Supporting Information

Structural diversity of supramolecular networks formed between polycyanometalates and sulfur-based chalcogen bond donors

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Table of Contents

Experimental Section

S-(Trifluoromethyl)dibenzothiophenium trifluoromethanesulfonate was commercially obtained from Fischer Scientific and used as a stock solution in CH_2Cl_2. $[PPh_4]_2[Ni(CN)_4]$[1], $[PPh_4]_2[Zn(CN)_4]$[1], $[NBu_4]_3[W(CN)_8]$[2], $[NBu_4]_3[Fe(CN)_6]$[3] were prepared using literature reported procedures. All reactions were carried out in previously heated glassware under an atmosphere of argon using standard Schlenk techniques and an oil pump vacuum of 10^{-3} mbar. Solvents were dried over activated 3 Å molecular sieves and stored under argon.

Removal of all ionic side products and excess starting materials was not possible due to the small scale.

S-(Trifluoromethyl)dibenzothiophenium octacyanotungstate(III):

$[NBu_4]_3[W(CN)_8]$ (0.010 g, 0.009 mmol, 1.00 equiv.) was dissolved in CH_2Cl_2 (0.3 mL) and a layer of CH_2Cl_2 (0.3 mL) was placed on top at room temperature. S-(Trifluoromethyl)dibenzothiophenium trifluoromethanesulfonate (0.086 g, 0.214 mmol, 8 equiv.) dissolved in CH_2Cl_2 (0.15 mL) was layered on top and the mixture was placed in a −20 °C freezer. After a day dark yellow crystals suitable for X-ray diffraction analysis had formed.

S-(Trifluoromethyl)dibenzothiophenium tetracyanozincate(II):

$[PPh_4]_2[Zn(CN)_4]$ (0.010 g, 0.012 mmol, 1.00 equiv.) was dissolved in CH_2Cl_2 (0.3 mL) and a layer of CH_2Cl_2 (0.3 mL) was placed on top at room temperature. S-(Trifluoromethyl)dibenzothiophenium trifluoromethanesulfonate (0.020 g, 0.049 mmol, 4 equiv.) dissolved in CH_2Cl_2 (0.15 mL) was layered on top and the mixture was placed in a −20 °C freezer. After a day colorless crystals formed suitable for X-ray diffraction analysis.

S-(Trifluoromethyl)dibenzothiophenium hexacyanoferrate(III):

$[NBu_4]_3[Fe(CN)_6]$ (0.010 g, 0.010 mmol, 1.00 equiv.) was dissolved in CH_2Cl_2 (0.3 mL) and a layer of CH_2Cl_2 (0.3 mL) was layered on top at room temperature. S-(Trifluoromethyl)dibenzothiophenium trifluoromethanesulfonate (0.034 g, 0.204 mmol, 6 equiv.) dissolved in CH_2Cl_2 (0.15 mL) was layered on top of the mixture. The mixture was placed in a −20 °C freezer. After a day yellow crystals of the desired product could be obtained which where suitable for X-ray diffraction analysis.

S-(Trifluoromethyl)dibenzothiophenium tetracyanonickelate(II):

$[PPh_4]_2[Ni(CN)_4]$ (0.010 g, 0.012 mmol, 1.00 equiv.) was dissolved in CH_2Cl_2 (0.3 mL) and a layer of CH_2Cl_2 (0.3 mL) was layered on top at room temperature. S-(Trifluoromethyl)dibenzothiophenium trifluoromethanesulfonate (0.060 g, 0.148 mmol, 4 equiv.) dissolved in CH_2Cl_2 (0.15 mL) was layered on top of the mixture. The mixture was

placed in a −20 °C freezer. After a day beige crystals of the desired product could be obtained which where suitable for X-ray diffraction analysis.

Crystallographic Details

X-Ray data were collected on a BRUKER D8 Venture system. Data were collected at 105(2) K using graphite-monochromated Mo Kα radiation (λα = 0.71073 Å). The strategy for the data collection was evaluated by using the Smart software. The data were collected by the standard "ψ-ω scan techniques" and were scaled and reduced using Saint+software. The structures were solved by using Olex2,[4] the structure was solved with the XT[5] structure solution program using Intrinsic Phasing and refined with the XL[6] refinement package using Least Squares minimization. If it is noted, bond length and angles were measured with Diamond Crystal and Molecular Structure Visualization Version 3.1.[7] Drawings were generated with Mercury.[8]

Identification code	$[CF_3SC_{10}H_8^+]_2$ $[Ni(CN)_4]^{2-} \bullet CH_2Cl_2$	$[CF_3SC_{10}H_8^+]_2$ $[Zn(CN)_4]^{2-} \bullet H_2O \bullet CH_2Cl_2$
CCDC Number	2352918	2352919
Empirical formula	$C_{16}H_{10}Cl_2F_3N_2Ni_{0.5}S$	$C_{31}H_{20}Cl_2F_6N_4OS_2Zn$
Formula weight	419.584	778.90
Temperature/K	105.0	105.0
Crystal system	triclinic	triclinic
Space group	P-1	P-1
a/Å	7.5146(3)	9.2339(4)
b/Å	10.6915(5)	13.5275(7)
c/Å	12.0434(5)	14.9019(8)
α/°	103.512(2)	105.866(2)
β/°	103.720(2)	107.532(2)
γ/°	106.570(2)	94.354(2)
Volume/Å³	852.48(7)	1681.72(15)
Z	2	2
ρ_{calc}g/cm³	1.635	1.538
μ/mm⁻¹	1.069	1.079
F(000)	423.5	784.0
Crystal size/mm³	0.1 × 0.1 × 0.1	0.1 × 0.1 × 0.1
Radiation	Mo Kα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.6 to 52.08	3.636 to 50.804
Index ranges	-9 ≤ h ≤ 9, -13 ≤ k ≤ 13, -14 ≤ l ≤ 14	-11 ≤ h ≤ 11, -16 ≤ k ≤ 16, -17 ≤ l ≤ 17
Reflections collected	19125	23898
Independent reflections	3348 [R_{int} = 0.0483, R_{sigma} = 0.0308]	6162 [R_{int} = 0.0678, R_{sigma} = 0.0658]
Data/restraints/parameters	3348/0/223	6162/0/427
Goodness-of-fit on F²	0.870	1.020
Final R indexes [I>=2σ (I)]	R_1 = 0.0278, wR_2 = 0.0787	R_1 = 0.0431, wR_2 = 0.0827
Final R indexes [all data]	R_1 = 0.0338, wR_2 = 0.0817	R_1 = 0.0669, wR_2 = 0.0936
Largest diff. peak/hole / e Å⁻³	0.34/-0.35	0.81/-0.67
Flack parameter	-	-

Identification code	[CF$_3$SC$_{10}$H$_8$$^+$]$_3$ [Fe(CN)$_6$]$^{3-}$·CH$_2$Cl$_2$	[CF$_3$SC$_{10}$H$_8$$^+$]$_3$ [W(CN)$_8$]$^{3-}$
CCDC Number	2352920	2352921
Empirical formula	C$_{46}$H$_{26}$Cl$_2$F$_9$FeN$_6$S$_3$	C$_{48.5}$H$_{27}$Cl$_3$F$_9$N$_8$S$_3$W
Formula weight	1056.693	1279.16
Temperature/K	105.0	105.0
Crystal system	triclinic	monoclinic
Space group	P1	C2/c
a/Å	10.2010(5)	38.630(5)
b/Å	11.0689(11)	14.822(2)
c/Å	11.4836(12)	18.028(2)
α/°	115.214(2)	90
β/°	97.954(2)	101.077(4)
γ/°	104.048(2)	90
Volume/Å^3	1094.00(17)	10130(2)
Z	1	8
ρ$_{calc}$g/cm^3	1.604	1.677
μ/mm^{-1}	0.692	2.640
F(000)	534.4	5024.0
Crystal size/mm^3	0.1 × 0.1 × 0.1	0.1 × 0.1 × 0.1
Radiation	Mo Kα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.3 to 52.08	4.298 to 50.748
Index ranges	-12 ≤ h ≤ 12, -13 ≤ k ≤ 13, -14 ≤ l ≤ 14	-46 ≤ h ≤ 46, -17 ≤ k ≤ 17, -21 ≤ l ≤ 21
Reflections collected	29759	166640
Independent reflections	8365 [R$_{int}$ = 0.0531, R$_{sigma}$ = 0.0447]	9273 [R$_{int}$ = 0.0905, R$_{sigma}$ = 0.0363]
Data/restraints/parameters	8365/3/605	9273/0/613
Goodness-of-fit on F^2	1.062	1.035
Final R indexes [I>=2σ (I)]	R$_1$ = 0.0317, wR$_2$ = 0.0677	R$_1$ = 0.0270, wR$_2$ = 0.0618
Final R indexes [all data]	R$_1$ = 0.0404, wR$_2$ = 0.0719	R$_1$ = 0.0396, wR$_2$ = 0.0658
Largest diff. peak/hole / e Å^{-3}	0.39/-0.28	0.47/-0.81
Flack parameter	0.016(9)	-
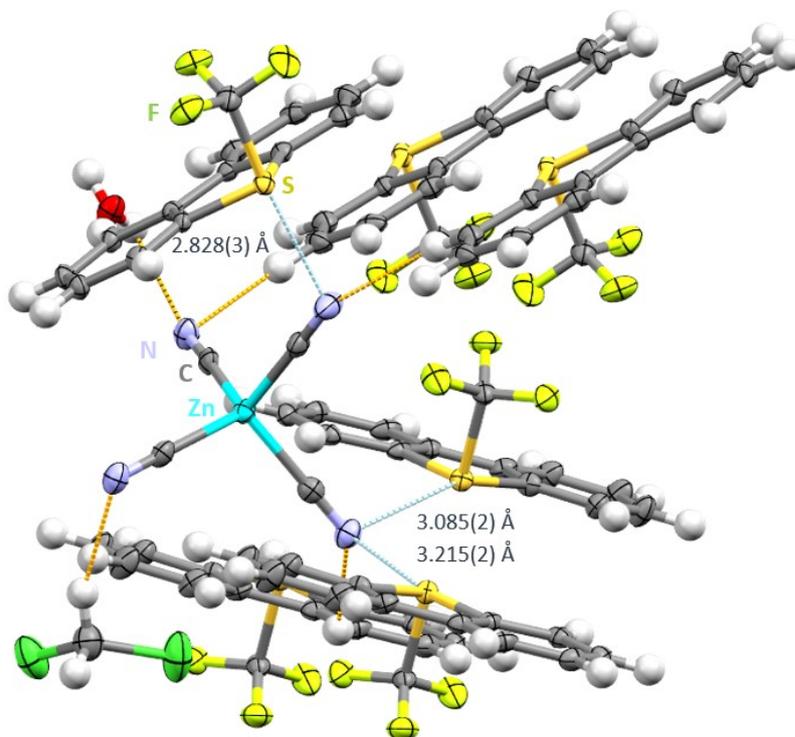
Fig. S1 Intermolecular S···N contacts in the crystal structure of [Ume$^+$]$_2$[Zn(CN)$_4$]$^{2-}$·H$_2$O·CH$_2$Cl$_2$. Thermal ellipsoids at the 50% probability level. Chalcogen bonds in light blue and hydorgen bonds in orange.

Fig. S2 Intermolecular S···N contacts in the crystal structure of [Ume+]$_3$[W(CN)$_8$]$^{3-}$. Thermal ellipsoids at the 50% probability level. Chalcogen bonds in light blue and hydrogen bonds in orange.

Computational Details

The energy calculations were carried out using the Turbomole 7.7 program[9] and the PBE0[10]-D3[11]/def2-TZVP[12] level of theory. For W, the def2-TZVP basis set used in this work includes effective core potentials (ECP),[13] and relativistic effects are used for the inner electrons.[12] The crystallographic coordinates have been used to evaluate the interactions in the solid state of the compounds, since we are interested to study the interactions as they stand in the solid state. The assemblies extracted from the solid-state structures were selected to study the chalcogen bonding interactions. The interaction energies were computed by subtracting the sum of the energies of the monomers to that of the assembly. The Bader's "Atoms in molecules" theory (QTAIM)[14,15] was used to study the interactions discussed herein using the Multiwfn program[16] and represented using the VMD visualization software.[17] The molecular electrostatic potential (MEP) surfaces were computed using the 0.001 a.u. isosurface as best estimation of the van der Waals surface at the same level of theory and represented using the GaussView program.[18] The utilization of the van der Waals surface is commonly used in the literature convenient to rationalize noncovalent interactions where the intermolecular distances are similar to the sum of the van der Waals radii. Natural bond orbital (NBO)[19] calculations

were performed using the NBO7.0 program.[20] The potential energy density (V) and the bond CP was used as energy predictor to estimate the HB and CH contributions. We have used the equation proposed by Espinosa et al. (E = 0.5 * V).[21]

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