	2170 (2171)	$[Si(CN)_5]^-$	$\{cat_2[Si(CN)_5]\}^+$ $\{cat_3[Si(CN)_5]_2\}^+$
$[^nPr_3NH]_2[Si(CN)_6]$ yield = 50 %	176	2170 (2172)	$[Si(CN)_5]^-$	[d]
$Li_2[Si(CN)_6]$ yield = 62 %	260	2282 (2206)	$[Si(CN)_5]^-$	[d]
$K_2[Si(CN)_6]$ yield = 68 %	219	2185 (2189)	$[Si(CN)_5]^-$	$\{cat_3an_1\}^+$
$[BMIm]_2[Si(CN)_6]$ Yield = 91 %	220 [c]	2168 (2173)	$[Si(CN)_5]^-$ $\{cat_3an_2\}^-$	[d]

[a] most intensive IR (Raman) band; [b] species found in NI / PI - ESI: negative / positive-ion electron spray ionization, [c] melting point: 72°, [d] no ion pair found

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Spectroscopic data of synthesized cyanidosilicate species are summarized in Table 1. All isolated cyanidosilicates were thermally stable up to 140 °C. Interestingly, the $[BMIm]^+$ salt melted at 72 °C and did not start to decompose until 220 °C. Thus, it can be referred to as ionic liquid. As expected, cyanidosilicates containing the decomposable $[R_3NH]^+$ ions were considerably less stable than the $[R_4N]^+$ / M^+ salts. Combined IR and TGA experiments of $[^{n}Pr_3NH]_2[Si(CN)_6]$ showed that, as expected, this salt decomposed into free amine $^{n}Pr_3N_{(g)}$, $HCN_{(g)}$ and $Si(CN)_{4(g)}$ at temperatures above 176 °C (eq. 3 in Scheme 3, Figure S79). By means of ESI-TOF measurements, it was possible to observe either the $[SiF(CN)_4]^-$ or $[Si(CN)_5]^-$ monoanions in case of the $[SiF(CN)_5]^{2-}$ salts, while for all $[Si(CN)_6]^{2-}$ salts always the $[Si(CN)_5]^-$ monoanion was detected in the negative mode. Only for $[BMIm]_2[Si(CN)_6]$, we were able to observe a larger cluster ion $\{[BMIm]_3[Si(CN)_6]_2\}^-$, indicating that this species can be transferred into the gas phase without decomposing the $[Si(CN)_6]^{2-}$ dianion. In the positive mode it was possible to detect singly charged salt cluster ions of the composition $\{cat_2[Si(CN)_5]\}^+$, $\{cat_3[Si(CN)_5]_2\}^+$, containing a formal $[Si(CN)_5]^-$ moiety, and both the $\{cat_3[Si(CN)_5F]\}^+$ and the $\{cat_3[Si(CN)_6]\}^+$ for some of the studied species (Table 1, cat = specific cation).[54,55]

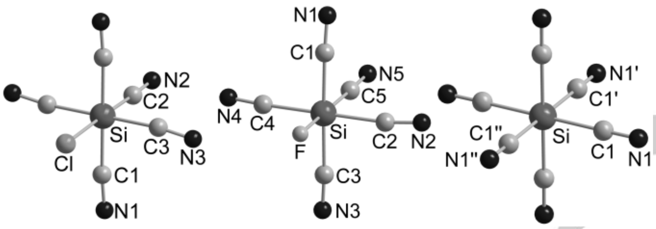

Figure 1. Ball-and-stick representation of the molecular anion structure in the crystal: Left: $[Ph_4P]_2[SiCl_{0.78}(CN)_{5.22}] \cdot 4\ CH_3CN$. Middle: $[^{n}Pr_3NH]_2[SiF(CN)_5]$, Right: $[^{n}Pr_3NH]_2[Si(CN)_6]$. Cations and solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: Left: Si-Cl 2.24(2), Si-C1 1.929(5), Si-C2 1.94(1), Si-C3 1.967(8); Cl-Si-C2 177.060(7), Cl-Si-C3 89.954(6), C2-Si-C3 90.989(7). Middle: Si-F 1.68(1), Si-C1 1.914(9), Si-C2 1.965(9), Si-C5 1.95(2); F-Si-C5 178.9(9), F-Si-C1 92.5(5), C1-Si-C2 88.8(4), C1-Si-C3 177.7(4). Right: Si-C1 1.952(1), C1-Si-C1' 91.24(5), C1-Si-C1'' 88.76(5), C11-Si-C1'' 180.0. Symmetry code: (') 1-y, 1-z, 1-x, ('') y, z, x.

Next, we investigated the stability towards moisture, mineral acids and bases. It should be noted that a typical, but weak odour of hydrogen cyanide (HCN) was noticed when adding water to a prepared NMR sample. However, a signal for free HCN ($\delta[^{13}C]$ = 113 ppm) was only observed after four days and even then most of the $[Si(CN)_6]^{2-}$ species remained intact. Besides, instant and strong release of $HCN_{(g)}$ could be detected by a BW GasAlert Detector when a droplet of concentrated aqueous HCl (12 M) was added to solid $[Et_3NH]_2[Si(CN)_6]$. When using less concentrated HCl (0.1 M) evolution of HCN was observed as well, but the anion decomposed much slower and even after two days, most of the $[Si(CN)_6]^{2-}$ could still be observed beside a small signal for HCN according to time-dependent ^{13}C NMR studies, even at slightly elevated temperatures (50°C, see Figure S82). Encouraged by this result and in the hope to be able to isolate a H_3O^+ or $H_5O_2^+$ salt, $K_2[Si(CN)_6]$ dissolved in water was rinsed over a column filled with the protic cation exchange resin Amberlyst-15. NMR spectroscopic investigation of the strong acidic solution (pH = 1) revealed a new signal for the proton at 4.3 ppm in ^1H NMR spectra and a still intact $[Si(CN)_6]^{2-}$ ion according to ^{13}C NMR experiments (Figure S80). The isolation of the free acid in the form of a solid was not successful until now, because the slow evaporation of the solution in a desiccator or the much faster removal of all volatile components in vacuum only led to decomposition caused by the loss of HCN.

All structure determinations of the ammonium silicate salts unequivocally proved the presence of either almost C_{4v} symmetrical $[SiX(CN)_5]^{2-}$ (X = F, Cl) or octahedral $[Si(CN)_6]^{2-}$ anions (Figure 1), featuring both a hexacoordinated silicon atom with bond angles close to 90 and 180° (Figure 1, Table S13 and Figures S1-13). These structures consist of separated ions with no significant interionic contacts as expected for a weakly coordinating cation, that is, the silicate dianions are surrounded by the $[WCC]^+$ ions and vice versa (e.g. see Figures S2 and S4). Both the Si-Cl (2.24(2) Å) and the Si-F (1.68(1) Å) bond lengths are in the expected range of a Si-X single bond (cf. Σr_{cov} (Si-X),[56] 1.78 X = F and 2.15 Å X = Cl). The experimentally determined Si-C bond lengths for the $[SiCl(CN)_5]^{2-}$ ion is also in the range for a single bond (average 1.945 Å), in accord with those found for $[SiF(CN)_5]^{2-}$ (average 1.951 Å) and $[Si(CN)_6]^{2-}$ (1.952 Å, cf. Σr_{cov} (Si-C) = 1.91 Å).[56] Since the $[Si(CN)_6]^{2-}$ ion is able to form coordination polymers by coordinating with Lewis acidic centers,[57] it was of interest to crystallize metal salts and investigate their structures (e.g. Li^+ and K^+).

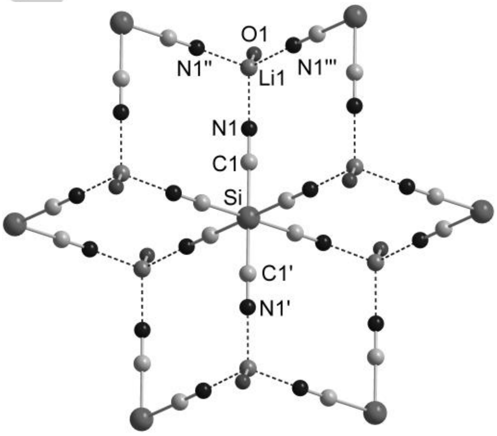

Figure 2. Ball-and-stick representation of a section of the molecular structure in in the crystal of $Li_2[Si(CN)_6] \cdot 2\ H_2O$. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si-C1 1.947(1), Li1-N1 2.40(2), Li1-O1 1.913(4); C1-Si-C1' 180.0, N1-Li1-N1'' 102.2(1). Symmetry code: (') –x + y, -x, z; ('') x - y, 1 - y, -z; (''') 1 - x, 1 – x + y, -z.

Crystals of $Li_2[Si(CN)_6] \cdot 2\ H_2O$ suitable for X-ray analysis were received by slow evaporation of a concentrated solution of water in the desiccator (Figure 2). Colourless crystals of $Li_2[Si(CN)_6] \cdot 2\ H_2O$ crystallized in the trigonal space group $P\bar{3}m1$ with one formula unit per cell. The octahedral $[Si(CN)_6]^{2-}$ ion coordinates to six different Li^+ ions, while the distorted tetrahedrally coordinated Li^+ ion is linked via the N atom of the cyanido ligand with three different adjacent $[Si(CN)_6]^{2-}$ ions besides one water molecule. These coordination modes lead to the formation of planar 12-membered $Li_2Si_2(CN)_4$ rings, which are connected either perpendicularly (edge shared at silicon) or coplanar (corner shared). The Si-C bonds are in the expected range (Si-C1 1.947(1), cf. Σr_{cov} (Si-C) = 1.91 Å), while the Li-N donor acceptor bonds are slightly elongated (d(Li1-N1) = 2.40(2), Σr_{cov}(Li-N) = 2.04 Å,[56] cf. 2.06 Å in LiCN).[58] Colourless crystals of $K_2[Si(CN)_6] \cdot 6\ CH_3CN$ were obtained after re-crystallization from acetonitrile. They crystallized in the monoclinic space group $P2_1/n$ with two formula units per unit cell. The $[Si(CN)_6]^{2-}$ is octahedrally surrounded by six K^+ ions and always linked by the nitrogen atom. As depicted in Figure 3, each K^+ ion coordinates via three nitrogen atoms of three adjacent cyanido ligands to three different $[Si(CN)_6]^{2-}$ anions (d(K-N$_{anion}$) between 2.766(1) - 2.790(1) Å), in addition to three further, slightly longer $K^+ \cdots NC\text{-}CH_3$ donor-acceptor bonds (d(K-N$_{acetonitrile}$) between 2.819(7) - 2.933(2) Å). Hence, the coordination around K^+ is best described as [3 + 3] coordination mode with a strongly distorted KN_6 core ($\measuredangle$(N1-K-N2) = 159.42(3), $\measuredangle$(N3-K-N5) = 166.1(2), $\measuredangle$(N6-K-N4) = 174.1(6) °). The main structural motif consists of edge linked 12-membered and 18-membered rings, finally leading to the formation of a 3d network, in which the acetonitrile molecules are located inside the large pores (d_{pore} = 10.4 Å, Figure 3 bottom, Figure S10).

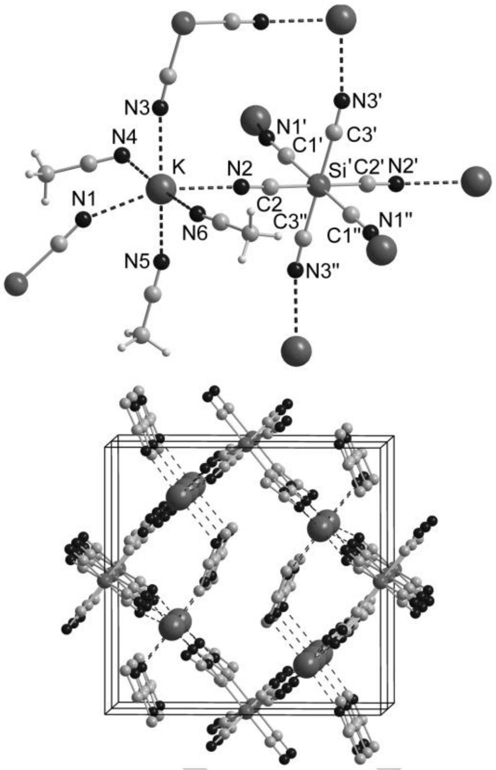

Figure 3. Top: Ball-and-stick representation of a section of the molecular structure in the crystal of $K_2[Si(CN)_6] \cdot 6\ CH_3CN$. View of the unit cell along [100]. Selected bond lengths [Å] and angles [°]: Si-C1 1.946(1), Si-C2 1.9427, Si-C3 1.949(1), K-N1 2.766(1), K-N2 2.776(1), K-N3 2.790(1), K-N4 2.933(2), K-N5 2.819(7), K-N6 2.848(2); C-Si-C 180.0, N1-K-N2 159.42(3), N3-K-N5 166.1(2), N6-K-N4 174.1(6). Symmetry codes: (') –0.5 + x, 0.5 - y, 0.5 + z; ('') 0.5 - x, 1.5 + y, 1.5 - z.

Finally, we have computed the standard Gibbs energies, $\Delta_R G°_{298}$, for the stepwise formation of the $[Si(CN)_6]^{2-}$ ion starting from $[SiF_6]^{2-}$ at 298 K using the PBE1PBE-D3BJ/aug-cc-pVTZ level of theory (for details see ESI). Experimentally, we could show that salts, bearing the $[Si(CN)_6]^{2-}$ dianion, can be prepared from $[SiF_6]^{2-}$ and $Me_3Si\text{-}CN$ and in agreement with these results the gas phase Gibbs energies for the consecutive substitution reactions of the first four steps are exergonic, decreasing for n = 1 - 4 ($\Delta_R G°_{298}$: –5.71, –3.01, –1.70, –0.72 kcal mol^{-1}), but slightly endergonic for n = 5 - 6 (1.56 and 3.51 kcal mol^{-1}, Tables S15 - 16). It should be noted that, although the last two steps are slightly endergonic, the reaction was carried out with a 20-fold excess of $Me_3Si\text{-}CN$ and the generated $Me_3Si\text{-}F$ was removed constantly from the equilibrium, thereby allowing the formation $[SiF(CN)_5]^{2-}$ and $[Si(CN)_6]^{2-}$ ions.

In conclusion, we present here a facile, high yield synthesis and isolation of salts featuring air stable $[SiF(CN)_5]^{2-}$ and $[Si(CN)_6]^{2-}$ dianions, respectively. However, as soon as a drop of water or an undried polar solvent are added, the smell of HCN can be perceived. Salts with completely alkylated ammonium cations and one-proton-containing ammonium cations of the general formula $[R_3NR']^+$ (R = Et, ^{n}Pr, ^{n}Bu; R' = H, Me) were isolated and fully characterized. In particular the $[R_3NH]^+$ salts, containing decomposable anions, can be utilized to generate easily metal hexacyanidosilicates simply by using metal bases such as MOH, which leads to the decomposition of the ammonium ion into R_3N and water as well as the formation of $M_2[Si(CN)_6]$ salts. The $[Si(CN)_6]^{2-}$ ion could also be utilized for the synthesis of $[BMIm]_2[Si(CN)_6]$, an ionic liquid, and as building block for the design of coordination polymers, when Lewis acidic metals were used as counter ions. Therefore, we expect that salts, containing $[SiF(CN)_5]^{2-}$ or $[Si(CN)_6]^{2-}$ dianions, could 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 counter ions.

Experimental Section

Caution! HCN as well as $Me_3Si\text{-}CN$ are highly toxic! Appropriate safety precautions (HCN detector, gas mask, low temperatures) should be taken. Experimental details including all spectra and ORTEP representations can be found in the supporting information.

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Keywords: cyanides • silicates • ionic liquids • structure • synthesis

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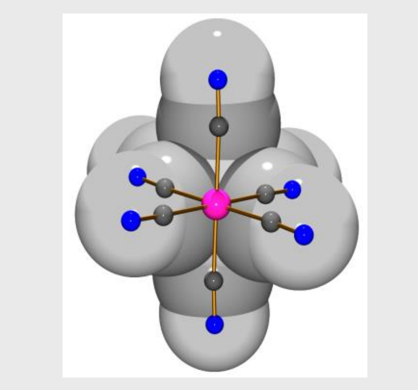
COMMUNICATION

The dose makes the hexacyanidosilicates. Treatment of $[R_4N]_2[SiF_6]$ with an excess of $Me_3Si\text{-}CN$ at 25 ° or 100 °C, respectively, led to the formation of salts bearing either the $[SiF(CN)_5]^{2-}$ or the $[Si(CN)_6]^{2-}$ dianion. The $[Si(CN)_6]^{2-}$ ion was shown to be utilized for the synthesis of ionic liquids as well as building block for the design of coordination polymers, when Lewis acidic metals are used as counter ions.



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