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Molecular Networks Based on CN Coordination Bonds

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This study examines the use of tetrahedral $[E(O–C_6X_4–CN)_4]^–$ anions (E = B, Al; X = H, F), which can be synthesized from the reaction of tetrahedral $NaBH_4/LiAlH_4$ and $HO–C_6X_4–CN$, as anionic linkers for the generation of 2D and 3D crystalline coordination polymer networks. Such polymer networks were obtained by the connection of tetrahedral *p*-cyanophenoxy aluminate or borate linkers with monocationic metal centers such as Li^+, Na^+, Ag^+, and Cu^+. These studies are specifically focused on the synthesis, structure, and stability of such polymers. Additionally, the perfluorinated $O–C_6F_4–CN$ linker was used to study electronic influences. Salts bearing the perfluorinated $[E(O–C_6F_4–CN)_4]^–$ anion decompose into $E(O–C_6F_4–CN)_3$ and $[O–C_6F_4–CN]^–$, which is also observed when a Lewis acid such as $B(C_6F_5)_3$ is added. Moreover, addition of $B(C_6F_5)_3$ leads to the formation of molecular-ion pairs because the cyano groups are now either completely or partly blocked. The structures of $M[Al(O–C_6H_4–CN)_4]$ (M = Li, Ag, Cu), $Na[B(O–C_6H_4–CN)_4]$, and $Li[Al(O–C_6F_4–CN)_4]$ as well as of the decomposition products $Na(O–C_6F_4–CN)$, $(THF)Al[O–C_6H_4–CN·B(C_6F_5)_3]_3$ (THF = tetrahydrofuran), $Na[(F_5C_6)_3B·O–C_6H_4–CN·B(C_6F_5)_3]$, and $Li[NC–C_6F_4–O–Al\{O–C_6F_4–CN·B(C_6F_5)_3\}_3]$ are discussed.

Introduction

The directed synthesis of coordination polymers[1] with two- or three-dimensional framework structures can be achieved through the connection of molecular building blocks through hydrogen bonds,[2,3] donor–acceptor bonds,[4] halogen bonds,[5] metal–metal,[6] CH–π,[7] and π–π interactions.[8] The synthesis and characterization of infinite two- and three-dimensional networks has been an area of rapid growth, because many applications of their useful electronic, magnetic, optical, and catalytic properties are expected.

Coordination polymers are composed of connectors and linkers.[1] We decided to study tetraphenoxyaluminates and borates of the type $[E(O–C_6X_4–CN)_4]^–$ (E = B, Al; X = H, F) with one cyano group as binding site per phenoxy group as linker. Transition-metal ions such as silver or copper ions are often utilized as versatile connectors in the construction of coordination polymers. Depending on the metal and its oxidation state, different coordination numbers and geometries, such as linear, tetrahedral, square planar, square pyramidal, trigonal bipyramidal, octahedral, etc. are obtained.[1] Tetraphenoxyaluminates and borates[9,10] and also their fluorinated analogs[11] have been studied and widely applied, for example, in catalysis, however, to the best of our knowledge the cyano-substituted anions are not known yet. The only known cyanoborates and aluminates are of the type $[B(C_6H_4–CN)_4]^–$[12] and $[B(CN)_4]^–$.[13] In addition, there is a great wealth of compounds based on polycyanometallates,[4b,14] $[C(CN)_3]^–$,[15] or Si(*p*-$C_6H_4–CN)_4$.[16]

Herein, we describe crystalline coordination polymer networks that were obtained through the connection of tetrahedral *p*-cyanophenoxy aluminate or borate linkers with monocationic transition metal center such as Ag^+ and Cu^+. A common feature of these supramolecular polymers is the presence of dative M–NC bonds (M = Ag, Cu), which are crucial structure-directing elements in addition to the tetrahedral $[E(O–C_6X_4–CN)_4]^–$ building block.

Results and Discussion

Ligands, such as *p*-cyanophenoxy linkers, with the potential for supplemental Lewis base interactions are finding increasing utility for the stabilization of electrophilic metal centers (metal = alkali, Cu, Ag, etc.).[17] For the synthesis of salts bearing the aluminate and borate anions, $[E(O–C_6H_4–CN)_4]^–$ (E = Al, B), $LiAlH_4$ and $NaBH_4$ were treated with four equivalents of 4-hydroxybenzonitrile, $HO–C_6H_4–CN$, at low temperatures in tetrahydrofuran (THF, Scheme 1). The resulting solution was heated to reflux for two hours. After filtration and removal of the solvent in vacuo, a colorless solid was obtained, which was washed with Et_2O to remove the excess 4-hydroxybenzonitrile. In both cases, the pure $Li[Al(O–C_6H_4–CN)_4]$ (**1**) or Na[B(O–

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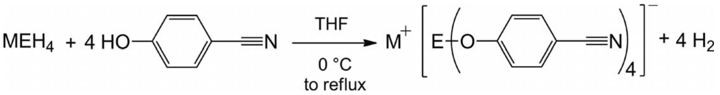
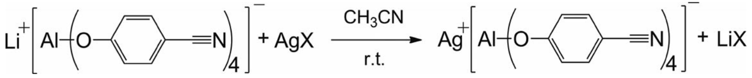


Scheme 1. Synthesis of Li[Al(O–C_6H_4–CN)$_4$] (**1**) and Na[B(O–C_6H_4–CN)$_4$] (**2**).

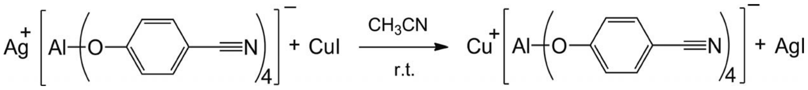
C_6H_4–CN)$_4$] salt (**2**) was obtained in yields between 60–70%. Li[Al(O–C_6H_4–CN)$_4$] (**1**) is highly soluble in THF and acetonitrile, whereas Na[B(O–C_6H_4–CN)$_4$] (**2**) is slightly less soluble. Both salts are almost insoluble in CH_2Cl_2 and aromatic solvents such as benzene or toluene.

By utilizing salt metathesis reactions with different silver salts AgX (X = NO_3^-, CF_3COO^-, $CF_3SO_3^-$), the exchange of the Li^+ ions by Ag^+ ions was achieved (Scheme 2) to afford Ag[Al(O–C_6H_4–CN)$_4$] (**3**) in yields between 40–50%. The copper salt Cu[Al(O–C_6H_4–CN)$_4$] (**4**) was obtained in the reaction of Ag[Al(O–C_6H_4–CN)$_4$] with CuI, which, unlike AgI, is soluble in acetonitrile (50% yield, Scheme 3). In comparison to the lithium salt, the M[Al(O–C_6H_4–CN)$_4$] salts (M = Ag, Cu) are also very good soluble in acetonitrile but considerably less soluble in THF. Whereas the silver and lithium salt can be crystallized as solvent-free species, solvent molecules occupy the voids in the copper species.

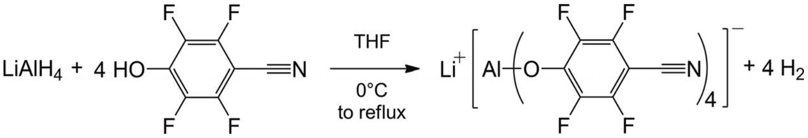
In a second series of experiments, we tried to synthesize the analogous perfluorinated salts Li[E(O–C_6F_4–CN)$_4$] (E = B, Al). Although the aluminate salt Li[Al(O–C_6F_4–CN)$_4$] (**5**) is easily generated in good yields (51%) by utilizing 4-cyano-2,3,5,6-tetrafluorophenol, HO–C_6F_4–CN, as shown in Scheme 4, in the reaction of $NaBH_4$ with HO–C_6F_4–CN in acetonitrile only the formation of Na(O–C_6F_4–CN) (**6**), the free acid B(O–C_6F_4–CN)$_3$, and molecular hydrogen (Scheme 5) is observed. If the Na^+ ion is not stabilized by significant donor–acceptor interactions as in compounds **1**–**5**, the "naked" Na^+ ion seems to be the stronger Lewis acid, which results in the abstraction of O–C_6F_4–CN^- from the [B(O–C_6F_4–CN)$_4$]$^-$ ion and yields Na(O–C_6F_4–CN) and B(O–C_6F_4–CN)$_3$. Obviously, the driving force for the formation of **6** is the instability of the [B(O–C_6F_4–CN)$_4$]$^-$ anion towards strong electrophilic ions. The whole process can formally be regarded as a Lewis acid/Lewis base reaction. A similar Lewis acid/Lewis base reaction is assumed to occur for weakly coordinating anions of the type [Al(OR^F)$_4$]$^-$ or [B(C_6F_5)$_4$]$^-$ in the presence of very electrophilic cations, in which the decomposition is initiated either by ligand (R^FO^-,[18,19] $C_6F_5^-$)[20] or fluoride ion abstraction.[21]



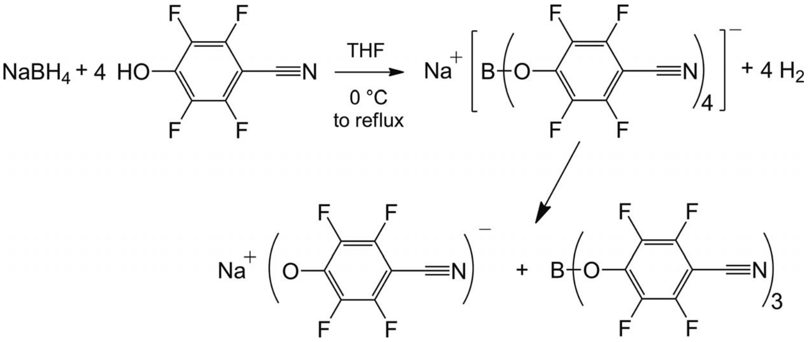
Scheme 2. Synthesis of Ag[Al(O–C_6H_4–CN)$_4$] (**3**).



Scheme 3. Synthesis of Cu[Al(O–C_6H_4–CN)$_4$] (**4**).



Scheme 4. Synthesis of Li[Al(O–C_6F_4–CN)$_4$] (**5**).



Scheme 5. Synthesis of Na(O–C_6F_4–CN) (**6**).

Finally, we studied the stability of salts bearing the $[E(O–C_6X_4–CN)_4]^-$ anion towards strong Lewis acids such as $B(C_6F_5)_3$. The idea was to see if either the very bulky adduct anions[22–25] of the type $[E(O–C_6X_4–CN·B(C_6F_5)_3)_4]^-$ are formed or if Lewis acid assisted degradation occurs leading to the formation of $M[O–C_6X_4–CN·B(C_6F_5)_3]$. The reaction of $Li[Al(O–C_6H_4–CN)_4]$ with an excess of $B(C_6F_5)_3$ led to the isolation of the solvent-stabilized Lewis acids $(THF)_2Al[O–C_6H_4–CN·B(C_6F_5)_3]_3$ (**7**) and $Li[(F_5C_6)_3B·O–C_6H_4–CN·B(C_6F_5)_3]$ [Equation (1)]; and the addition of $B(C_6F_5)_3$ to a solution of $Na[B(O–C_6H_4–CN)_4]$ gave $Na[(F_5C_6)_3B·O–C_6H_4–CN·B(C_6F_5)_3]$ (**8a**) as confirmed by X-ray structure analysis. In the latter case, it can be assumed that the free acid $(Et_2O)_2B[O–C_6H_4–CN·B(C_6F_5)_3]_3$ is also formed; however, this could not be isolated [Equation (1)]. Only when $Li[Al(O–C_6F_4–CN)_4]$ was treated with $B(C_6F_5)_3$, was no decomposition observed, however, the tri-adduct $Li[(NC–C_6F_4–O)Al\{O–C_6F_4–CN·B(C_6F_5)_3\}_3]$ (**9**) and not the tetra-adduct was obtained as shown by X-ray structure analysis.

$$\begin{aligned}2\ \text{solvent} + [E\{O–C_6H_4–CN·B(C_6F_5)_3\}_4]^- + B(C_6F_5)_3 &\rightleftarrows \\ (\text{solvent})_2E[O–C_6H_4–CN·B(C_6F_5)_3]_3 &+ \\ [(F_5C_6)_3B·O–C_6H_4–CN·B(C_6F_5)_3]^- &\quad (1)\end{aligned}$$

Properties

Salts bearing the $[E(O–C_6X_4–CN)_4]^-$ anion (E = B, Al; X = H, F) are neither air- nor considerably moisture-sensitive. They dissolve in solvents such as CH_3CN or THF but not in CH_2Cl_2 or benzene. They slowly decompose in water with the formation of the free alcohol $HO–C_6X_4–CN$ and $B_2O_3·nH_2O$ and $Al_2O_3·nH_2O$ as shown by ^1H, ^{19}F, and ^{11}B NMR studies. All mentioned $[E(O–C_6X_4–CN)_4]^-$ salts are easily prepared in bulk and are indefinitely stable when stored in a sealed tube in the dark (silver salts). All considered salts bearing the $[E(O–C_6X_4–CN)_4]^-$ ion are thermally stable up to at least 270 °C (Table 1). The thermal stabilities nicely correlate with the trends found for $M[B(CN)_4]$ (M = Li 500, Cu 470, Ag 440 °C).[26] The decomposition products were analyzed by powder XRD (PXRD) measurements and were identified as $LiAlO_2$ (for **1**), $NaBO_2$ (for **2**), Ag (for **3**), and a mixture of Cu_2O, CuO, and Cu (for **4**).

Spectroscopic Studies

The ^{13}C NMR spectroscopic data along with the IR/Raman data for the compounds described in this work are listed in Table 1. The IR and Raman data of all considered CN-group-containing anions in Table 1 show sharp bands in the expected 2220–2320 cm^{-1} region, which can be assigned to the ν_{CN} stretching frequencies. Interestingly, there is almost no difference between free $HO–C_6X_4–CN$ (X = H: 2231; X = F: 2252 cm^{-1}) and the metal salts containing the $[E(O–C_6X_4–CN)_4]^-$ ion (shift $< 10\ cm^{-1}$; X = H: 2223–2236; X = F: 2252–2256 cm^{-1}). On the contrary, the coordination of a Lewis acid such as $B(C_6F_5)_3$ to a NC–R species causes a significant band shift to higher wave numbers ($\Delta\tilde{\nu}$ = 76 in **7**, 78 in **8a**, and 66 cm^{-1} in **9**).[27] For the $B(C_6F_5)_3$ adducts, ^{11}B spectroscopy is also particularly well suited to distinguish between three-coordinate borane and the four-coordinate boron found in the Lewis acid–base adducts for which the ^{11}B resonance (**7**: –11.8, **8**: –10.1, and **9**: –8.5 ppm) is shifted to lower frequency with respect to free $B(C_6F_5)_3$ by more than 65 ppm [cf. $B(C_6F_5)_3$ in CD_2Cl_2: 59.1 ppm].[28–33]

X-ray Structure Analysis

The structures of compounds **1**–**9** have been determined. Tables 2 and 3 present the X-ray crystallographic data of species **1**–**5**, **7**, and **8a**. X-ray quality crystals of all considered species were selected in Kel-F-oil (Riedel-de Haën) or Fomblin YR-1800 (Alfa Aesar) at ambient temperature. All samples were cooled to –100(2) °C during the measurement. More details are found in the Supporting Information.

$Li[Al(O–C_6H_4–CN)_4]$ (1)

Crystals suitable for X-ray crystallographic analysis were obtained by adding three drops of CH_2Cl_2 to a saturated THF solution of **1** and storing it at 7 °C for 2 d. Complex **1** crystallized as colorless blocks in the tetragonal space group $I\bar{4}$ with two formula units per unit cell. Both metal ions have a tetrahedral coordination environment and all *p*-cyanophenoxy linker molecules (tetrahedrally attached to Al atoms through O atoms and to Li atoms through N

Table 1. Thermal analysis: melting and decomposition points (from DSC measurements); spectroscopic data: IR, Raman, and ^{13}C NMR spectroscopic data of $HO–C_6X_4–CN$(X = H, F) based species along with the data of free *p*-cyanophenols.

	M.p. [°C]	^{13}C NMR $\delta_{(CN)}$ [ppm]	IR υ_{CN} [cm^{-1}]	Raman υ_{CN} [cm^{-1}]
$HO–C_6H_4–CN$	113	119.6	2231 (s)	2239(10)
$HO–C_6F_4–CN$	268	107.8	2252 (s)	2267(1), 2252(10)
$Li[Al(O–C_6H_4–CN)_4]$ (**1**)	349[a]	120.8	2236 (s)	2244(2), 2235(10), 2217(4)
$Na[B(O–C_6H_4–CN)_4]$ (**2**)	362[a]	119.4	2226 (m)	2230(10)
$Ag[Al(O–C_6H_4–CN)_4]$ (**3**)	243[a]	120.7	2223 (s)	2244(10)
$Cu[Al(O–C_6H_4–CN)_4]$ (**4**)	281[a]	120.9	2231 (m)	2235(10), 2181(1)
$Li[Al(O–C_6F_4–CN)_4]$ (**5**)	271	109.7	2256 (m)	2266(10)
$Na(O–C_6F_4–CN)$ (**6**)	367	113.0	2253 (s)	2252(10)
$(thf)_2Al[O–C_6H_4–CN·B(C_6F_5)_3]_3$ (**7**)	137[a]	115.6	2307 (s)	2312(10)
$Na[(F_5C_6)_3B·O–C_6H_4–CN·B(C_6F_5)_3]$ (**8a**)	155	114.7	2309 (s)	2312(10)
$Li[(NC–C_6F_4–O)Al\{O–C_6F_4–CN·B(C_6F_5)_3\}_3]$ (**9**)	319[a]	114.8	2318 (m), 2263 (w)	2324(10)

[a] Decomposition temperature.

Table 2. Crystallographic details of Li[Al(O–C_6H_4–CN)$_4$] (**1**), Na[B(O–C_6H_4–CN)$_4$] (**2**), Ag[Al(O–C_6H_4–CN)$_4$] (**3**).

	1	**2**	**3**
Empirical formula	$C_{28}H_{16}AlLiN_4O_4$	$C_{46}H_{52}BN_4NaO_{8.5}$	$C_{28}H_{16}AgAlN_4O_4$
Formula weight. [g mol^{-1}]	506.37	830.72	607.3
Color	colorless	colorless	colorless
Crystal system	tetragonal	triclinic	tetragonal
Space group	$I\bar{4}$	$P1$	$I\bar{4}$
a [Å]	6.9524(8)	11.3778(4)	6.9541(3)
b [Å]	6.95424(8)	14.5700(6)	6.9541(3)
c [Å]	25.457(7)	14.8545(6)	26.2002(15)
α [°]	90	83.928(2)	90
β [°]	90	76.016(2)	90
γ [°]	90	70.325(2)	90
V [Å^3]	1230.5(4)	2249.2(2)	1267.0(1)
Z	2	2	2
μ [mm^{-1}]	0.13	0.09	0.87
λ Mo-K_α [Å]	0.71073	0.71073	0.71073
T [K]	173	173	173
Measured reflections	4206	38231	5766
Independent reflections	2153	11158	2274
Reflections with $I > 2\sigma(I)$	2053	7149	2167
R_{int}	0.03	0.044	0.022
F(000)	520	880	1480
R_1 $\{R[F_2 > 2\sigma(F_2)]\}$	0.036	0.067	0.026
wR_2 (all data)	0.091	0.204	0.048
GooF	1.08	0.99	1.002
Parameters	87	644	87

Table 3. Crystallographic details of Cu[Al(O–C_6H_4–CN)$_4$]·2CH_2Cl_2 (**4**), Li[Al(O–C_6F_4–CN)$_4$] (**5**), and (THF)$_2$Al[O–C_6H_4–CN·B(C_6F_5)$_3$]$_3$ (**7**).

	4	**5**	**7**
Empirical formula	$C_{30}H_{20}AlCl_4CuN_4O_4$	$C_{48}H_{40.8}AlF_{16}LiN_4O_9$	$C_{83.5}H_{29}AlClB_3F_{45}N_3O_5$
Formula weight [g mol^{-1}]	732.82	1155.55	2103.96
Color	colorless	colorless	colorless
Cryst. system	monoclinic	monoclinic	triclinic
Space group	$P2_1/c$	$C2/c$	$P\bar{1}$
a [Å]	12.4486(6)	23.49(2)	16.921(9)
b [Å]	15.0360(6)	13.024(9)	17.643(9)
c [Å]	16.5961(7)	33.99(2)	18.37(1)
α [°]	90	90	62.08(2)
β [°]	92.074(2)	98.59(2)	62.87(2)
γ [°]	90	90	83.93(2)
V [Å^3]	3104.4 (2)	10280(12)	4271(4)
Z	4	8	2
μ [mm^{-1}]	1.12	0.16	0.21
λ Mo-K_α [Å]	0.71073	0.71073	0.71073
T [K]	173	173	173
Measured reflections	36748	43873	71398
Independent reflections	7508	11625	20425
Reflections with $I > 2\sigma(I)$	4900	6878	11411
R_{int}	0.058	0.032	0.041
F(000)	1480	4710	2082
R_1 $\{R[F_2 > 2\sigma(F_2)]\}$	0.043	0.051	0.055
wR_2 (all data)	0.110	0.138	0.174
GooF	1.06	1.05	0.99
Parameters	442	846	1365

atoms) bridge the two metal ions to form a 3D framework structure as shown in Figures 1 and 2. Each nitrile group in the structure is coordinated to a lithium atom with a Li–N length of 2.054(1) Å (cf. Σr_{cov} = 2.05 Å) and an Al–O bond length of 1.7329(9) (cf. Σr_{cov} = 1.89 Å).[34] These values are similar to those observed for phenoxyaluminates and lithium nitrile complexes.[35] Both the AlO_4 tetrahedron and the LiN_4 moiety are slightly distorted with one smaller [N1–Li1–N1′ 106.78(3) and O1′–Al1–O1 107.43(3)°] and one larger angle [N1′–Li1–N1′′ 115.00(6) and O1′–Al1–O1′′ 113.63(7)°]. Whereas the LiN_4 tetrahedra are almost linearly attached to the phenoxy linker [C7–N1–Li1 160.0(1)°], the AlO_4 tetrahedra display a bent structure [C1–O1–Al1 134.20(8)°].

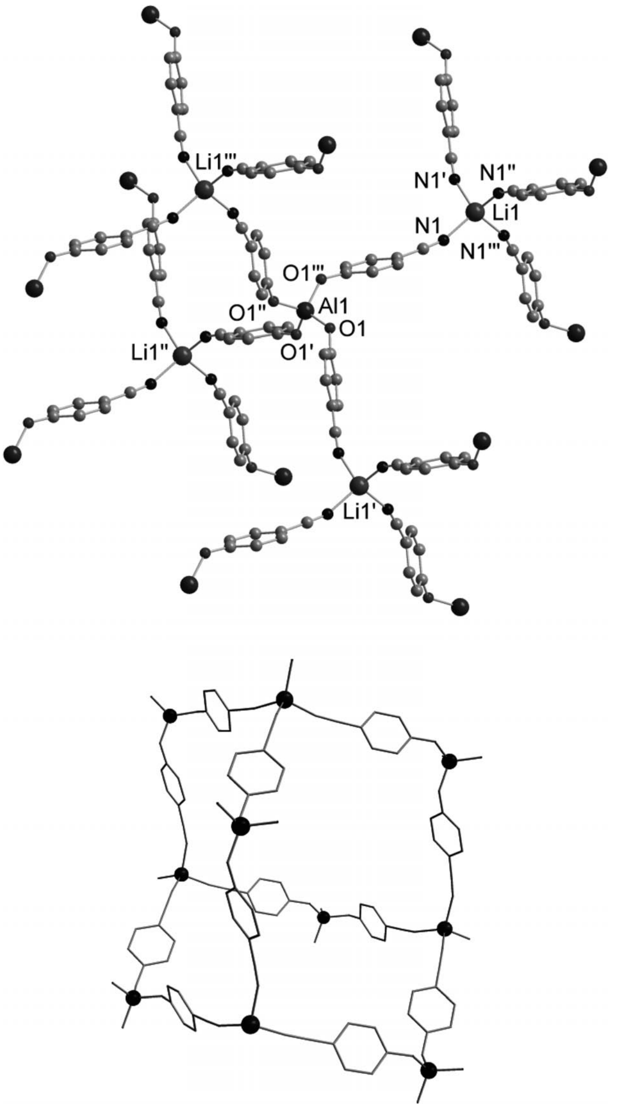


Figure 1. Top: Ball-and-stick drawing of the local environment about the tetrahedral centers in **1** (hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Al1–O1 1.7329(9), O1–C1 1.338(1), C7–N1 1.149(2), N1–Li1 2.054(1); O1′–Al1–O1 107.43(3), O1′–Al1–O1′′ 113.63(7), N1–Li1–N1′ 106.78(3), N1′–Li1–N1′′ 115.00(6), C1–O1–Al1 134.20(8), C7–N1–Li1 160.0(1). Bottom: adamantane structural motif in **1**.

A closer look at the 3D network of **1** revealed a highly interpenetrated structure, which does not possess large free channels or pores. It consists of five independent infinite frameworks, each with diamond-like topology (Figure 2). The interpenetrated framework of **1** is related to some classic inorganic frameworks, as it features the adamantane structural motif known from diamondlike frameworks such as that of zinc cyanide, which consists of two independent infinite frameworks, each with diamondlike topology.[36] Interpenetrating diamond-related nets with *n* = 5 (*n* = number of nets) have been describe for adamantane-1,3,5,7-tetracarboxylic acid,[37] [Cu(L)$_2$](BF$_4$) (L = 1,4-dicyanobenzene)[38] and [Cu(bpe)$_2$](BF$_4$) [with CH$_3$CN or CH$_2$Cl$_2$ as guest molecules, bpe = 1,4-bis(4-pyridyl)butadiyne].[39]

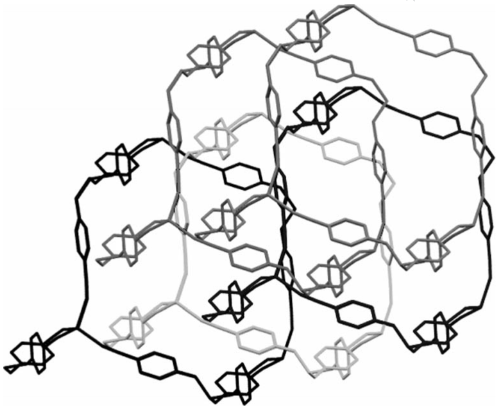


Figure 2. Five interpenetrating diamond-like frameworks in the structure of **1** showing the translational relationship between independent nets.

An inherent feature of such entangled interpenetrated structures is that they can be disentangled only by breaking internal connections.[1a] Furthermore, N$_2$ sorption measurements with compound **1** did not show significant permanent porosity (approximately 4 m^2 g^{-1} of BET surface). The structural collapse seems to occur in one step at 349 °C upon thermal treatment and results in the formation of LiAlO$_2$.

Ag[Al(O–C6H4–CN)4] (3)

Compound **3** crystallizes isostructurally to compound **1** with very similar cell parameters [cf. Li: 6.9524(8), 6.9524(8), 25.457(7) vs. Ag: 6.9541(3), 6.9541(3), 26.200(2) Å; Table 2]. Only the *c* axis is slightly elongated. All the structural features discussed before for compound **1**

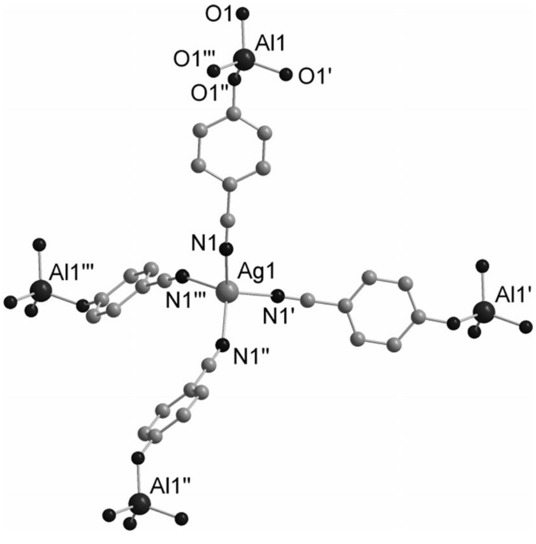


Figure 3. Ball-and-stick drawing of the local environment about the tetrahedral centers in **3** (hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Ag1–N1 2.286(2), Al1–O1 1.736(1), N1–C7 1.144(3); N1′–Ag1–N1 117.76(7), N1′–Ag1–N1′′ 105.49(3), O1′′–Al1–O1 112.7(1), O1′–Al1–O1 107.89(5), C7–N1–Ag1 154.0(2), C1–O1–Al1 131.4(1).

(Figure 1) are similarly found in the silver salt (Figure 3). Only slight differences arise from the longer Ag–N bond length of 2.286(2) compared to 2.054(1) Å for Li–N in **1**; the Al–O distances are essentially identical and the angles are also very similar.

$Cu[Al(O{-}C_6H_4{-}CN)_4]{\cdot}2CH_2Cl_2$ (4)

Single crystals of **4** were grown by slow vapor diffusion of CH_2Cl_2 into a saturated acetonitrile solution of the compound overnight at ambient temperature. In contrast to the isostructural complexes **1** and **3**, the copper salt crystallizes in the monoclinic space group $P2_1/c$ with four formula units per unit cell. Again, both metal centers sit in a slightly distorted tetrahedral environment (Figure 4, top) with an average Cu–N distance of 1.995 Å {cf. 1.979 Å in [Cu_2(1,2,4,5-tetracyanobenzene)$_3$]$(PF_6)_2(Me_2CO)_4$ or 1.977 Å in $Cu[B(CN)_4]$}[26] and 1.732 Å for the Al–O bond lengths [cf. 1.733 and 1.736(1) Å in compounds **1** and **3**, respectively]. The solid-state structure possesses relatively large cavities despite fourfold interpenetration (see Supporting Information Figure S2), and the cavities are filled by two solvent molecules per formula unit. As illustrated in Figure 4 (bottom), the major difference in the solid-state structure of **4** compared to the those of compounds **1** and **2** arises from the smaller degree of interpenetration in **4** leading to larger voids, which are filled with disordered CH_2Cl_2 solvent molecules. Thermogravimetric analysis (TGA) indicates that the solvent can be fully removed at 90 °C. However, removal of the solvent leads to a loss of crystallinity (single-crystal integrity is not maintained), as evidenced by powder X-ray diffraction analysis (see Supporting Information). No specific surface could be found by nitrogen sorption experiments of the desolvated compound.

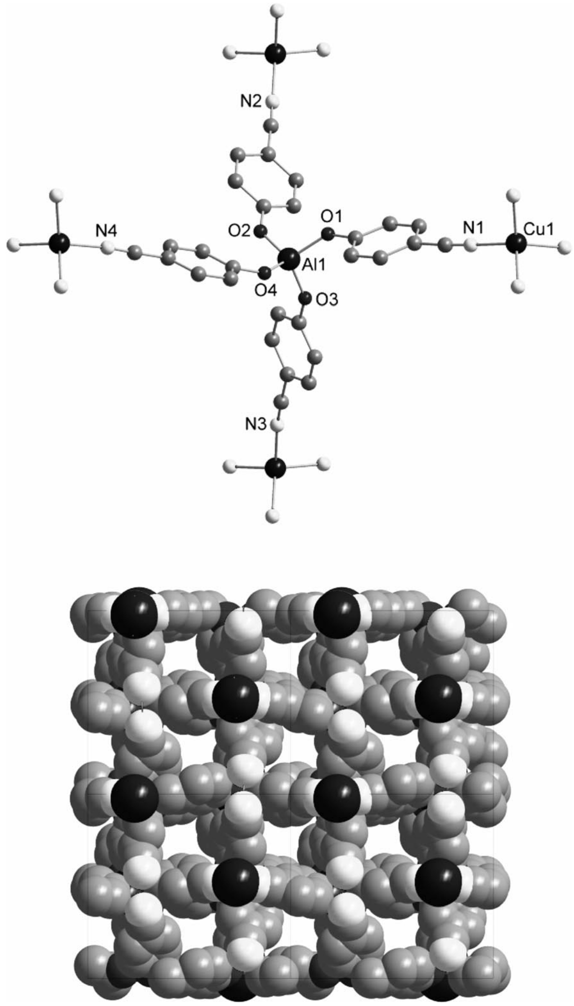


Figure 4. Top: Ball-and-stick drawing of the local environment about the tetrahedral centers in **4** (hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Al1–O2 1.735(2), Al1–O4 1.735(2), Al1–O1 1.739(2), Al1–O3 1.722(2), Cu1–N1 1.975(2), Cu1–N2 2.018(2), Cu1–N3 1.992(2), Cu1–N4 1.996(2); N1–Cu1–N3 110.1(1), N1–Cu1–N4 118.07(9), N3–Cu1–N4 101.55(9), N1–Cu1–N2 105.10(9), N3–Cu1–N2 111.68(9), N4–Cu1–N2 110.53(9), O3–Al1–O2 115.55(9), O3–Al1–O4 107.38(9), O2–Al1–O4 108.39(9), O3–Al1–O1 105.25(9), O2–Al1–O1 108.42(9), O4–Al1–O1 111.90(9). Bottom: space filling model of a section of **4**, view along *a* axis, disordered solvent molecules (CH_2Cl_2) inside the pores are omitted for clarity.

$Na[B(O{-}C_6H_4{-}CN)_4]{\cdot}8THF$ (2)

Crystals suitable for X-ray crystallographic analysis were obtained by adding three drops of CH_2Cl_2 to a saturated THF solution and storing it at ambient temperature. Complex **2** crystallizes in the triclinic space group $P\bar{1}$ with two formula units per unit cell. As the Na^+ ions prefer an octahedral rather than a tetrahedral coordination sphere (in contrast to Li^+ or Cu^+, see above), the coordination sphere around the sodium ions is either composed of four square planar arranged N atoms of the *p*-cyanophenoxy linker and two O atoms of THF molecules (Na1) with a linear O5–Na1–O5′ moiety (180.0°) or two N atoms of the *p*-cyanophenoxy linker (N4–Na2–N4′ 180.0°) and four square planar arranged O atoms of THF molecules as observed for Na2 (Figure 5, top). The boron atom is in a distorted tetrahedral environment with an average O–B–O angle of 108.8°. Interestingly, only three of the *p*-cyanophenoxy linkers act as bridging ligands between both metal ions and the fourth remains uncoordinated (N1 in Figure 5). Obviously, no stable network can be composed with octahedral Na^+ ions and a tetrahedral BO_4 building block in the presence of a donating solvent such as THF. Thus a 2D network with three different parallel layers is formed as depicted in Figure 5 (bottom). In addition to the six coordinated THF molecules, two further uncoordinated THF molecules per unit cell are found between these layers. The average B–O distance is 1.466 Å, which is slightly longer than the sum of the covalent radii (1.38 Å).[34] The C–N distance of the uncoordinated CN group is slightly shorter than those that are attached to Na^+ ions [1.137(3) vs. 1.143(3), 1.141(2), and 1.148(2) Å].

$[Li(THF)_{3.6}(Et_2O)_{0.4}][(THF)Al(O{-}C_6F_4{-}CN)_4]$ (5)

Crystals of **5** were obtained by a slow diffusion method. Et_2O was layered above a saturated THF solution of **5**, stored at –30 °C, and after one day crystals had formed near the original solvent interface. Complex **5** crystallized as colorless prisms in the monoclinic space group $C2/c$ with

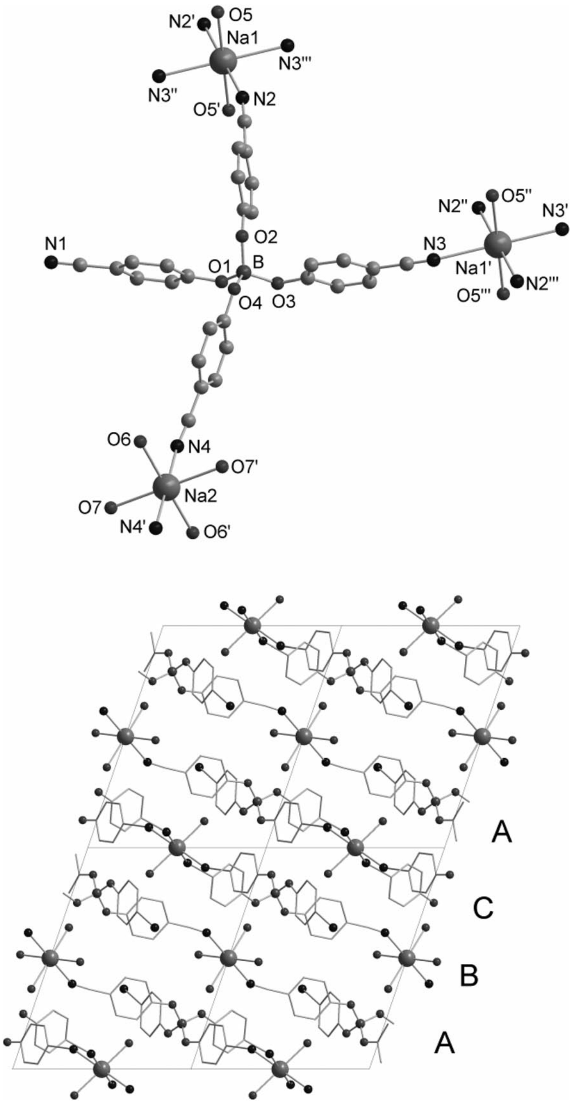


Figure 5. Top: Ball-and-stick drawing of the local environment about the tetrahedral centers in **2** (hydrogen atoms omitted for clarity, only the O atoms of the coordinated THF molecules are shown). Selected bond lengths [Å] and angles [°]: B–O1 1.463(2), B–O4 1.467(2), B–O2 1.467(2), B–O3 1.468(2), N2–Na1 2.443(2), N3–Na1 2.572(2), N4–Na2 2.541(2), Na1–O5 2.375(1), Na2–O6 2.419(5), N1–C7 1.137(3), N2–C14 1.143(3), N3–C21 1.141(2), N4–C28 1.148(2), Na2–O7 2.44(1); O1–B–O4 114.7(1), O1–B–O2 113.9(2), O4–B–O2 100.5(1), O1–B–O3 101.0(1), O4–B–O3 113.6(2), O2–B–O3 113.7(1), O5′–Na1–O5 180.00(9), O5–Na1–N2 86.50(6), O5–Na1–N2′ 93.50(6), O5–Na1–N2 93.50(6), O5–Na1–N2 86.50(6), N2′–Na1–N2 180.0(1), O5–Na1–N3 93.86(5), O5–Na1–N3 86.14(5), N2–Na1–N3 83.34(6), N2–Na1–N3 96.66(6), O5–Na1–N3 86.14(5), N2–Na1–N3 96.66(6), N3–Na1–N3′ 180.0(1), O6–Na2–O6′ 180.0(1), O6–Na2–O7 92.7(4), O6–Na2–O7 87.3(4), O7–Na2–O7′ 180.000(2). Bottom: view along *c* axis displaying parallel layers (A, B, C) of the 2D network (hydrogen atoms and all uncoordinated THF molecules omitted for clarity, only O atoms of coordinating THF molecules are shown).

eight crystallographically equivalent $[Li(THF)_{3.6}(Et_2O)_{0.4}]$-$[(THF)Al(O–C_6F_4–CN)_4]$ asymmetric units per unit cell. As illustrated in Figure 6, the asymmetric unit consists of the separated complex ion pair $[Li(THF)_{3.6}(Et_2O)_{0.4}]^+$ and $[(THF)Al(O–C_6F_4–CN)_4]^-$, which display no significant interactions since all CN groups remain uncoordinated. The Li^+ ion is tetrahedrally surrounded exclusively by either THF or Et_2O molecules. Hence, no network is formed. Obviously, perfluorination at the phenyl rings results in a dramatic decrease of the basicity of the CN groups; therefore, the Li^+ ions favor coordination by solvent molecules. The positions of four THF molecules in **5** were found to be disordered and were split in two parts. The occupancy of each part was refined freely (for details see Supporting Information). The position of the fifth THF molecule in **5** was found to be partially displaced by Et_2O and was split in two parts. The occupancy of each part was refined freely (THF/Et_2O: 0.606(7)/0.394(7)).

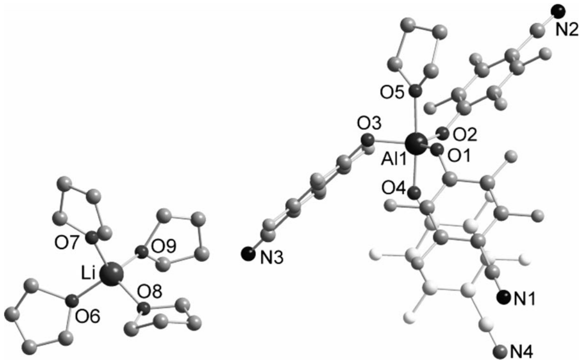


Figure 6. Ball-and-stick drawing of the asymmetric unit in **5** (hydrogen atoms omitted for clarity, disorder not shown). Selected bond lengths [Å] and angles [°]: Al1–O2 1.765(2), Al1–O1 1.766(2), Al1–O3 1.771(2), Al1–O4 1.821(2), Al1–O5 1.966(2), N1–C7 1.138(3), N2–C14 1.136(3), N3–C21 1.135(3), N4–C28 1.137(3); O2–Al1–O1 122.46(9), O2–Al1–O3 116.49(9), O1–Al1–O3 120.17(9), O2–Al1–O4 92.55(8), O1–Al1–O4 95.97(8), O3–Al1–O4 90.63(9), O2–Al1–O5 90.15(8), O1–Al1–O5 84.84(7), O3–Al1–O5 85.76(9), O4–Al1–O5 176.19(8), C1–O1–Al1 132.3(2), C8–O2–Al1 141.3(2), C15–O3–Al1 129.2(2), C22–O4–Al1 147.3(2).

Probably the most interesting feature of the molecular structure of **5** is the pentacoordination of the Al^{3+} in the complex anion, which displays a distorted trigonal bipyramidal arrangement of the O atoms around the Al^{3+} center. The one coordinating THF molecule adopts an apical position with an O4–Al1–O5 angle of 176.19(8)°. As expected the $Al–O_{ax}$ bond lengths [Al1–O4 1.821(2) and Al1–O5 1.966(2) Å] are considerably elongated compared to the $Al–O_{eq}$ bond lengths [Al1–O2 1.765(2), Al1–O1 1.766(2), and Al1–O3 1.771(2) Å]. In contrast to compounds **1**–**4**, the perfluorinated *p*-cyanophenoxy linker, $–O–C_6F_4–CN$, is considerably less basic and thus allows pentacoordination at the Al^{3+} center and prevents the cyano groups from coordinating to the Li^+ ion. Moreover, the perfluorinated *p*-cyanophenoxy linker does not provide sufficient steric hindrance to prevent solvent coordination. The oxygen-pentacoordinate aluminate is well known and can be found in aluminium containing alcoholates[40] or can be achieved by additional solvent coordination.[41] Furthermore, pentacoordination by nitrogen and oxygen containing ligands is known.[42]

Na(O–C_6F_4–CN)·3THF and Na(O–C_6F_4–CN)·nCH_3CN

Crystals of Na(O–C_6F_4–CN) were obtained from THF (**6a**) and CH_3CN (**6b**) solutions. As the X-ray data sets for both species were rather poor, the structural details cannot be discussed in detail, but the data allowed us to establish the connectivity as displayed in Figures 7 and 8. In **6a** the oxygen atom of the –O–C_6F_4–CN linker bridges two Na^+ ions thus forming chains of planar Na_2O_2 rings connected by two perfluorinated *p*-cyanophenoxy linkers. In **6b**, the oxygen of the perfluorinated *p*-cyanophenoxy coordinates in a μ^3 coordination mode to three adjacent Na^+ ions resulting in the formation of a distorted Na_4O_4 cube (Figure 8 bottom). These cubes are linked by the nitrogen and oxygen atoms of the *p*-cyanophenoxy linker leading to the formation of 3D network with channels and voids as illustrated in Figure 8 (top). Moreover, one CH_3CN solvent molecules is attached to each Na^+ center.

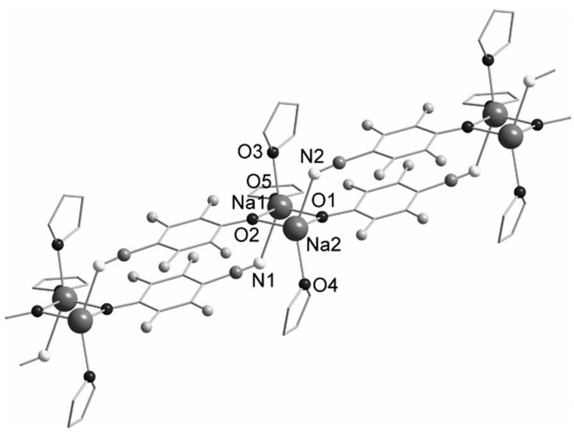


Figure 7. Drawing of the chains in **6a** (hydrogen atoms omitted for clarity, disorder not shown).

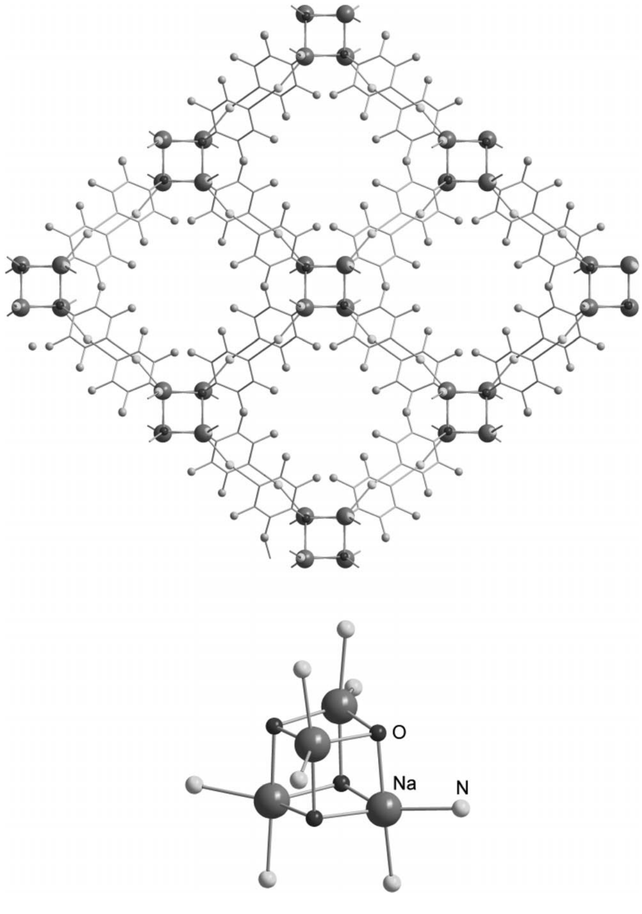


Figure 8. Top: view along the *a* axis of the 3D network in **6b**; bottom: Na_4O_4 cube in **6b**, each Na^+ center is attached to one N atom of the phenoxy linker and one of the CH_3CN molecule.

$(THF)_2Al\{O–C_6H_4–CN·B(C_6F_5)_3\}_3$ (7)

Compound **7** crystallizes in the triclinic space group $P\bar{1}$ with two formula units per unit cell. There are no significant interactions between adjacent $(THF)_2Al[O–C_6H_4–CN·B(C_6F_5)_3]_3$ molecules. As shown in Figure 9, species **7** can be considered as a solvent-stabilized $Al[O–C_6H_4–CN·B(C_6F_5)_3]_3$ Lewis acid with a trigonal pyramidal coordinated Al center with O_{eq}–Al–O_{eq} angles close to 120° [O1–Al1–O3 118.85(9), O1–Al1–O2 121.53(9), O3–Al1–O2 119.58(9)°] and an almost linear O_{ax}–Al–O_{ax} unit [O5–Al1–O4 177.70(8)°]. Both THF solvent molecules occupy axial positions, and the $B(C_6F_5)_3$ molecules are attached to the N atom of the cyano group thus preventing the formation of 2D or 3D networks. The average Al–O_{eq} bond length is 1.742 Å (cf. Al–O_{ax} 1.976 Å).

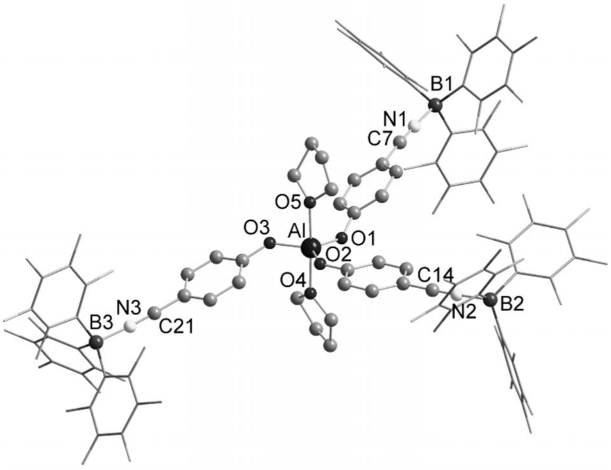


Figure 9. Drawing of the molecular structure of **7** (hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Al1–O1 1.722(2), Al1–O3 1.748(2), Al1–O2 1.755(2), Al1–O4 1.986(2), Al1–O5 1.965(2), N1–C7 1.137(3), N2–C14 1.142(3), N3–C21 1.139(3), N1–B1 1.588(4), N2–B2 1.581(3), N3–B3 1.574(3); O1–Al1–O3 118.85(9), O1–Al1–O2 121.53(9), O3–Al1–O2 119.58(9), O1–Al1–O5 92.1(1), O3–Al1–O5 88.30(9), O2–Al1–O5 91.63(9), O1–Al1–O4 88.5(1), O3–Al1–O4 89.47(8), O2–Al1–O4 89.94(8), O5–Al1–O4 177.70(8), C7–N1–B1 176.7(2), C14–N2–B2 177.3(2), C21–N3–B3 175.5(2).

$[Na(Et_2O)_4][(C_6F_5)_3B–NC–C_6H_4–O–B(C_6F_5)_3]$ (8a), $[Na(Et_2O)_4][(C_6F_5)_3B–NC–C_6F_4–O–B(C_6F_5)_3]$ (8b),[43] and $Li[(NC–C_6F_4–O)Al\{O–C_6F_4–CN·B(C_6F_5)_3\}_3]$ (9)

Compounds **8a**, **8b**, and **9** crystallize as ion pairs. As the X-ray data sets for **8b** and **9** were rather poor, structural details cannot be discussed in detail. The connectivity of all three species is displayed in Figures 10 (anions of **8a** and **8b**) and 11 (ion pair in **9**). Whereas no significant cation···anion interactions are observed for **8**, in **9** the $[Li(Et_2O)_3]^+$ ion is strongly coordinated to one unblocked cyano group of the $[(NC–C_6F_4–O)Al\{O–C_6F_4–CN·B(C_6F_5)_3\}_3]$ anion. However, there are no interactions between the ion pairs of **9** worthy of discussion. For both species, the metal ions as well as the Al and B centers are tetrahedrally coordinated. (Figure 11).

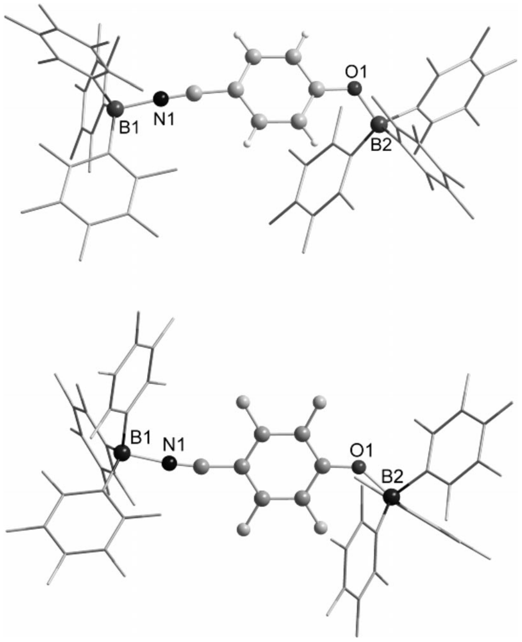


Figure 10. Drawing of the molecular structures of the anion in **8a** (top) and **8b** (bottom).

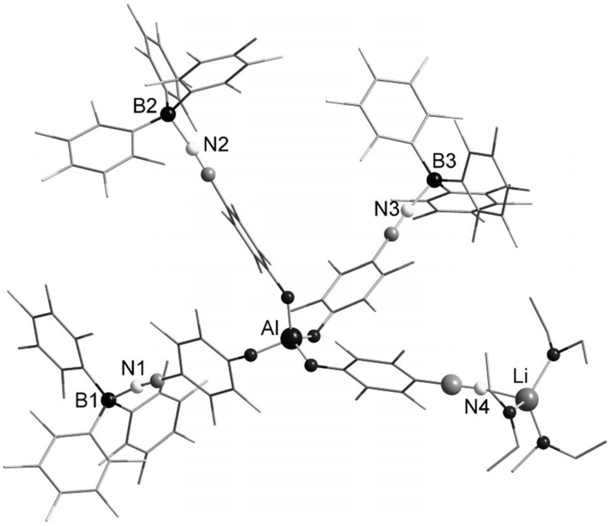


Figure 11. Drawing of the molecular structure of **9**.

Conclusions

Crystalline coordination polymer networks were obtained by connection of *p*-cyanophenoxy linker units, tetrahedrally attached to either aluminium or boron, with monocationic metal centers (M) such as Li^+, Na^+, Ag^+, and Cu^+. An interesting common feature of these supramolecular polymers is the presence of dative metal–nitrogen bonds as crucial structure-directing elements besides the tetrahedral $[E(O–C_6H_4–CN)_4]^-$ (E = Al, B) anion. Utilizing the perfluorinated $O–C_6F_4–CN$ linker leads to a decrease in the stability of the $[E(O–C_6H_4–CN)_4]^-$ anion with respect to decomposition into $E(O–C_6H_4–CN)_3$ and $(O–C_6H_4–CN)^-$, which is also observed when a Lewis acid such as $B(C_6F_5)_3$ is added. Moreover, addition of $B(C_6F_5)$ leads to the formation of molecular ion pairs because now the cyano groups are either completely or partly blocked.

Experimental Section

General Information: All manipulations were carried out under oxygen- and moisture-free conditions under argon using standard Schlenk or drybox techniques.

Dichloromethane and acetonitrile were heated to reflux over CaH_2; tetrahydrofuran and Et_2O were dried with Na/benzophenone and freshly distilled prior to use. Lithium aluminium hydride (Alfa Aeser) was purified by recrystallization from Et_2O prior to use. 4-Hydroxybenzonitrile (Merck) was sublimated in vacuo at 60 °C prior use. $AgNO_3$ (VEB Arzneimittelwerk, Dresden) was recrystallized from water, powdered, and dried in vacuo for 10 h. $NaBH_4$ (Merck) and KOH (VWR) were used as received. ^1H, ^{11}B and ^{13}C NMR spectra were obtained with Bruker Avance 250 (250 MHz) and Avance 300 (300 MHz) spectrometers and were referenced externally. CD_2Cl_2 and $CDCl_3$ were dried with P_4O_{10}, $[D_6]DMSO$ and CD_3CN were dried with CaH_2, and C_6D_6 was dried with sodium. FTIR spectra were obtained with a Nicolet 380 FTIR spectrometer with a Smart Orbit attenuated total reflectance (ATR) device. Raman spectra were obtained with a Bruker Vertex 70 FTIR spectrometer with a RAM II FT-Raman module equipped with a Nd:YAG laser (1064 nm) or Kaiser Optical Systems RXN1–785 nm microprobe. CHN analyses were conducted with an Analysator Flash EA 1112 instrument from Thermo Quest or C/H/N/S-Mikronalysator TruSpec-932 instrument from Leco. Differential scanning calorimetry (DSC) measurements were obtained with a Mettler-Toledo 823e instrument (heating rate 5 °C/min). Thermogravimetric analysis (TGA) measurements were performed with a Setaram LapSys 1600 TGA-DSC under an argon atmosphere (heating rate 5 °C/min). Nitrogen sorption experiments were performed at –192 °C with a Thermo Sorptomatic 1990 instrument.

X-ray Structure Determination: X-ray quality crystals were selected in Fomblin YR-1800 perfluoroether (Alfa Aesar) at ambient temperatures. The samples were cooled to 173(2) K during measurement. The data were collected with a Bruker Apex Kappa-II CCD diffractometer using graphite monochromated Mo-K_α radiation (λ = 0.71073 Å). The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares procedures (SHELXL-97). Semi-empirical absorption corrections were applied (SADABS). All non-hydrogen atoms were refined anisotropically, hydrogen atoms were included in the refinement at calculated positions using a riding model.

XRD: Powder XRD patterns were collected with a Stoe Stadi P diffractometer using a position sensitive detector and germanium-monochromatized Cu-$K_{\alpha 1}$ radiation (λ = 1.5406 Å) at ambient temperature.

Syntheses[44]

Li[Al(O–C_6H_4–CN)$_4$] (1): 4-Hydroxybenzonitrile (2 g, 17 mmol, 4.25 equiv.) dissolved in THF (18 mL) was added slowly to a stirred solution of activated $LiAlH_4$ (0.152 g, 4 mmol, 1 equiv.) in THF (24 mL) at 0 °C. The resulting solution was heated to reflux for two hours. The solution was filtered, and the solvent was removed in vacuo to yield a colorless solid. This crude product was washed two times with Et_2O (10 mL) to remove the excess 4-hydroxybenzonitrile. The pure product was dried for three hours in vacuo at 70 °C; yield 1.32 g (65%). M.p. (DSC): (onset) 349.4 °C, (peak) 353.9 °C. $C_{28}H_{16}AlLiN_4O_4$ (506.37): calcd. C 66.41, H 3.18, N 11.06; found C 65.35, H 3.54, N 10.68. ^{1}H NMR (CD_3CN, 300 MHz, 25 °C): δ = 7.49–7.42 (m, 8 H, C*H*–C–CN), 6.90–8.84 (m, 8 H, C*H*–C–O) ppm. ^{13}C NMR (CD_3CN, 300 MHz, 25 °C): δ = 164.9 (s, 1 C, *C*O), 135.0 (s, 1 C, *C*–C–CN), 121.1 (s, 1 C, *C*N), 120.8 (s, 1C, *C*–C–O), 101.4 (s, 1 C, *C*–CN) ppm.

Na[B(O–C_6H_4–CN)$_4$] (2): 4-Hydroxybenzonitrile (2.728 g, 23 mmol, 4.25 equiv.) dissolved in THF (18 mL) was rapidly added to a stirred suspension of $NaBH_4$ (0.205 g, 5.4 mmol, 1 equiv.) in THF (24 mL) at 0 °C. The resulting suspension was heated to reflux for three hours. A colorless solid was obtained after filtration and removal of the solvent in vacuo. This crude product was washed two times with Et_2O (10 mL) to remove the excess 4-hydroxybenzonitrile. The pure product was dried for six hours in vacuo at 70 °C; yield 1.56 g (67%); decomp. (DSC): (onset) 362.1 °C. $C_{28}H_{16}B\ N_4NaO_4$ (506.26): calcd. C 66.43, H 3.19, N 11.07; found C 66.10, H 3.39, N 10.25. ^{1}H NMR ([d$_6$]DMSO, 300 MHz, 25 °C): δ = 7.55–7.45 (m, 8 H, C*H*–CCN), 7.12–7.04 (m, 8 H, C*H*–C–O) ppm. ^{13}C NMR (CD_3CN, 250 MHz, 25 °C): δ = 165.3 (s, 1 C, *C*O), 133.1 (s, 1 C, *C*–C–CN), 119.4.6 (s, 1 C, *C*N), 119.1 (s, 1 C, *C*-C-O), 100.6 (s, 1 C, *C*–CN) ppm. ^{11}B NMR (CD_3CN, 300 MHz, 25 °C): δ = 2.55 (s) ppm.

Ag[Al(O–C_6H_4–CN)$_4$] (3): Lithium tetrakis-(4-cyanophenyl)aluminate (4 mmol, 2.0255 g) and silver triflate (4.5 mmol, 1.1562 g) were each dissolved in acetonitrile (40 mL). The silver salt solution was added to the stirred aluminate solution through a dropping funnel at ambient temperature. The turbid deep red solution was filtered, and the volume of the solvent was reduced to ca. 40mL and filtered again. The microcrystalline product was crystallized overnight in a freezer at –30 °C from the clear red solution. The solvent was removed by decantation and the product was dried in vacuo for 2 h. After powdering and drying again for 2 h in high vacuum a light red-gray powder was obtained; yield 1.038 g (42.71% with respect to Al); decomp. (DSC): (onset) 243 °C. $C_{28}H_{16}AlAgN_4O_4$ (607.31): calcd. C 55.38, H 2.66, N 9.23; found C 54.57, H 2.49, N 8.84. ^{1}H NMR (CD_3CN, 300 MHz, 25 °C): δ = 7.50–7.42 (m, 8 H, C*H*–C–CN), δ = 6.89–6.81 (m, 8 H, C*H*–C–O) ppm. ^{13}C NMR (CD_3CN, 300 MHz, 25 °C): δ = 164.6 (s, 1 C, *C*O), 135.0 (s, 1 C, *C*–C–CN), 120.7 (s, 1 C, *C*N), 119.7 (s, 1 C, *C*–C–O), 101.6 (s, 1 C, *C*–CN) ppm.

Cu[Al(O–C_6H_4–CN)$_4$](4): A solution of Ag[Al(O–C_6H_4–CN)$_4$] (607.3 mg, 1 mmol) in acetonitrile (40 mL) was added to a stirred yellow colored solution of CuI (190.4 mg, 1 mmol) in acetonitrile (15 mL) at ambient temperature. A white precipitate was formed, and the solution turned slightly green. The reaction mixture was allowed to stir for ten minutes, and the precipitate was allowed to settle out. The solution was filtered and the residue was washed with acetonitrile (15mL). The solution was filtered again, and the solvent was removed under reduced pressure. The white solid was dried for twelve hours at ambient temperature to yield the desired product (316.6 mg, 51% yield). Dec (DSC): (Onset) 281 °C. $C_{28}H_{16}AlCuN_4O_4$ (562.89): calcd. C 59.74, H 2.86, N 9.95; found C 58.84, H 3.44, N 9.65. ^{1}H NMR (CD_3CN, 250 MHz, 25 °C): δ = 7.50–7.41 (m, 8 H, C*H*–C–CN), 6.90–6.82 (m, 8 H, C*H*–C–O) ppm. ^{13}C NMR (CD_3CN, 250 MHz, 25 °C): δ = 164.9 (s, 1 C, *C*O), 135.0 (s, 1 C, *C*–C–CN), 121.1 (s, 1 C, *C*N), 120.7 (s, 1 C, *C*–C–O), 101.4 (s, 1 C, *C*–CN) ppm.

Li[Al(O–C_6F_4–CN)$_4$] (5): 4-Hydroxy-2,3,5,6-tetrafluorobenzonitrile (5.52 g, 28.87 mmol, 4.2 equiv.) dissolved in THF (18 mL) was added slowly to a stirred solution of activated $LiAlH_4$ (0.26 g, 6.87 mmol, 1 equiv.) in THF (24 mL) at 0 °C. The resulting solution was heated to reflux for two hours. The solution was filtered, and the solvent was removed in vacuo to yield the desired product as a colorless solid. This crude product was washed two times with CH_2Cl_2 (10 mL) to remove the excess 4-hydroxy-2,3,5,6-tetrafluorobenzonitrile. The pure product was dried for ten hours in vacuo at 80 °C; yield 3.5 g (64.16%). M.p. (DSC): (onset) 271.2 °C, (peak) 281.4 °C; dec. (onset) 361 °C. $C_{28}AlF_{16}LiN_4O_4$ (794.23): calcd. C 42.34, N 7.05; found C 42.15, N 6.75. ^{13}C NMR (CD_3CN, 300 MHz, 25 °C): δ = 149.1 (dm, $^1J_{C,F}$ = 251.7 Hz, 1 C, *C*F–CO), 145.2 (m, 1 C, *C*O), 141.2 (dm, $^1J_{C,F}$ = 242.2 Hz, 1 C, *C*F–CCN), 109.7 (t, $^3J_{C,F}$ = 3.6 Hz, 1 C, *C*N), 84.9 (m, 1 C, *C*–CN) ppm. ^{19}F NMR (CD_3CN, 282.4 MHz, 25 °C): δ = –139.1 (d, $^1J_{C,F}$ = 11.23 Hz, 8 F), –161.4 (d, $^1J_{C,F}$ = 14.83 Hz, 8 F) ppm.

Na(O–C_6F_4–CN) (6): To a stirred suspension of $NaBH_4$ (0.257 g, 6.75 mmol, 1 equiv.) in THF (24 mL), cooled to 0 °C, 4-hydroxy-2,3,5,6-tetrafluorobenzonitrile (5.435 g, 28.5 mmol, 4.2 equiv.) dissolved in freshly distilled THF (18 mL) was added. The resulting suspension was heated to reflux for three hours. The suspension was filtered, and the solvent was removed in vacuo to give a colorless solid. The solid was washed two times with freshly distilled Et_2O (10 mL) to remove the excess 4-hydroxy-2,3,5,6-tetrafluorobenzonitrile; decomp. (DSC): (onset) 366.56 °C, (peak) 371.11 °C. C_7F_4NNaO (213.07): calcd. C 39.46, N 6.57; found C 39.40 N 6.20. ^{13}C NMR ([D$_6$]DMSO, 75.5 MHz, 25 °C): δ = 153.7 (d, $^1J_{C,F}$ = 260.4 Hz, 2 C, *C*–CO), 146.9 (tt, $^2J_{C,F}$ = 13.9, $^3J_{C,F}$ = 4.5 Hz, 1 C, *C*O), 140.3 (d, $^1J_{C,F}$ = 247.6 Hz, 2 C, *C*–CN), 112.7 (t, $^3J_{C,F}$ = 3.77 Hz, 1 C, *C*N), 63.4 (t, $^2J_{C,F}$ = 18.1 Hz, 1 C, *C*–CN). ^{19}F NMR ([D$_6$]DMSO, 282.4 MHz, 25 °C, ppm): δ = –144.8 (m, 2 F), –167.7 (m, 2 F) ppm.

(THF)Al[O–C_6H_4–CN·B(C_6F_5)$_3$]$_3$ (7): To a stirred solution of B(C_6F_5)$_3$ (2.56 g, 5 mmol, 5 equiv.) in THF (50 mL), solid Li[Al(O–C_6H_4–CN)] (0.505 g, 1 mmol, 1 equiv.) was added in one portion and the resulting solution was stirred overnight. Removal of the solvent yielded a colorless solid, which was washed two times with *n*-hexane (50 mL). The residual *n*-hexane was removed in vacuo, and the solid was dissolved in Et_2O (20 mL). The resulting solution was filtered and concentrated to 6 mL. Storage over 48 h at 7 °C resulted in the precipitation of (THF)$_2$Al[O–C_6H_4–CN·B(C_6F_5)$_3$]$_3$; yield 0.6 g (31%). For analytical experiments the solid was dried in vacuo for six hours at 70 °C and (THF)Al{O–C_6H_4–CN·B(C_6F_5)$_3$}$_3$ was obtained; decomp. (DSC): (onset) 136.8 °C. $C_{79}H_{20}AlB_3F_{45}N_3O_4$ (1989.37): calcd. C 47.70, H 1.01, N, 2.11; found C 47.43, H 1.33, N 1.71. ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ = 7.54–7.48 (m, 6 H, C*H*–C–CN), 6.77–6.71 (m, 6 H, C*H*–CO) ppm. ^{13}C NMR ($CDCl_3$, 300 MHz, 25 °C): δ = 166.4 (s, 3 C, *C*O), 147.2 (m, 6 C, *C*F–CB), 139.7 (m, 3 C, *C*F–CF–CF–CB), 136.3 (m, 6 C, *C*F–CF–CB), 136.0 (s, 6 C, *C*H–C–CN), 120.4 (s, 6 C, *C*H–CO), 115.6 (s, 3 C, *C*N), 114.9 (br., 3 C, *C*–B), 92.2 (s, 3 C, C–CN) ppm. ^{19}F NMR ($CDCl_3$, 282 MHz, 25 °C): δ = –135.1 to –135.2 (m, 6 F, C*F*–CB), –157.9 (t, $^3J_{F,F}$ = 20.3 Hz, 3 F, C*F*–CF–CF–CB), –164.7 to –164.8 (m, 6 F, C*F*–CF–CB) ppm. ^{11}B NMR ($CDCl_3$, 96 MHz, 25 °C): δ = –11.7 (s, 3 B) ppm.

$Na[(F_5C_6)_3B\cdot O{-}C_6H_4{-}CN\cdot B(C_6F_5)_3]$ (8a): A Schlenk flask was loaded with $B(C_6F_5)_3$ (2.56 g, 5 mmol, 5 equiv.) and $Na[B(O{-}C_6H_4{-}CN)]$ (0.505 g, 1 mmol, 1 equiv.). To this mixture Et_2O (50 mL) was added to obtain a suspension. The suspension was stirred overnight and a colorless solution was obtained. After removal of the solvent in vacuo a solid was obtained, which was washed three times with *n*-hexane (20 mL). The residual *n*-hexane was removed in vacuo, and the solid was dissolved in Et_2O (15 mL). The resulting solution was filtered and concentrated to 5 mL. Colorless crystals of $[Na(Et_2O)_4][(F_5C_6)_3B\cdot O{-}C_6H_4{-}CN\cdot B(C_6F_5)_3]$ suitable for X-ray crystallographic analysis were grown by storage at –30 °C overnight. The crystallized product was dried in vacuo for six hours at 70 °C to give the solvent-free product $Na[(F_5C_6)_3B\cdot O{-}C_6H_4{-}CN\cdot B(C_6F_5)_3]$ for analytical experiments; yield 0.25 g (21%). M.p. (DSC): (onset) 154.7 °C, (peak) 164.4 °C; dec. (onset) 303.9 °C. $C_{51}H_{28}B_2F_{30}NNaO_5$ (1349.3): calcd. C 45.40, H 2.09, N 1.04; found C 45.22, H 1.46, N 1.04. ^1H NMR ($CDCl_3$, 300 MHz, 25 °C, ppm): δ = 7.71–7.47 (m, C*H*–C–CN, 2 H), 6.96–7.78 (m, 2 H, C*H*–CO). ^{13}C NMR ($CDCl_3$, 300 MHz, 25 °C, ppm): δ = 163.5 (s, 1C, *C*–O), 148.0 (m, 12C, *C*F–CB), 139.5 (m, *C*F–CF–CF–CB, 6C), 137.4 (m, 12C, *C*F–CF–CB), 136.6 (s, 2C, *C*H–C–CN), 117.8 (s, 2C, *C*H–CO), 115.0 (br., 6C, *C*–B), 114.7 (s, 1C, *C*N), 96.3 (s, 1C, *C*–CN). ^{19}F NMR ($CDCl_3$, 300 MHz, 25 °C): δ = –134.4 to –134.5 (m, 12 F, C*F*–CB), –156.2 (t, 6 F, C*F*–CF–CF–CB, $^3J_{F,F}$ = 19.3 Hz), –163.2 to –163.4 (m, 12 F, C*F*–CF–CB). ^{11}B NMR ($CDCl_3$, 300 MHz, 25 °C): δ = –11.7 (s, 1B, *B*·NC), –2.9 (s, 1B, *B*·O).

$Li[NC{-}C_6F_4{-}O{-}Al\{O{-}C_6F_4{-}CN\cdot B(C_6F_5)_3\}_3]$ (9): A Schlenk flask was loaded with $B(C_6F_5)_3$ (1.03 g, 2 mmol, 4 equiv.) and $Li[Al(O{-}C_6F_4{-}CN)]$ (0.4 g, 0.5 mmol, 1 equiv.). To this mixture Et_2O (25 mL) was added to obtain a suspension. The suspension was stirred overnight and a colorless solution was obtained. The solution was filtered and the volume of the solvent reduced to 10 mL. Storage at –40 °C overnight gave colorless crystals of $[(Et_2O)_3Li][(NC{-}C_6F_4{-}O)Al\{O{-}C_6F_4{-}CN{-}B(C_6F_5)_3\}_3]$ suitable for X-ray crystallographic analysis. The crystallized product was dried in vacuo for six hours at 70 °C to give the solvent-free product $Li[(NC{-}C_6F_4{-}O)Al\{O{-}C_6F_4{-}CN{-}B(C_6F_5)_3\}_3]$ for analytical experiments; yield 0.86 g (74%); decomp. (DSC): (onset) 318.7 °C. $C_{82}AlB_3F_{61}LiN_4O_4$ (2330.17): calcd. C 42.27, N 2.40; found C 41.92, N 1.81. ^{13}C NMR ($CDCl_3$, 300 MHz, 25 °C, ppm): δ = 151.23 (m, 1C, *C*F–C–CN), 149.83 (m, *C*O), 148.24 (dm, *C*F–C–B), 145.93 (dm, *C*F–CF–CF–CB), 142.87 (m, *C*F–CO), 137.53 (dm, *C*F–CF–CB), 107.92 (m, *C*N). ^{19}F NMR ($CDCl_3$, 300 MHz. 25 °C, ppm): δ = –130.93 (s), –133.78 (s), –155.82 (s), –156.46 (s), –163.19 (s). ^{11}B NMR ($CDCl_3$, 300 MHz, 25 °C): δ = 2.5 to –41.5 (br).

CCDC-901962 (for **1**), -901963 (for **5**), -901964 (for **3**), -901965 (for **4**), -901966 (for **7**), -901967 (for **2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Details of crystallography experiments, figure showing the interpenetration in the solid state structure of **4**, IR and Raman spectroscopic data.

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[43] Fluorinated species **8b** was prepared for comparison from Na[O–C_6F_4–CN] and B(C_6F_5)$_3$.

[44] IR and Raman data can be found in the Supporting Information.

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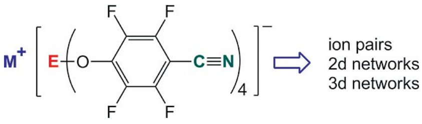
Coordination Polymer Networks

Tetrahedral [E(O–C_6X_4–CN)$_4$]$^-$ anions (E = B, Al; X = H, F) were synthesized and used as anionic linkers for the generation of 2D and 3D crystalline coordination polymer networks.



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Molecular Networks Based on CN Coordination Bonds

Keywords: Coordination polymers / Aluminates / Borates / Silver / Copper / Bridging ligands