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Structure and Bonding of Tetracyanopyrrolides

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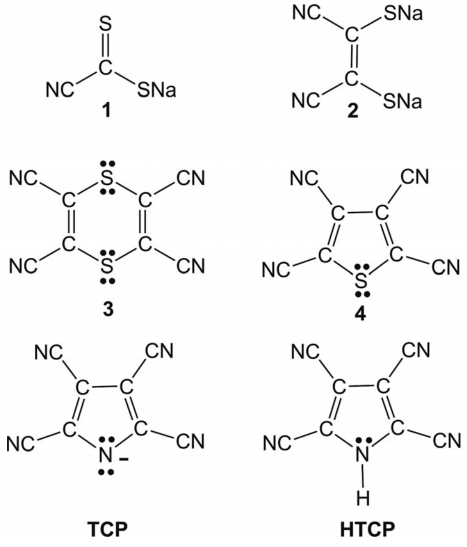
Salts bearing the tetracyanopyrrolide anion (TCP) were synthesized from tetracyano-1,4-dithiin and sodium azide according to a modified synthetic protocol. The solid-state structures of HTCP, MeTCP, Me_4NTCP, NaTCP, and the ionic liquid EMIMTCP (EMIM = 1-ethyl-3-methylimidazolium) are discussed for the first time. According to experimental and computational data, the TCP anion can be regarded as a pseudohalide with π bonds highly delocalized over the entire anion including the four cyano groups. The planar anion is C_{2v} symmetric and represents a multifunctional binary CN ligand, which is capable of forming classic coordination bonds through the lone pairs of the CN groups or the ring nitrogen atom. In addition, noncovalent interactions such as π–π interactions are found and can be used to strengthen structural and electronic communication between organic ligands.

Introduction

The chemistry of thiacyanocarbons (Scheme 1) was developed by Bähr and Schleitzer as early as 1955–1957.[1] They started from CS_2 and NaCN to yield sodium cyanodithioformiate, which dimerizes under oxidizing conditions to give disodium dimercaptomaleodinitrile (**2**) as shown in Scheme 2. Both **1** or **2** can be oxidized to afford tetracyano-1,4-dithiin (**3**) in high yield.[1,2] The reactive dithiin **3** extrudes sulfur at elevated temperatures to give tetracyanothiophene **4**, and also undergoes a remarkable reaction with sodium azide in ethanol (Scheme 2) at 25 °C to form sodium tetracyanopyrrolide (NaTCP).[3,4]

The free acid (HTCP) of the TCP ion is easily obtained by ion exchange utilizing acidic Amberlite resin. HTCP, which is a medium strong acid,[15] forms salts bearing the tetracyanopyrrolide anion (TCP) upon addition of strong bases such as MOH (M = R_4N, alkali metal) or even ammonia.[5]



Scheme 1. Thiacyanocarbons and tetracyanopyrrolides.

The parent anion of TCP, the pyrrolide anion $[H_4C_4N]^-$ is composed of a five-membered ring with six delocalized π electrons and represents a strong base (pK_b = –3.51). In comparison, pyrrole, the corresponding acid, is a very weak acid (pK_a = 17.51).[6] Substitution of all four H atoms by cyano groups in $[H_4C_4N]^-$ dramatically decreases the basicity of the anion (pK_b = 11.29) and thus its conjugate acid HTCP represents a medium–strong acid (pK_a = 2.71),[15] This situation resembles the situation in nonlinear resonance-stabilized pseudohalides such as in the tricyanomethanide anion $[C(CN)_3]^-$[7] or dicyanoamide $[N(CN)_2]^-$[8] compared to $[CH_3]^-$ and $[NH_2]^-$.[9] The pseudohalogen concept can be generalized and extended to planar highly delocalized heterocycle anions such as tetracyanopyrrolide or the five-membered ring anion $[CS_2N_3]^-$,[10,11] which can be obtained in the reaction of carbon disulfide and sodium azide as shown by Sommer[12] in 1915. Such heterocyclic anions can also be classified as pseudohalides when they fulfill the well-known criteria with respect to halogen-like chemical behavior:[13,14] a pseudohalogen (X) forms a singly charged anion (X^-), a pseudohalogen hydrogen acid of the type HX, and low solubility salts of the type $M(X)_n$ with

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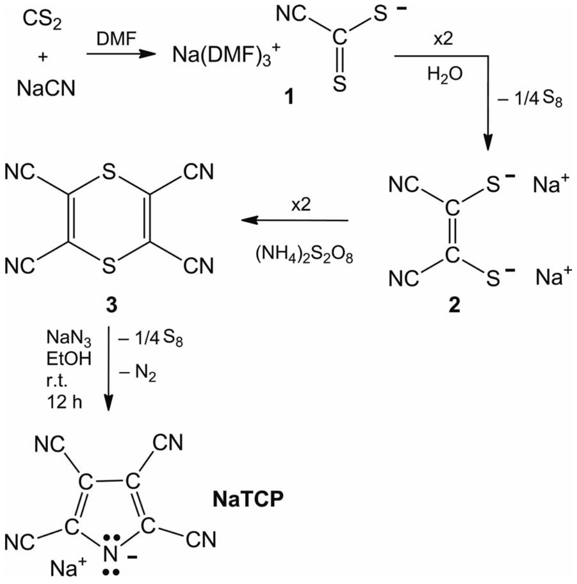


Scheme 2. Synthesis of sodium tetracyanopyrrolide (NaTCP).

silver, lead and mercury, etc. However, not all criteria are always met. In case of TCP it is already known that it forms a low solubility silver salt AgTCP.[15]

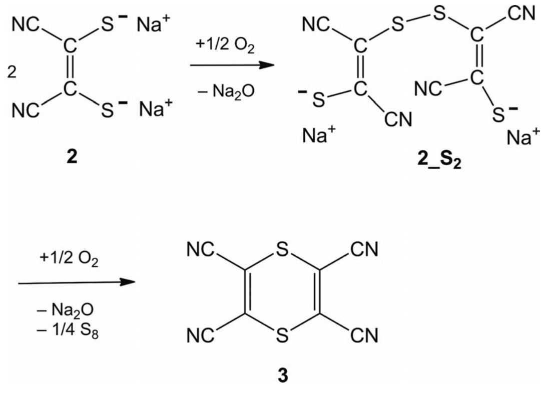
We report here on the (modified) syntheses and full characterization of tetracyanopyrrolide-based compounds along with their first structural characterization including the starting materials and the thiacyanocarbons **2** and **3**. The structure and bonding of the tetracyanopyrrolides are discussed on the basis of the pseudohalogen concept.

Results and Discussion

The TCP anion belongs to the class of resonance stabilized binary CN anions such as tricyanomethanide $[C(CN)_3]^-$,[7] dicyanoamide $[N(CN)_2]^-$, or its trimerization product the melaminate $[C_3N_6(CN)_3]^{3-}$.[8,16,17] In the last decade, these anions have been the object of great interest by several groups,[14,16,18,19–22] especially in the fields of solid state chemistry and coordination chemistry.[16,18,19] Thus, it is was vital to have a feasible high-yielding synthesis and to find ways to obtain single crystals suitable for a single crystal structure elucidation.

Synthesis

The starting material for the synthesis of TCP salts, dithiin **3**, can be generated in a three-step synthesis. The pathway as shown in Scheme 2 involves the synthesis of sodium cyanodithioformiate (**1**), which is obtained in good yields (>68%) as a DMF solvate. Slow decomposition of **1** occurs at slightly elevated temperatures (> 80 °C) in the solid state. Conversion of **1** into the dithiolate **2** is easily achieved in $CHCl_3$ (yield > 88%) under reflux conditions. Compound **2** is easily prepared in bulk, almost indefinitely stable when stored in a sealed tube under argon, and decomposes at temperatures above 374 °C. However, when **2** was stored in air, slow oxidation to yield the disulfide species **2_S$_2$** was observed as depicted in Scheme 3. Compound **2_S$_2$** could be isolated and characterized by X-ray crystallography (Figure 1). The final product of the oxidation process is dithiin **3**. A much better alternative for the synthesis of dithiin **3** is the direct oxidation of **2** in H_2O with ammonium peroxodisulfate as shown in Scheme 2 (yield >60%, Figure 2). Decomposition of **3** starts at 170 °C with the release of sulfur.



Scheme 3. Stepwise oxidation of **2**.

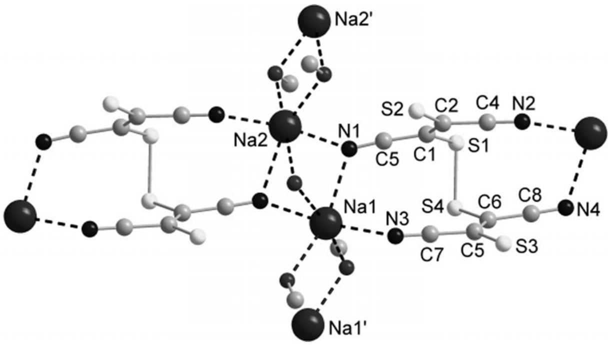


Figure 1. Molecular structure of $[Na(MeOH)_{1.5}]_2[C_8N_4S_4]$ (**2_S$_2$**). Parts of the MeOH molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: S1–C1 1.753(2), S1–S4 2.1031(7), S2–C2 1.689(2), S3–C5 1.695(2), S4–C6 1.755(2), C1–C2 1.377(3), C1–C3 1.421(3), C2–C4 1.454(3), C5–C6 1.377(3), C5–C7 1.459(3), C6–C8 1.426(3), N1–C3 1.148(2), N2–C4 1.144(2), N3–C7 1.143(2), N4–C8 1.149(2); C1–S1–S4 100.81(6), C6–S4–S1 99.96(7), C2–C1–C3 118.0(2), C2–C1–S1 124.7(1), C3–C1–S1 117.3(2), C5–C6–S4 124.1(1), C8–C6–S4 117.8(2), N3–C7–C5 177.1(2), N4–C8–C6 177.9(2).

Starting from dithiin **3**, different routes to salts bearing the TCP^- ion were checked (Schemes 2 and 4). For practical reasons it is best to react tetracyano-1,4-dithiin with an equimolar amount of sodium azide in ethanol but without isolating NaTCP. Once the release of nitrogen is finished, the dark red reaction mixture is filtered to remove elemental sulfur. The filtrate is evaporated to dryness and re-dissolved in water. This aqueous filtrate is decolorized with activated charcoal, and tetramethylammonium chloride is added as a saturated aqueous solution. The immediate precipitation of Me_4NTCP is observed. Pure NaTCP can now be generated by utilization of an ion-exchange resin column. A similar

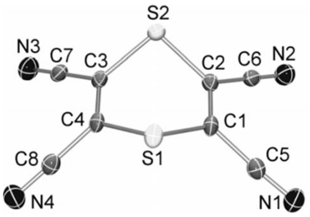
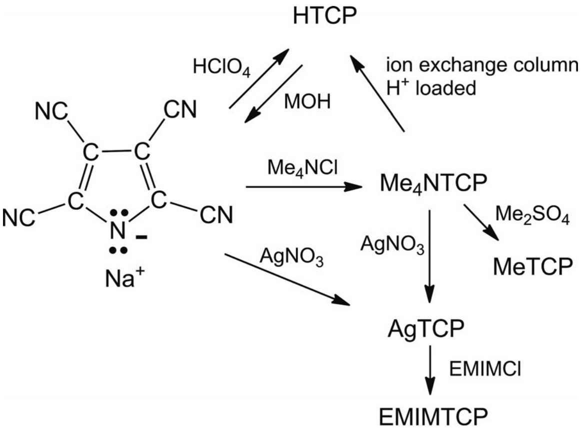


Figure 2. ORTEP drawing of the molecular structure of **3**. Thermal ellipsoids with 50% probability at 173 K. Selected bond lengths [Å] and angles [°]: S1–C1 1.762(2), S1–C4 1.763(2), S2–C2 1.762(2), S2–C3 1.763(2), C1–C2 1.341(2), C1–C5 1.437(2), C2–C6 1.434(2), C3–C4 1.338(2), C3–C7 1.434(2), C4–C8 1.433(2), N1–C5 1.142(2), N4–C8 1.141(2), N2–C6 1.144(2), N3–C7 1.139(2); C1–S1–C4 96.95(8), C4–C3–S2 121.7(1), C2–S2–C3 97.24(8), C2–C1–C5 120.5(2), C2–C1–S1 121.70 (13), C5–C1–S1 117.8(1), N1–C5–C1 176.6(2), N2–C6–C2 176.8 (2), N3–C7–C3 179.4(2), N4–C8–C4 178.1(2).

procedure can be used to prepare HTCP when the ion exchange column is loaded with H^+ instead of Na^+. Moreover, HTCP can be obtained from NaTCP upon addition of $HClO_4$. Methylation of the TCP ion in Me_4NTCP by means of Me_2SO_4 yields MeTCP. The low solubility silver salt AgTCP can be generated from NaTCP or Me_4NTCP dissolved in a water/acetone mixture when $AgNO_3$ is added.



Scheme 4. Synthesis of TCP compounds.

As ionic liquids are increasingly receiving attention because of their wide spectrum of applications (as reaction media, as lubricants, or as electrolytes particularly for solar and fuel cells),[23–31] the EMIM (1-ethyl-3-methylimidazolium) salt of TCP was also prepared and fully characterized. By a salt metathesis reaction, the silver salt can be transferred into EMIMTCP, an ionic liquid with a melting point of 30 °C {cf. $EMIM_3[C_3N_6(CN)_3]$: –20 °C,[17] $EMIM[N(CN)_2]$: –12 °C[32]}. EMIMTCP is thermally stable to over 230 °C {cf. $EMIM_3[C_3N_6(CN)_3]$: 253 °C,[17] $EMIM[N(CN)_2]$: 275 °C[33]}. The melting and decomposition points of all TCP species along with selected vibrational data are summarized in Table 1. The IR and Raman data of all considered TCP species show sharp bands in the expected region between 2217–2256 cm^{-1}, which can be assigned to the υ_{CN} stretching frequencies.

Table 1. Melting points, decompositions points [°C], and IR/Raman data of the υ_{CN} stretching modes [cm^{-1}].

	M.p. [°C]	$T_{dec.}$ [°C]	IR υ_{CN} [cm^{-1}]	Raman υ_{CN} [cm^{-1}]
NaTCP	401	>600	2241(sh), 2226(s)	2247(10)
Me_4NTCP	119	423	2220(s)	2228(10), 2229(sh)
EMIMTCP	30	230	2225(s), 2217(s)	2230(10)
HTCP	202	202	2251(s), 2241(s)	2256(10)
MeTCP	187	362	2242(s), 2236(s)	2245(10)

X-ray Crystallography

As far as we know there are no structural data available of the starting material or of any TCP species. The structures of the starting materials as well of the TCP species HTCP, $HTCP{\cdot}2H_2O$, NaTCP, MeTCP, Me_4NTCP, and the ionic liquid EMIMTCP have been determined. Tables 2, 3, and 4 present the X-ray crystallographic data. X-ray quality crystals of all considered species were selected in Kel-F-oil (Riedel deHaen) or Fomblin YR-1800 (Alfa Aesar) at ambient temperature. All samples were cooled to –100(2) °C during the measurement.

Table 2. Crystallographic details of **1**, **2_S₂**, and dithiin **3**.

	1	**2_S₂**	**3**
Formula	$C_{11}H_{21}N_4NaO_3S_2$	$C_{11}H_{12}N_4Na_2O_3S_4$	$C_8N_4S_2$
Fw [$g\,mol^{-1}$]	344.43	422.47	216.24
Color	yellow	orange	brown
Cryst. system	hexagonal	triclinic	monoclinic
Space group	$P\bar{6}2c$	$P\bar{1}$	$P2_1/n$
a [Å]	12.5185(6)	8.6772(3)	6.8962(3)
b [Å]	12.5185(6)	9.9270(4)	18.3391(7)
c [Å]	6.4790(4)	13.0318(5)	6.9796(3)
α [°]	90	96.233(2)	90
β [°]	120	106.649(2)	90.345(2)
γ [°]	90	112.217(2)	90
V [$Å^3$]	879.31(7)	965.40(6)	882.69(6)
Z	2	2	4
μ [mm^{-1}]	0.34	0.55	0.56
λ Mo-K_α [Å]	0.71073	0.71073	0.71073
T [K]	173	173	173
Measured refl.	6609	28721	8219
Ind. refl.	1000	6151	2111
Refl. with $I > 2\sigma(I)$	848	3960	1610
$R_{int.}$	0.029	0.064	0.031
$F(000)$	364	432	432
R_1 {$R[F_2 > 2\sigma(F_2)]$}	0.033	0.043	0.033
wR_2 (all data)	0.075	0.094	0.071
GooF	1.06	1.02	1.06
Parameters	54	239	127
CCDC	891163	891164	891165

The molecular structures of disulfide species **2_S₂**, dithiin species **3**, and all TCP species are shown in Figures 1, 2, 3, 4, 5, 6, 7, 8, and 9, along with selected bond lengths and angles. More details are found in the Supporting Information including the data for compound **1**, **2**, and **2_S₂**.

Table 3. Crystallographic details of HTCP, HTCP·2H_2O, and MeTCP.

	HTCP	HTCP·2H_2O	MeTCP
Formula	C_8HN_5	C_8HN_5·2H_2O	$C_9H_3N_5$
Fw [g mol^{-1}]	167.14	203.17	181.16
Color	colorless	colorless	colorless
Cryst. system	orthorhombic	orthorhombic	orthorhombic
Space group	$Pna2_1$	$Pna2_1$	$Pca2_1$
a [Å]	11.4239(4)	13.854(3)	12.667(1)
b [Å]	7.5869(3)	10.023(2)	6.4604(7)
c [Å]	9.6957(3)	6.858(2)	10.9375(9)
α [°]	90	90	90
β [°]	90	90	90
γ [°]	90	90	90
V [Å^3]	840.35(5)	952.3(4)	895.1(1)
Z	4	4	4
μ [mm^{-1}]	0.09	0.11	0.09
λ Mo-K_α [Å]	0.71073	0.71073	0.71073
T [K]	173	173	173
Measured refl.	14732	6106	7164
Indep. refl.	2483	2283	2462
Refl. with $I > 2\sigma(I)$	2258	1549	2101
$R_{int.}$	0.029	0.054	0.027
$F(000)$	336	416	368
R_1 $\{R[F_2 > 2\sigma(F_2)]\}$	0.036	0.043	0.037
wR_2 (all data)	0.083	0.089	0.089
GooF	1.07	0.95	1.09
Parameters	123	156	129
CCDC	911668	891167	891168

Table 4. Crystallographic details of Me_4NTCP, EMIMTCP and NaTCP·2.33(THF).

	Me_4NTCP	EMIMTCP	NaTCP·2.33THF
Formula	$C_{12}H_{12}N_6$	$C_{14}H_{11}N_7$	C_8N_5Na·2.33C_4H_8O
Fw [g mol^{-1}]	240.28	277.30	357.36
Color	colorless	colorless	colorless
Cryst. system	orthorhombic	monoclinic	triclinic
Space group	$Cmca$	$P2_1/c$	$P\bar{1}$
a [Å]	6.6339(5)	7.1996(4)	12.6752(3)
b [Å]	20.819(2)	11.4526(5)	15.2851(4)
c [Å]	19.878(1)	17.5271(9)	17.3205(5)
α [°]	90	90	67.384(1)
β [°]	90	92.885(2)	70.118(1)
γ [°]	90	90	72.894(1)
V [Å^3]	2745.4(3)	1443.4(1)	2861.0(1)
Z	8	4	6
μ [mm^{-1}]	0.08	0.09	0.11
λ Mo-K_α [Å]	0.71073	0.71073	0.71073
T [K]	173	173	173
Measured refl.	4349	11495	70690
Indep. refl.	989	2805	15118
Refl. with $I > 2\sigma(I)$	698	2251	10313
$R_{int.}$	0.037	0.034	0.049
$F(000)$	1008	576	1124
R_1 $\{R[F_2 > 2\sigma(F_2)]\}$	0.042	0.056	0.044
wR_2 (all data)	0.104	0.154	0.127
GooF	1.02	1.08	1.07
Parameters	107	217	919
CCDC	891169	891170	891171

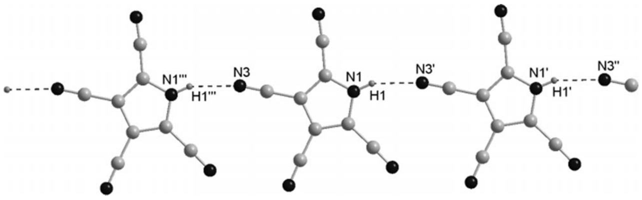


Figure 3. Hydrogen bonding in solvent free HTCP [d(N1···N3′) = 2.897 Å] leading to planar chains of HCTP molecules.

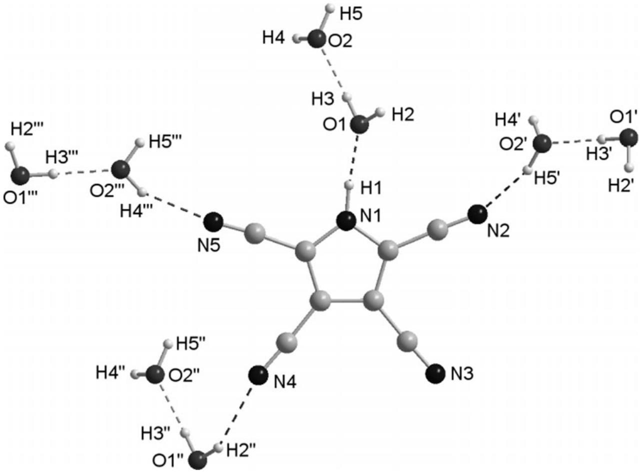


Figure 4. Ball-and-stick representation of HTCP·2H_2O displaying hydrogen bonding around one TCP ion. Selected bond lengths [Å] and angles [°]: N1–C4 1.348(3), N1–C1 1.361(3), N2–C5 1.136(3), N3–C6 1.145(3), N4–C7 1.145(3), N5–C8 1.140(3), C1–C2 1.389(3), C1–C5 1.422(3), C2–C3 1.410(3), C2–C6 1.423(3), C3–C4 1.380(3), C3–C7 1.428(3), C4–C8 1.423(3), O1···O2 2.703(3); C4–N1–C1 108.2(2), N1–C1–C2 109.2(2), N1–C1–C5 122.2(2), C2–C1–C5 128.6(2), C1–C2–C3 106.1(2), C1–C2–C6 124.7(2), C3–C2–C6 129.1(2), C4–C3–C2 106.8(2), C4–C3–C7 124.5(2), C2–C3–C7 128.7(2), N1–C4–C3 109.7(2), N1–C4–C8 124.0(2), C3–C4–C8 126.3(2), N2–C5–C1 178.0(3), N3–C6–C2 178.0(3), N4–C7–C3 177.2(3), N5–C8–C4 175.8(3).

Sulfide Bridged 2_S_2

Compound **2_S_2** was recrystallized from MeOH to yield $[Na(MeOH)_{1.5}]_2[C_8N_4S_4]$. Compound **2_$S_2$** crystallizes in the triclinic space group $P\bar{1}$ with two formula units per unit cell (Figure 1). The sodium cations are octahedrally coordinated by three O atoms of the MeOH solvent molecules and three N atoms of the cyano groups leading to a two-dimensional network. A slightly distorted C_2 symmetry is found for the $[C_8N_4S_4]^{2-}$ anion with two almost planar $C_4N_2S_2$ moieties linked by the S–S bridge [d(S1–S4) = 2.1031(7) Å cf. Σr_{cov}(S–S) = 2.06 Å].[34] Both cyano groups are part of these planes. The sulfur–carbon bond lengths amount to 1.762–1.763 Å, in accord with a typical S–N single bond [cf. Σr_{cov}(S–N) = 1.78 Å].[34] All C–CN units are almost linear with angles between 177–179°.

Dithiin 3

The molecular compound **3** crystallizes in the monoclinic space group $P2_1/n$ (Z = 4, see Figure 1). There are only four

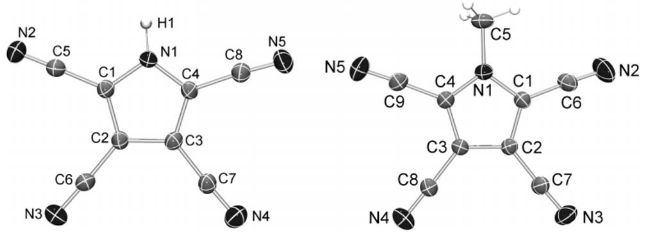


Figure 5. ORTEP drawing of the molecular structure of HTCP (left) and MeTCP (right). Thermal ellipsoids with 50% probability at 173 K. Selected bond lengths [Å] and angles [°]: HTCP: N1–C1 1.354(2), C1–C2 1.384 (2), N1–C4 1.354(2), C1–C5 1.424(2), C2–C3 1.412(2), N2–C5 1.140(2), C2–C6 1.429(2), N3–C6 1.139(2), C3–C4 1.386(2), N4–C7 1.144(2), C3–C7 1.422(2), N5–C8 1.143(2), C4–C8 1.424(2); N1–C4–C3 108.9(1), N1–C1–C2 108.52(9), N1–C4–C8 123.5(1), N1–C1–C5 123.5(1), C3–C4–C8 127.6(1), C2–C1–C5 128.0(1), N2–C5–C1 176.0 (1), C1–C2–C3 107.0(1), N3–C6–C2 179.9(2), C1–C2–C6 125.8(1), N4–C7–C3 177.9(1), C3–C2–C6 127.2(1), N5–C8–C4 177.2(1); MeTCP: N1–C4 1.353(2), N1–C1 1.361(2), N1–C5 1.465(2), N2–C6 1.137(2), N3–C7 1.137(2), N4–C8 1.136(2), N5–C9 1.137(2), C1–C2 1.376(2), C1–C6 1.419(2), C2–C3 1.406(2), C2–C7 1.419(2), C3–C4 1.381(2), C3–C8 1.421(2), C4–C9 1.422(2); C4–N1–C1 108.1(1), C4–N1–C5 125.5(1), C1–N1–C5 126.3(1), N1–C1–C2 109.1(1), N1–C1–C6 123.0(1), C2–C1–C6 127.9(1), C1–C2–C3 106.9(1), C1–C2–C7 124.5(1), C3–C2–C7 128.6(1), N2–C6–C1 177.4(2), N3–C7–C2 177.2(2), N4–C8–C3 177.4(2), N5–C9–C4 177.4(2).

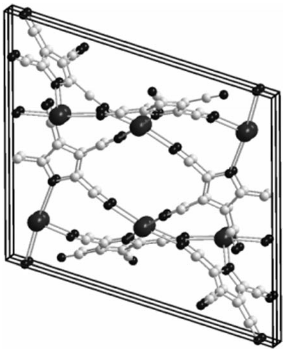


Figure 6. View along the *a* axis in NaTCP displaying layers with no significant interactions between these layers (THF molecules omitted for clarity).

weak S···NC van der Waals interactions with intermolecular distances between 3.27–3.4 Å [cf. $\Sigma r_{\mathrm{vdW}}(\mathrm{S}\cdots\mathrm{N})$ = 3.4 Å].[35] A slightly distorted C_{2v} symmetry is found for **3** with a strongly folded central six-membered S_2C_4 ring (<C1–C2–S2–C3 45.03°). Both S_2C_2 moieties are planar (deviation from planarity <0.6°). Interestingly, both cyano groups are also part of these planes. The sulfur–carbon bond lengths are in the range 1.762–1.763 Å, in accord with a typical single bond [cf. $\Sigma r_{\mathrm{cov}}(\mathrm{S{-}C})$ = 1.78 Å]. The C–C bonds within the ring amount to 1.338–1.341 Å indicating double bonds, whereas the exocyclic C–C bonds are significantly longer at 1.434–1.437 Å [cf. $\Sigma r_{\mathrm{cov}}(\mathrm{C{-}C})$ = 1.50 vs. $\Sigma r_{\mathrm{cov}}(\mathrm{C{=}C})$ = 1.34 Å].[34]

HTCP and HTCP·2H$_2$O

The free acid crystallizes either as a dihydrate or as a solvent-free species in the orthorhombic space group $Pna2_1$

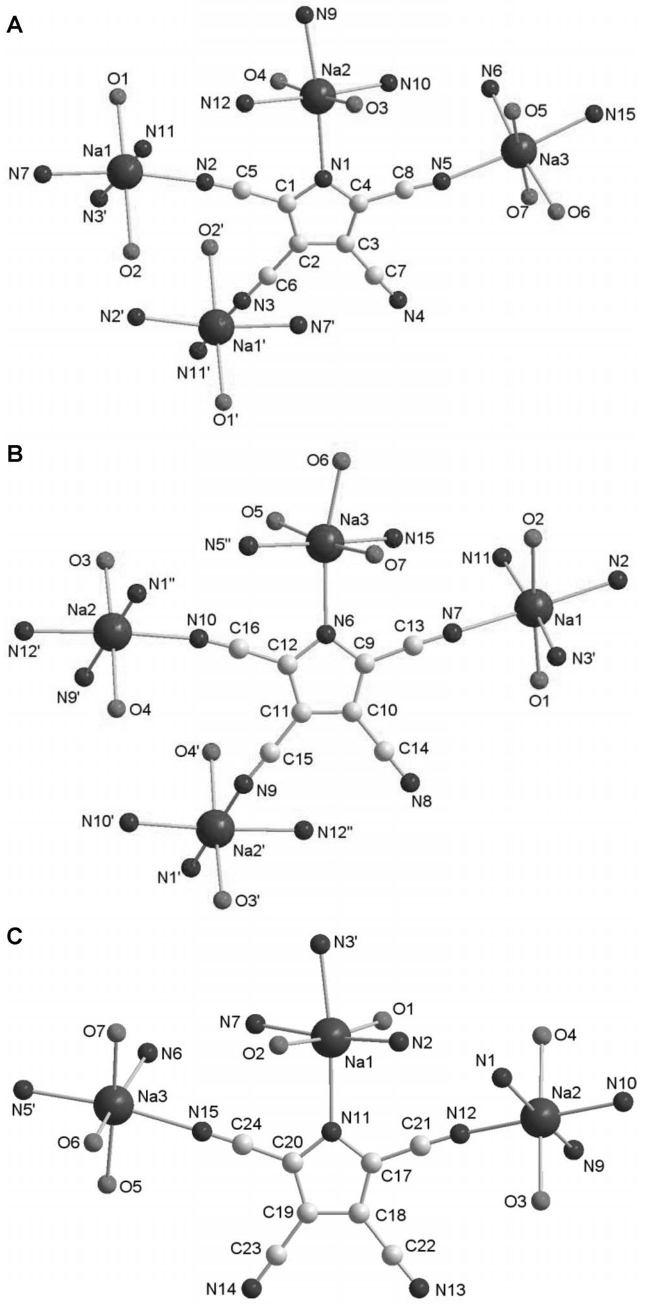


Figure 7. Ball-and-stick representation of the coordination environment of the three independent NaTCP ion pairs (**A**, **B**, and **C**). For the Na$^+$ ions only the coordinating atoms are shown. Selected bond lengths [Å] and angles [°]: N1–C1 1.355(2), N1–C4 1.356(2), N2–C5 1.142(2), N3–C6 1.140(2), N4–C7 1.140(2), N5–C8 1.140(2), N6–C9 1.356(2), N6–C12 1.358(2), N7–C13 1.142(2), N8–C14 1.139(2), N9–C15 1.142(2), N10–C16 1.144(2), N11–C17 1.354(2), N11–C20 1.358(2), N12–C21 1.141(2), N13–C22 1.138(2), N14–C23 1.138(2), N15–C24 1.139(2), C1–C2 1.394(2), C1–C5 1.432(2), C2–C3 1.403(2), C2–C6 1.423(2), C3–C4 1.397(2), C3–C7 1.425(2), C4–C8 1.432(2), C9–C10 1.397(2), C9–C13 1.429(2), C10–C11 1.405(2), C10–C14 1.424(2), C11–C12 1.401(2), C11–C15 1.420(2), C12–C16 1.425(2), C17–C18 1.394(2), C17–C21 1.428(2), C18–C19 1.403(2), C18–C22 1.422(2), C19–C20 1.395(2), C19–C23 1.422(2), C20–C24 1.428(2); N2–C5–C1 175.3(1), N3–C6–C2 177.5(1), N4–C7–C3 177.7(2), N5–C8–C4 174.9(1), N7–C13–C9 176.5(2), N8–C14–C10 178.4(2), N9–C15–C11 177.5(2), N10–C16–C12 175.9(1), N12–C21–C17 176.6(1), N13–C22–C18 178.6(2), N14–C23–C19 179.5(2), N15–C24–C20 177.6(1).

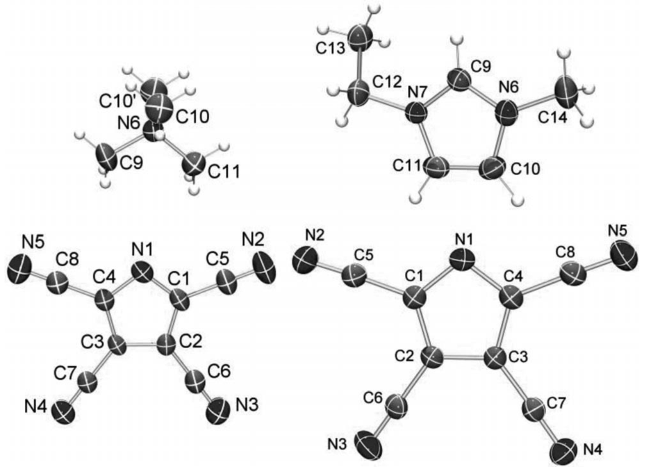


Figure 8. ORTEP drawing of the molecular structure of Me_4NTCP (left) and EMIMTCP (right). Thermal ellipsoids with 50% probability at 173 K. Selected bond lengths [Å] and angles [°]: Me_4NTCP: N1–C4 1.354(3), C2–C6 1.417(4), N1–C1 1.354(3), C3–C4 1.405(4), N2–C5 1.141(4), C3–C7 1.409(4), N3–C6 1.150(4), C4–C8 1.433(4), N4–C7 1.150(4), N6–C11 1.486(4), N5–C8 1.139(4), N6–C10 1.488 (3), N6–C9 1.491(4); N2–C5–C1 180.0(4), N3–C6–C2 179.5(3), N4–C7–C3 180.0(3), N5–C8–C4 179.8 (3); EMIMTCP: N1–C4 1.355(3), N1–C1 1.355(3), N2–C5 1.148(3), N3–C6 1.148(3), N4–C7 1.148(3), N5–C8 1.148(3); N2–C5–C1 177.5(2), N3–C6–C2 179.5(3), N4–C7–C3 178.1(2), N5–C8–C4 178.6(3).

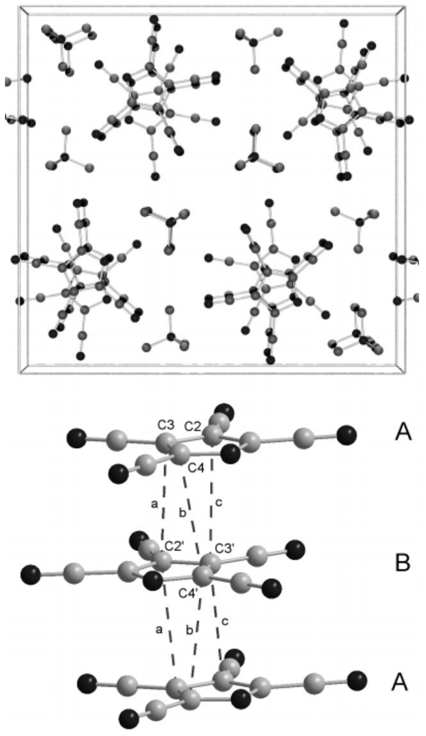


Figure 9. Top: view along the *a* axis displaying layers. Bottom: significant van der Waals interactions between these layers (right). Distances [Å] < 3.4: a = 3.384, b = 3.350, c = 3.384; cf. $\Sigma r_{\mathrm{vdW}}(\mathrm{C}\cdots\mathrm{C}) = 3.4$, $\Sigma r_{\mathrm{vdW}}(\mathrm{C}\cdots\mathrm{N}) = 3.3$.

with four formula units per unit cell. One strong hydrogen bond along N1–H1···N3′ with a heavy-atom distance of 2.897 Å is found for HTCP in the solid state, which leads to chains of planar HCTP molecules (Figure 3). A slightly different picture is observed for $HTCP{\cdot}2H_2O$ (Figure 4). Here, both water molecules are linked by strong hydrogen bonds (O1···O2 2.703 Å) and form a Zundel ion. Such a dihydrate moiety is closely attached through O1 by a second strong hydrogen bond with the acidic proton (H1) of the TCP ion as illustrated in Figure 4 (N1···O1 2.595 Å). Additionally, three of the four cyano groups also form weak hydrogen bonds with heavy-atom distances between 2.96–3.01 Å. The main molecular structural motif of HTCP and $HTCP{\cdot}2H_2O$ is the almost C_{2v}-symmetric tetracyanopyrrolide unit as shown in Figures 3, 4, and 5. All four cyano groups are linearly attached to the five-membered ring with $NC–C_{ring}$ distances between 1.422–1.423 Å, which are only slightly longer than the $C_{ring}–C_{ring}$ distances [e.g. C1–C2 1.389(3), C2–C3 1.410(3), and C3–C4 1.380(3) Å in $HTCP{\cdot}2H_2O$] indicating partial double bond character and delocalization of π-electron density along the carbon framework in HTCP (vide infra). The CN distances range from 1.136–1.145 Å in accord with the values for typical CN triple bonds [cf. $\Sigma r_{\mathrm{cov}}(\mathrm{C{\equiv}N}) = 1.14$ Å].[34]

MeTCP

In contrast to $HTCP{\cdot}2H_2O$, MeTCP crystallizes without significant intermolecular interactions in the orthorhombic space group $Pca2_1$ with four formula units in the unit cell. The asymmetric unit consists of a planar C_{2v}-symmetric molecule with a disordered methyl group, which was split into two parts (Figure 5, right). The metrical parameters are very similar to those found in HTCP (vide supra).

NaTCP

Three independent NaTCP ion pairs are found within the triclinic unit cell of this compound (space group $P\bar{1}$, Z = 6), which only differ with respect to the coordination modes around the Na^+ and $TCP^–$ ions as depicted in Figure 6. Thus, the unit cell contains six NaTCP moieties and in addition seven THF solvent molecules, which are linked by numerous interactions. The Na^+ ions have either a 4N + 2O or a 3N + 3O coordination leading to a distorted octahedral environment for all sodium ions (Figure 7). Although, the pyrrolide nitrogen atom always takes part in the Na^+ coordination, either one (Figure 7, structure **A** and **B**) or two CN groups (structure **C**) remain uncoordinated. Owing to these strong interactions, layers are formed, however, no interpenetration is observed as shown in Figure 6. The C_4N rings are superimposed but between these layers neither considerable interionic interactions nor π-stacking effects are observed. Two slightly different sets of Na–N bond lengths are found: $d(\mathrm{Na–N_{cyano}})$ = 2.44–2.53 and $d(\mathrm{Na–N_{pyrrolide}})$ = 2.54–2.59 Å. It is interesting to note that no significant difference in the CN bond lengths is observed depending on the coordination mode (1.138–1.144 Å) and even the uncoordinated cyano groups are within this range.

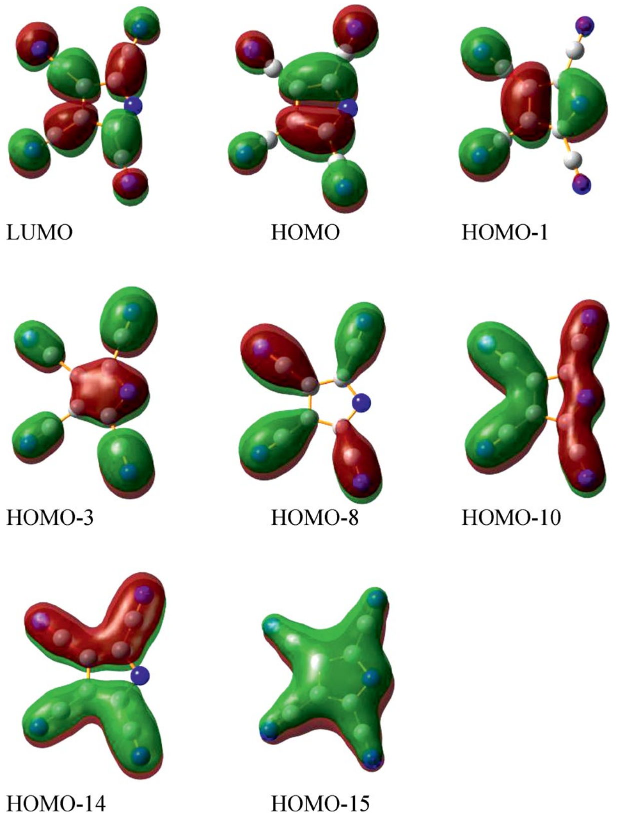
Although the coordination environment around the TCP ion does not support C_{2v} symmetry, the coordinated anion retains almost local C_{2v} symmetry. Again the metrical parameters compare well with those found in HTCP (vide supra).

Me_4NTCP and EMIMTCP

Me_4NTCP crystallizes in the orthorhombic space group *Cmca* with eight formula units per unit cell (Figure 8, left), and EMIMTCP crystallizes in the monoclinic space group $P2_1/c$ with four formula units per unit cell (Figure 8, right). In contrast to NaTCP, no coordinative interactions between cations and anions are detected for Me_4NTCP and EMIMTCP. However, as illustrated in Figure 9, anion···anion π–π stacking[36,37] is observed in both compounds, which is more pronounced in Me_4NTCP as indicated by the shorter distances between the TCP layers (Me_4NTCP: 3.4–3.5, EMIMTCP: 3.5–3.6 Å). X-ray crystal structure analysis for Me_4NTCP and EMIMTCP showed that the TCP anion possesses high planarity and nearly C_{2v} symmetry (Figures 8 and 9). The atoms of the NC_4 skeleton deviate by only 0.009 (MeTCP) and 0.0011 (EMINTCP) Å, respectively, from the least-squares plane. The TCP anions are uniformly stacked along the *a* axis with an interplanar distance of about 3.4 Å in Me_4NTCP, nearly equal to the sum of the van der Waals radii of the carbon atoms of the two TCP planes [cf. $\Sigma r_{\mathrm{vdW}}(\mathrm{C}) = 1.7$, $r_{\mathrm{vdW}}(\mathrm{N}) = 1.6$].[34,35] The neighboring TCP columns are not linked with each other and, therefore, no three-dimensional structure is observed as found for NaTCP (vide supra). The cations are located in vacant channels.

Computations

Calculations were carried out with the Gaussian 03 package of molecular orbital programs to gain further insight into the electronic situation in the TCP ion.[38] The structures of the TCP ion and for comparison the parent ion $[H_4C_4N]^-$ were optimized within the DFT approach at the pbe1pbe level with an aug-cc-pVDZ basis set.[39] Vibrational frequencies were also computed to characterize all structures as minima on the potential energy surface. A natural bond orbital analysis (NBO)[40] was performed at the same level, to study the charge distribution, bond polarization, and hybridization effects. The C_4N core in the parent anion $[H_4C_4N]^-$ possesses a charge of –1.74*e* which decreases upon substitution of all H atoms by CN groups to –0.80*e* corresponding to a total loss of 0.95*e*. In accord with the pseudohalogen concept (vide supra), the basicity of the ring nitrogen atom also decreases as displayed by the change in the partial charge (–0.63 vs. –0.45*e*). As the entire TCP ion is planar, strong in-plane and out-of-plane delocalization of π electrons is found in the MO and NBO picture, respectively, leading among other things to fairly short C–CN and C–C distances, in accord with partial double bond character (see above). A close inspection of the π MOs reveals a strong mixing of the three occupied, mainly bonding MOs of the C_4N ring as known from $[H_4C_4N]^-$ with the out-of-plane π bond of the four cyano groups yielding seven occupied π-MOs with mainly bonding character as depicted in Figure 10.


LUMO HOMO HOMO-1

HOMO-3 HOMO-8 HOMO-10

HOMO-14 HOMO-15

Figure 10. π MOs in the TCP ion displaying a strong delocalization into the CN groups.

Conclusions

Salts bearing the tetracyanopyrrolide anion were synthesized in good yields starting from tetracyano-1,4-dithiin (**3**) and sodium azide. The structure and bonding of such salts is discussed for the first time and the anion can be referred to as a pseudohalide with π bonds highly delocalized over the entire anion including the four cyano groups. The planar anion is C_{2v} symmetric and represents a multifunctional binary CN ligand, which is capable of forming classic coordination bonds through the lone pairs of the CN groups or the ring nitrogen atom. In addition, noncovalent interactions such as π–π interactions are found and can be used to strengthen structural and electronic communication between organic ligands. With metal ions the multidentate TCP ligand forms a σ-conjugation network, with weakly coordinating cations such as Me_4N^+ or $EMIM^+$ isolated ion pairs are observed, in which anion···anion π–π stacking occurs, and in HTCP hydrogen bonds with water molecules dominate the solid-state structure. Interestingly, all four cyano groups are not always involved in the coordination chemistry. It can be concluded that the utilization of TCP ions in combination with transition metal ions will results in supramolecular chemistry and for the paramagnetic metals even molecular magnetism can be expected.

Experimental Section

General Information: All substances were used as received: NaCN (Alfa Aesar, 98 %), CS_2 (Riedel-de Haën, Germany), NaN_3 (Acros Organics, 99 %), NMe_4Cl (Merck, 98 %), $(NH_4)_2S_2O_8$ (Roth, 98 %).

NMR: ^1H and ^{13}C spectra were obtained with Bruker Avance 250 (250 MHz) and Avance 300 (300 MHz) spectrometers and were referenced externally. $[D_6]$DMSO was dried with molecular sieves (3 Å). IR spectra were recorded with a Nicolet 380 FTIR spectrometer equipped with a Smart Orbit attenuated total reflectance (ATR) device; Raman spectra were recorded 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 recorded with a from Mettler–Toledo 823e calorimeter. A sample of approximately 1 to 2 mg was placed in an aluminium crucible. The closed crucible was placed in the furnace. The closed furnace was flushed with nitrogen and the sampled was measured using a heating rate of 5 °C per minute. The heat flow was calculated based on a two point calibration (melting points of In and Zn) using the Metler software.

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).

Synthesis

Tetracyano-1,4-dithiin: A suspension of NaCN (49.0 g, 1 mol) and DMF (300 mL) was stirred vigorously and CS_2 (76.1 g, 1 mol) was added dropwise over one hour. H_2O (2.5 L) was added and the mixture was stored overnight at 6 °C. The precipitate (sulfur) was removed by filtration. A solution of H_2O (500 mL) and $(NH_4)_2S_2O_8$ (228.0 g, 1 mol) was added to the filtrate over an hour, the mixture was stirred over 30 min, and the product was collected by filtration. The yield of the raw product was 40–50 g (80–90 %) and was contaminated with sulfur (5 weight percentage). The resulting residue was applied to the top of an open-bed silica gel column. The column was eluted with ethyl acetate/*n*-heptane (v:v = 3:1). The resulting purified fractions were combined and evaporated under reduced pressure; yield 34–39 g (60–70 %); m.p. (DSC): 175.6 °C, T_{dec} = 257 °C. $C_8N_4S_2$ (216.23): calcd. C 44.43, N 25.91, S 29.66; found C 44.67, N 25.53, S 29.11. ^{13}C NMR ($[D_6]$DMSO, 63 MHz, 25 °C): δ = 125.4 (s, CN, 4 C), 112.4 (s, C_{quat}, 4 C) ppm. IR (ATR): $\tilde{\nu}$ = 2921 (m), 2852 (s), 2226 (m), 2212 (s), 1532 (m), 1486 (s), 1463 (s), 1455 (s), 1306 (s), 1160 (m), 1148 (m), 1122 (w), 1927 (w), 997 (w), 926 (w), 869 (w), 825 (w), 805 (s), 677 (w), 623 (m), 582 (s), 561 (s) cm^{-1}; Raman (50 mW, 1500 scans, 25 °C): $\tilde{\nu}$ = 2283 (1), 2218 (10), 2185 (3), 1560 (4), 620 (1), 472 (1), 349 (1) cm^{-1}. MS *m*/*z* (%) = 216 (100) [M], 184 (11) [M – S], 70 (34) [M – (NC–C–S)], 32 (31) [S].

Tetramethylammonium Tetracyanopyrrolide (Me_4NTCP): Tetracyano-1,4-dithiin (10.8 g, 0.05 mol), sodium azide (3.25 g, 0.05 mol), and 200 mL of ethanol was mixed and stirred overnight, and nitrogen slowly evolved. The dark red reaction mixture was filtered to remove elemental sulfur (1.15 g), and the filtrate was evaporated to dryness under reduced pressure. Water (200 mL) was added, and a brown solid (1.1 g) that contained appreciable amounts of elemental sulfur was removed by filtration. The aqueous filtrate was decolorized with "Darco" and stirred at 0 °C, tetramethylammonium chloride (11 g) was added as a saturated aqueous solution. Reddish brown tetramethylammonium tetracyanopyrrolide (7.25 g, 62.5 %) was removed by filtration, washed with water, and dried under reduced pressure; m.p. (DSC): 118.7 °C, T_{dec} = 423 °C. $C_{12}H_{12}N_6$ (240.27): calcd. C 59.99, H 5.03, N 34.98; found C 59.11, H 5.01, N 34.13. ^1H NMR ($[D_6]$DMSO, 300 MHz, 25 °C): δ = 3.09 (s, CH_3, 12 H) ppm. ^{13}C NMR ($[D_6]$DMSO, 75 MHz, 25 °C): δ = 119.8 (s, C_{quat}, 2 C), 114.5 (s, C_{quat}, 2 C), 112.5 (s, C_{quat}, 2 C), 102.0 (s, C_{quat}, 2 C), 54.4 (s, CH_3, 4 C) ppm. IR (ATR): $\tilde{\nu}$ = 3039 (w), 2220 (s), 1485 (s), 1475 (s), 1415 (m), 1372 (w), 1132 (w), 1074 (m), 948 (s), 677 (w) cm^{-1}; Raman (500 mW, 5 scans, 25 °C): $\tilde{\nu}$ = 2229 (10), 2228 (10) cm^{-1}.

1-Ethyl-3-methylimidazolium Tetracyanopyrrolide (EMIMTCP): To a solution of tetramethylammonium tetracyanopyrrolide (2.4 g, 10 mmol) in water/acetone was added $AgNO_3$ (2.2 g, 13 mmol) in water. After stirring for 2 h the brown silver salt was collected, washed three times with 20 mL of water and suspended in another 30 mL of water. To the suspension was added 1-ethyl-3-methylimidazolium iodide (1.9 g, 8 mmol) in water (20 mL). After stirring for 7 d, the suspension was filtered. Removal of the solvent of the filtrate led to light brown ionic liquid; yield 61 %; m.p. (DSC): 29.8 °C, $T_{dec.}$ = 230.4 °C. $C_{14}H_{11}N_7 \cdot 2.5H_2O$ (322.32): calcd. C 52.17, H 5.00, N 30.42; found C 51.99, H 4.25, N 30.91. ^1H NMR ($[D_6]$DMSO, 300 MHz, 25 °C): δ = 9.23 (s, NC*H*N, 1 H), 7.77 (s, NC*H*CHN, 1 H), 7.69 (s, NCHC*H*N, 1 H), 4.20 (q, $^3J_{H,H}$ = 7.4 Hz, 2 H, CH_2), 3.85 (s, 3 H, NCH_3), 1.41 (t, $^3J_{H,H}$ = 7.4 Hz, 3 H, CH_3) ppm. ^{13}C NMR ($[D_6]$DMSO, 75 MHz, 25 °C): δ = 136.5 (s, N*C*HN, 1 C), 123.6 (s, N*C*HCHN, 1 C), 122.0 (s, NCH*C*HN, 1 C), 119.8 (s, C_{quat}, 2 C), 114.6 (s, C_{quat}, 2 C), 112.5 (s, C_{quat}, 2 C), 102.5 (s, C_{quat}, 2 C), 44.2 (s, CH_2, 1 C), 35.7 (s, NCH_3, 1 C), 15.1 (s, CH_3, 1 C) ppm. IR (ATR): $\tilde{\nu}$ = 3414 (br), 3152 (w), 3121 (w), 2994 (w), 2755 (w), 2714 (w), 2225 (s), 2217 (s), 1598 (w), 1572 (m), 1471 (m), 1450 (m), 1347 (s), 1328 (s), 1167 (vs), 1076 (m), 1028 (w), 962 (w), 826 (s), 739 (s), 709 (w), 675 (w), 631 (m), 616 (vs) cm^{-1}; Raman (500 mW, 1000 scans, 25 °C): $\tilde{\nu}$ = 2230 (10), 1473 (1), 1414 (2), 1309 (2) cm^{-1}.

Tetracyanopyrrole (HTCP): A column containing Amberlyst 15 ion-exchange resin (200 g) was thoroughly washed with 10 mol-% HCl, deionized water, acetone, and acetonitrile. A solution of tetramethylammonium tetracyanopyrrolide (2.4 g, 0.01 mol) in acetonitrile (25 mL) was slowly added to the top of the column. The free pyrrole was eluted with acetonitrile and the eluent evaporated to dryness under reduced pressure. The resulting residue was applied to the top of an open-bed silica gel column. The column was eluted with ethyl acetate/*n*-heptane (v:v = 3:1). The resulting purified fractions were combined and evaporated under reduced pressure; yield 54 %, $T_{dec.}$ (DSC) = 202 °C $C_8HN_5 \cdot 2H_2O$ (203.16): calcd. C 47.30, H 2.48, N 34.47; found C 47.08, H 2.69, N 34.33. ^1H NMR (CD_3CN, 250 MHz, 25 °C): δ = 11.09 (s, 1 H, NH) ppm. ^{13}C NMR (CD_3CN, 63 MHz, 25 °C): δ = 113.5 (s, C_{quat}, 2 C), 110.1 (s, C_{quat}, 2 C), 109.0 (s, C_{quat}, 2 C), 107.0 (s, C_{quat}, 2 C) ppm. IR (ATR): $\tilde{\nu}$ = 3572 (m), 3501 (m), 3161 (w), 3047 (w), 2939 (w), 2796 (w), 2700 (m), 2557 (w), 2251 (s), 2241 (s), 1610 (m), 1493 (w), 1462 (m), 1443 (m), 1285 (m), 1083 (m), 893 (s), 673 (m) cm^{-1}; Raman

(500 mW, 1000 scans, 25 °C): $\tilde{\nu}$ = 2256 (10), 1491 (4), 1445 (5), 1351 (1), 1068 (1), 674 (1), 520 (1) cm^{-1}. MS *m/z* (%) = 167 (100) [M]. HRMS (EI): calcd. for C_8HN_5 167.02265; found 167.02256.

***N*-Methyltetracyanopyrrole (MeTCP):** To a solution of acetone and tetramethylammonium tetracyanopyrolide (2.2 g, 9.16 mmol), dimethyl sulfate (1.15 g, 9.16 mmol) was added, and the mixture was stirred overnight. For purification, ethyl acetate was added, and the mixture was filtered over a sintered glass filter filled with silica gel. The product was crystallized from dichloromethane (135 mg); yield 8%; m.p. (DSC): 187.45 °C, $T_{dec.}$ = 361.9 °C. $C_{12}H_{12}N_6$ (240.27): calcd. C 59.67, H 1.67, N 38.66; found C 59.53, H 1.59, N 37.59. ^{1}H NMR ([D$_6$]DMSO, 300 MHz, 25 °C): δ = 4.0 (s, 3 H, CH_3) ppm. ^{13}CNMR ([D$_6$]DMSO, 75 MHz, 25 °C): δ = 111.6 (s, 2 C, C_{quat}), 109.5 (s, 2 C, C_{quat}), 108.1 (s, 2 C, C_{quat}), 104.3 (s, 2 C, C_{quat}), 37.8 (s, 4 C, NCH_3) ppm. IR (ATR): $\tilde{\nu}$ = 3083 (w), 2959 (w), 2830 (w), 2299 (w), 2242 (s), 2236 (s), 2194 (w), 1532 (w), 1503 (s), 1462 (s), 1377 (s), 1262 (w), 1224 (w), 1186 (m), 1126 (w), 1013 (w), 965 (w), 934 (w), 899 (w), 838 (m), 836 (w), 806 (w), 705 (w), 678 (m), 550 (w) cm^{-1}; Raman (500 mW, 250 scans, 25 °C): $\tilde{\nu}$ = 2961 (0.3), 2245 (10.0), 1505 (2.1), 1464 (2.2), 1424 (1.6), 1380 (0.7), 517 (0.5), 134 (0.8), 111 (0.9), 82 (1.3) cm^{-1}. HRMS (ESI): calcd. 180.03157; found 180.03198.

Sodium Tetracyanopyrrolide (NaTCP): A column containing 200 g of AMBERLYST 15 ion-exchange resin was used for ion exchange. A solution of acetonitrile and tetramethylammonium tetracyanopyrrolide (1 g, 4.16 mmol) was added to the top of the column. After the whole solution was run through the column, the column was flushed with acetonitrile (100 mL) twice. All acetonitrile fractions were collected, and the solvents were evaporated to dryness. The yield of the raw product was 85%. For purification, the residue was crystallized from hot THF and *n*-heptane and then dissolved in hot ethanol. *n*-Heptane was added to form two phases (yellow/red). The mixture was stored overnight at –40 °C. The red phase with higher density evaporated until crystals formed at –40 °C. After addition of diethyl ether, the precipitation of white NaTCP was observed. The hygroscopic precipitate was collected by filtration through a sintered glass funnel and was washed three times with diethyl ether (yield 25%). Alternative route: Two equimolar solutions of tetramethylammonium tetracyanopyrrolide in acetonitrile and $NaClO_4$ in water were united, the acetonitrile was evaporated, and the solution was filtered. The filtrate was evaporated to dryness and the precipitate was dissolved in THF. When diethyl ether was slowly added the product crystallized. The crystallization step was repeated four times; m.p. 400.5 °C. DSC: M.p. 400.5 °C. C_8N_5Na (189.11): cald. C 50.81, N 37.03, found C 52.10, N 36.94. ^{13}C NMR ([D$_6$]DMSO, 63 MHz, 25 °C): δ = 119.8 (s, C_{quat}, 2 C), 114.5 (s, C_{quat}, 2 C), 112.5 (s, C_{quat}, 2 C), 102.0 (s, C_{quat}, 2 C) ppm. IR (ATR, 32 scans, 25 °C): $\tilde{\nu}$ = 3542 (w), 3131 (w), 2769 (vw), 2721 (vw), 2241 (vs), 2226 (vs), 1681 (w), 1478 (s), 1417 (m), 1329 (w), 1305 (vw), 1201 (vw), 1087 (m), 1043 (vw), 1012 (vw), 979 (vw), 728 (w), 692 (m), 679 (m), 536 (s) cm^{-1}; Raman (500 mW, 400 scans, 25 °C): $\tilde{\nu}$ = 2247 (10.0), 1482 (2.1), 1420 (2.4), 1318 (1.5), 1310 (1.6), 546 (0.5), 467 (0.4), 157 (0.6), 136 (1.6), 109 (0.7), 76 (0.8) cm^{-1}.

CCDC-891163 (for **1**), -891164 (for **2_S$_2$**), -891165 (for **3**), -891166 (for HTCP), -891167 (for HTCP·2H$_2$O), -891168 (for MeTCP), -891169 (for Me$_4$NTCP), -891170 (for EMIMTCP) and -891171 (for NaTCP·2.33THF) 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): Experimental and theoretical details.

Acknowledgments

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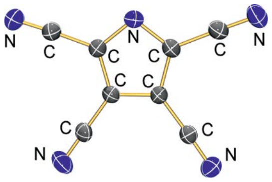
Coordination Chemistry

Salts containing the binary tetracyanopyrrolide anion (TCP) were synthesized from tetracyano-1,4-dithiin and sodium azide. The planar TCP anion, which might be regarded as a pseudohalide, is C_2v symmetric and represents a multifunctional binary CN ligand as demonstrated in a series of solid-state structures.



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Structure and Bonding of Tetracyanopyrrolides

Keywords: Coordination chemistry / Ligand design / N ligands / Main group elements / Pseudohalogen