Electronic Supplementary Material (ESI) for Faraday Discussions.

Supporting Information

Syntheses and investigation of metal complexes with macrocyclic polythiaether ligands

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UV-Vis spectroscopy

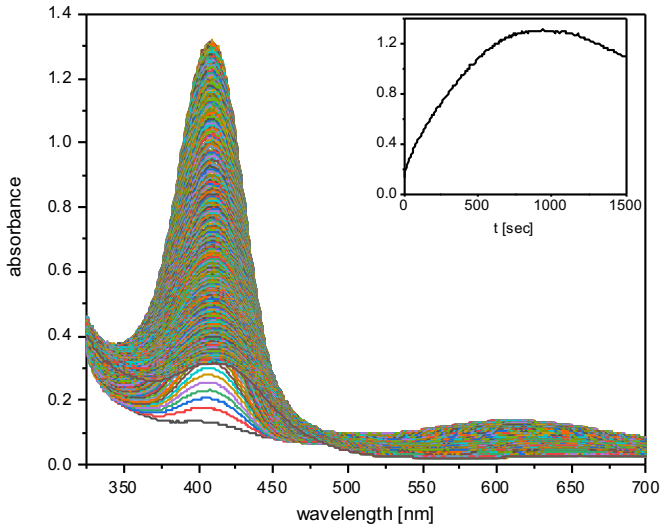


Figure S1. Low temperature time resolved stopped-flow UV/Vis spectra of the reaction of $[Cu^{I}(14\text{-}S_4)]PF_6$ with ozone in dichloromethane ($c_{complex}$ = 0.15 mmol/L after mixing) at -80.0 °C, total time: 1500 s. Inlay (timetrace): Absorbance vs. time at 408 nm.

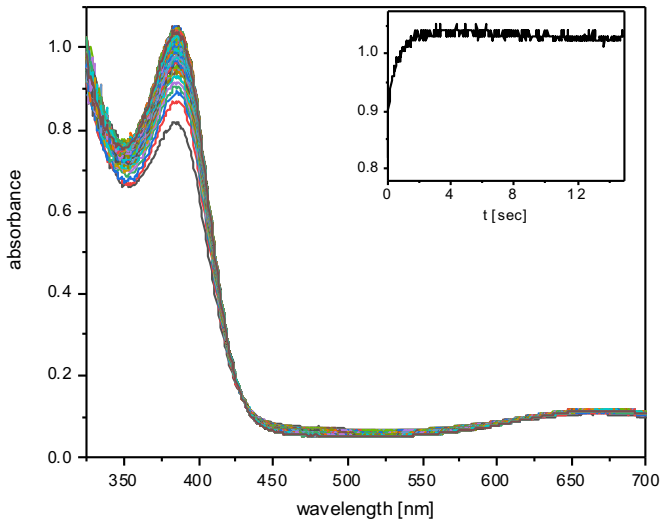


Figure S2. Low temperature time resolved stopped-flow UV/Vis spectra of the reaction of $[Cu^{I}(14\text{-}N_2S_2)]PF_6$ with ozone in dichloromethane ($c_{complex}$ = 0.2 mmol/L after mixing) at -80.0 °C, total time: 15 s. Inlay (timetrace): Absorbance vs. time at 385 nm.

Cyclic Voltammetry

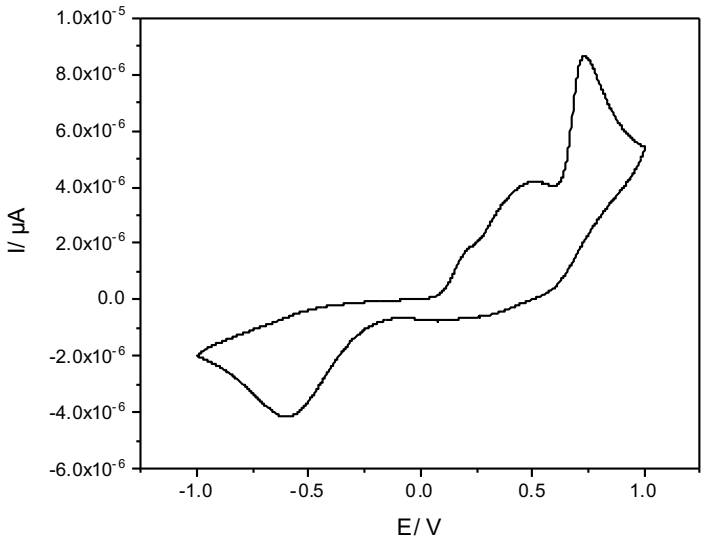


Figure S3. Cyclic voltammogramm of $[Fe^{II}(14\text{-}S_4)(MeCN)_2][(FeI_3)_2(14\text{-}S_4)]$ in MeCN ($c_{complex}$ = 2 mmol/L) at room temperature, Rate: 50 mV/s, Upper Limit 1000 mV, Lower Limit -1000 mV, E(Int/Fin): 100 mV, Cycles: 3).

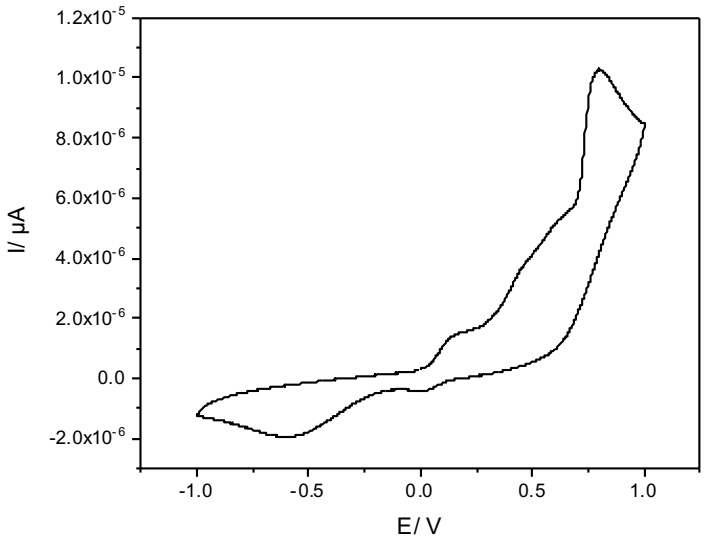


Figure S4. Cyclic voltammogramm of $[Fe^{II}(14\text{-}S_4)(MeCN)_2]FeI_4$ in MeCN ($c_{complex}$ = 2 mmol/L) at room temperature, Rate: 50 mV/s, Upper Limit 1000 mV, Lower Limit -1000 mV, E(Int/Fin): 100 mV, Cycles: 3).

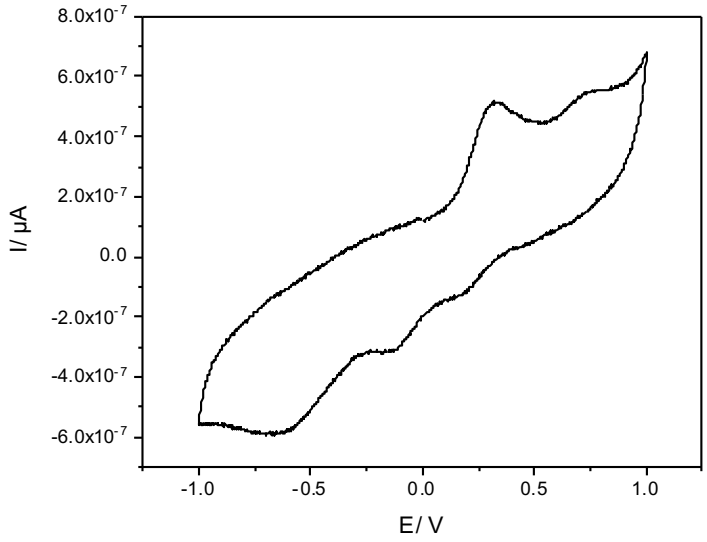


Figure S5. Cyclic voltammogramm of [Co^{II}(14-S_4)$(OTf)_2$] in MeCN ($c_{complex}$ = 0.5 mmol/L) at room temperature, Rate: 50 mV/s, Upper Limit 1500 mV, Lower Limit -1500 mV, E(Int/Fin): 100 mV, Cycles: 3).

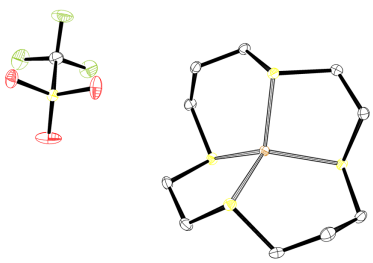
Single Crystal Diffraction Data

Details of X-ray crystal structure determination

Diffraction data for all structures was collected at low temperatures (100K) using φ- and ω-scans on a BRUKER D8 Venture system equipped with dual IμS microfocus sources, a PHOTON100 detector and an OXFORD CRYOSYSTEMS 700 low temperature system. Mo-K_α radiation with wavelength 0.71073 Å and a collimating Quazar multilayer mirror were used. Semi-empirical absorption correction from equivalents was applied using SADABS-2016/2[1][Krause, L.; Herbst-Irmer, R.; Sheldrick, G. M.; Stalke, D. *J. Appl. Cryst.* **2015**, 48, 3–10 and the structures were solved by direct methods using SHELXT2014/5[2][Sheldrick, G. M. *Acta Cryst. A* **2015**, 71, 3–8]. Refinement was performed against F^2 on all data by full-matrix least squares using SHELXL2018/3.[2][Sheldrick, G. M. *Acta Cryst. C* **2015**, 71, 3–8] All non-hydrogen atoms were refined anisotropically and C-H hydrogen atoms were positioned at geometrically calculated positions and refined using a riding model. NH-hydrogen atoms were located in the Fourier difference map and set to ideal distances. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2x or 1.5x (CH_3 hydrogen atoms) the U_{eq} value of the atoms they are linked to.

The crystallographic data has been deposited with the Cambridge Crystallographic Data Centre as CCDC No. 2107318-2107328 and can be obtained free of charge.[https://www.ccdc.cam.ac.uk/structures/]

[Cu^{I}(14-S_4)]OTf



The structure of [Cu^{I}(14-S$_4$)]OTf was solved in the monoclinic space group $P2_1/n$ and the asymmetric unit contains two cations and two anions of [Cu^{I}(14-S$_4$)]OTf.

Table S1. Crystal data and structure refinement for [Cu^{I}(14-S$_4$)]OTf.

CCDC No	2107318	
Empirical formula	C_{11} H_{20} Cu F_3 O_3 S_5	
Formula weight	481.11	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 19.3571(11) Å	α= 90°.
	b = 9.1791(5) Å	β= 93.921(2)°.
	c = 20.0178(12) Å	γ = 90°.
Volume	3548.5(4) Å^3	
Z	8	
Density (calculated)	1.801 Mg/m^3	
Absorption coefficient	1.856 mm^{-1}	
F(000)	1968	
Crystal size	0.797 x 0.644 x 0.534 mm^3	
Theta range for data collection	1.416 to 30.508°.	
Index ranges	-27 ≤ h ≤ 27, -13 ≤ k ≤ 13, -28 ≤ l ≤ 28	
Reflections collected	109254	
Independent reflections	10827 [R(int) = 0.0481]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10827 / 0 / 416	
Goodness-of-fit on F^2	1.032	

Final R indices [I>2σ(I)]	R1 = 0.0276, wR2 = 0.0576
R indices (all data)	R1 = 0.0390, wR2 = 0.0613
Extinction coefficient	0.00250(8)
Largest diff. peak and hole	0.458 and -0.410 e.Å^{-3}

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for [Cu^I(14-S_4)]OTf. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cu(1)	8869(1)	8386(1)	7877(1)	11(1)
S(1)	9885(1)	8691(1)	8492(1)	12(1)
S(2)	7994(1)	7870(1)	8548(1)	11(1)
S(3)	8287(1)	10135(1)	7264(1)	12(1)
S(4)	9262(1)	6606(1)	7214(1)	11(1)
C(1)	9634(1)	8192(2)	9327(1)	16(1)
C(2)	9002(1)	9084(2)	9509(1)	16(1)
C(3)	8310(1)	8291(2)	9404(1)	16(1)
C(4)	7487(1)	9489(2)	8306(1)	14(1)
C(5)	7439(1)	9642(2)	7545(1)	14(1)
C(6)	8210(1)	9516(2)	6395(1)	14(1)
C(7)	8352(1)	7905(2)	6272(1)	13(1)
C(8)	9113(1)	7432(2)	6389(1)	13(1)
C(9)	10179(1)	6923(2)	7440(1)	14(1)
C(10)	10297(1)	7040(2)	8201(1)	14(1)
Cu(11)	3888(1)	6333(1)	7816(1)	11(1)
C(11)	4870(1)	6155(2)	9235(1)	14(1)
S(11)	4948(1)	5980(1)	8338(1)	11(1)
S(13)	3234(1)	4629(1)	7247(1)	12(1)
C(13)	3544(1)	6152(2)	9320(1)	16(1)
S(12)	3089(1)	6882(1)	8563(1)	12(1)
C(12)	4238(1)	6951(2)	9466(1)	16(1)
S(14)	4244(1)	8138(1)	7134(1)	11(1)
C(15)	2415(1)	5268(2)	7549(1)	15(1)

C(16)	3151(1)	5223(2)	6374(1)	14(1)
C(17)	3306(1)	6820(2)	6241(1)	13(1)
C(18)	4075(1)	7250(2)	6323(1)	12(1)
C(19)	5172(1)	7904(2)	7342(1)	13(1)
C(20)	5301(1)	7737(2)	8099(1)	13(1)
C(14)	2485(1)	5420(2)	8311(1)	16(1)
S(21)	6154(1)	8479(1)	5869(1)	11(1)
F(21)	5910(1)	9615(1)	4671(1)	37(1)
F(22)	6474(1)	7608(1)	4677(1)	40(1)
F(23)	6988(1)	9584(1)	5012(1)	34(1)
O(21)	6725(1)	7622(1)	6149(1)	25(1)
O(22)	5511(1)	7706(1)	5762(1)	21(1)
O(23)	6108(1)	9920(1)	6147(1)	24(1)
C(21)	6392(1)	8836(2)	5018(1)	20(1)
S(31)	1092(1)	6643(1)	5881(1)	12(1)
F(31)	1559(1)	7106(1)	4696(1)	33(1)
F(32)	1774(1)	4955(1)	5087(1)	30(1)
F(33)	743(1)	5520(1)	4699(1)	31(1)
O(31)	861(1)	5337(1)	6190(1)	31(1)
O(32)	1738(1)	7218(2)	6164(1)	28(1)
O(33)	564(1)	7721(1)	5727(1)	21(1)
C(31)	1302(1)	6023(2)	5051(1)	18(1)

Table S3. Bond lengths [Å] and angles [°] for [Cu^{I}(14-S_4)]OTf.

Cu(1)-S(1)	2.2646(4)

Cu(1)-S(4)	2.2683(4)
Cu(1)-S(3)	2.2728(4)
Cu(1)-S(2)	2.2812(4)
S(1)-C(10)	1.8265(16)
S(1)-C(1)	1.8300(16)
S(2)-C(3)	1.8222(16)
S(2)-C(4)	1.8271(16)
S(3)-C(6)	1.8273(16)
S(3)-C(5)	1.8288(16)
S(4)-C(8)	1.8231(15)
S(4)-C(9)	1.8252(16)
C(1)-C(2)	1.537(2)
C(1)-H(1A)	0.9900
C(1)-H(1AB)	0.9900
C(2)-C(3)	1.525(2)
C(2)-H(2A)	0.9900
C(2)-H(2AB)	0.9900
C(3)-H(3A)	0.9900
C(3)-H(3AB)	0.9900
C(4)-C(5)	1.526(2)
C(4)-H(4A)	0.9900
C(4)-H(4AB)	0.9900
C(5)-H(5A)	0.9900
C(5)-H(5AB)	0.9900
C(6)-C(7)	1.528(2)
C(6)-H(6A)	0.9900
C(6)-H(6AB)	0.9900

C(7)-C(8)	1.537(2)
C(7)-H(7A)	0.9900
C(7)-H(7AB)	0.9900
C(8)-H(8A)	0.9900
C(8)-H(8AB)	0.9900
C(9)-C(10)	1.527(2)
C(9)-H(9A)	0.9900
C(9)-H(9AB)	0.9900
C(10)-H(10A)	0.9900
C(10)-H(10B)	0.9900
Cu(11)-S(11)	2.2618(4)
Cu(11)-S(13)	2.2698(4)
Cu(11)-S(12)	2.2808(4)
Cu(11)-S(14)	2.2827(4)
C(11)-C(12)	1.524(2)
C(11)-S(11)	1.8192(15)
C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900
S(11)-C(20)	1.8271(16)
S(13)-C(16)	1.8265(16)
S(13)-C(15)	1.8312(16)
C(13)-C(12)	1.541(2)
C(13)-S(12)	1.8283(16)
C(13)-H(13A)	0.9900
C(13)-H(13B)	0.9900
S(12)-C(14)	1.8284(16)
C(12)-H(12A)	0.9900

C(12)-H(12B)	0.9900
S(14)-C(18)	1.8252(15)
S(14)-C(19)	1.8300(16)
C(15)-C(14)	1.529(2)
C(15)-H(15A)	0.9900
C(15)-H(15B)	0.9900
C(16)-C(17)	1.524(2)
C(16)-H(16A)	0.9900
C(16)-H(16B)	0.9900
C(17)-C(18)	1.537(2)
C(17)-H(17A)	0.9900
C(17)-H(17B)	0.9900
C(18)-H(18A)	0.9900
C(18)-H(18B)	0.9900
C(19)-C(20)	1.526(2)
C(19)-H(19A)	0.9900
C(19)-H(19B)	0.9900
C(20)-H(20A)	0.9900
C(20)-H(20B)	0.9900
C(14)-H(14A)	0.9900
C(14)-H(14B)	0.9900
S(21)-O(22)	1.4370(12)
S(21)-O(21)	1.4378(13)
S(21)-O(23)	1.4399(13)
S(21)-C(21)	1.8238(17)
F(21)-C(21)	1.332(2)
F(22)-C(21)	1.333(2)

F(23)-C(21)	1.343(2)
S(31)-O(31)	1.4349(13)
S(31)-O(32)	1.4377(13)
S(31)-O(33)	1.4398(12)
S(31)-C(31)	1.8283(17)
F(31)-C(31)	1.338(2)
F(32)-C(31)	1.3386(19)
F(33)-C(31)	1.333(2)
S(1)-Cu(1)-S(4)	95.364(15)
S(1)-Cu(1)-S(3)	125.880(16)
S(4)-Cu(1)-S(3)	111.537(16)
S(1)-Cu(1)-S(2)	110.942(16)
S(4)-Cu(1)-S(2)	119.142(16)
S(3)-Cu(1)-S(2)	95.944(16)
C(10)-S(1)-C(1)	103.48(8)
C(10)-S(1)-Cu(1)	96.08(5)
C(1)-S(1)-Cu(1)	101.00(6)
C(3)-S(2)-C(4)	102.48(7)
C(3)-S(2)-Cu(1)	107.15(5)
C(4)-S(2)-Cu(1)	94.74(5)
C(6)-S(3)-C(5)	101.52(7)
C(6)-S(3)-Cu(1)	107.41(5)
C(5)-S(3)-Cu(1)	94.66(5)
C(8)-S(4)-C(9)	104.45(7)
C(8)-S(4)-Cu(1)	101.06(5)
C(9)-S(4)-Cu(1)	95.73(5)
C(2)-C(1)-S(1)	110.41(11)

C(2)-C(1)-H(1A)	109.6
S(1)-C(1)-H(1A)	109.6
C(2)-C(1)-H(1AB)	109.6
S(1)-C(1)-H(1AB)	109.6
H(1A)-C(1)-H(1AB)	108.1
C(3)-C(2)-C(1)	114.71(14)
C(3)-C(2)-H(2A)	108.6
C(1)-C(2)-H(2A)	108.6
C(3)-C(2)-H(2AB)	108.6
C(1)-C(2)-H(2AB)	108.6
H(2A)-C(2)-H(2AB)	107.6
C(2)-C(3)-S(2)	117.76(11)
C(2)-C(3)-H(3A)	107.9
S(2)-C(3)-H(3A)	107.9
C(2)-C(3)-H(3AB)	107.9
S(2)-C(3)-H(3AB)	107.9
H(3A)-C(3)-H(3AB)	107.2
C(5)-C(4)-S(2)	109.51(11)
C(5)-C(4)-H(4A)	109.8
S(2)-C(4)-H(4A)	109.8
C(5)-C(4)-H(4AB)	109.8
S(2)-C(4)-H(4AB)	109.8
H(4A)-C(4)-H(4AB)	108.2
C(4)-C(5)-S(3)	109.53(11)
C(4)-C(5)-H(5A)	109.8
S(3)-C(5)-H(5A)	109.8
C(4)-C(5)-H(5AB)	109.8

S(3)-C(5)-H(5AB)	109.8
H(5A)-C(5)-H(5AB)	108.2
C(7)-C(6)-S(3)	116.77(11)
C(7)-C(6)-H(6A)	108.1
S(3)-C(6)-H(6A)	108.1
C(7)-C(6)-H(6AB)	108.1
S(3)-C(6)-H(6AB)	108.1
H(6A)-C(6)-H(6AB)	107.3
C(6)-C(7)-C(8)	115.48(13)
C(6)-C(7)-H(7A)	108.4
C(8)-C(7)-H(7A)	108.4
C(6)-C(7)-H(7AB)	108.4
C(8)-C(7)-H(7AB)	108.4
H(7A)-C(7)-H(7AB)	107.5
C(7)-C(8)-S(4)	110.23(10)
C(7)-C(8)-H(8A)	109.6
S(4)-C(8)-H(8A)	109.6
C(7)-C(8)-H(8AB)	109.6
S(4)-C(8)-H(8AB)	109.6
H(8A)-C(8)-H(8AB)	108.1
C(10)-C(9)-S(4)	109.54(10)
C(10)-C(9)-H(9A)	109.8
S(4)-C(9)-H(9A)	109.8
C(10)-C(9)-H(9AB)	109.8
S(4)-C(9)-H(9AB)	109.8
H(9A)-C(9)-H(9AB)	108.2
C(9)-C(10)-S(1)	109.76(11)

C(9)-C(10)-H(10A)	109.7
S(1)-C(10)-H(10A)	109.7
C(9)-C(10)-H(10B)	109.7
S(1)-C(10)-H(10B)	109.7
H(10A)-C(10)-H(10B)	108.2
S(11)-Cu(11)-S(13)	126.244(16)
S(11)-Cu(11)-S(12)	111.280(16)
S(13)-Cu(11)-S(12)	95.787(16)
S(11)-Cu(11)-S(14)	94.586(15)
S(13)-Cu(11)-S(14)	112.379(16)
S(12)-Cu(11)-S(14)	118.497(16)
C(12)-C(11)-S(11)	117.67(11)
C(12)-C(11)-H(11A)	107.9
S(11)-C(11)-H(11A)	107.9
C(12)-C(11)-H(11B)	107.9
S(11)-C(11)-H(11B)	107.9
H(11A)-C(11)-H(11B)	107.2
C(11)-S(11)-C(20)	103.80(7)
C(11)-S(11)-Cu(11)	108.06(5)
C(20)-S(11)-Cu(11)	95.47(5)
C(16)-S(13)-C(15)	101.45(7)
C(16)-S(13)-Cu(11)	106.49(5)
C(15)-S(13)-Cu(11)	94.58(5)
C(12)-C(13)-S(12)	110.28(11)
C(12)-C(13)-H(13A)	109.6
S(12)-C(13)-H(13A)	109.6
C(12)-C(13)-H(13B)	109.6

S(12)-C(13)-H(13B)	109.6
H(13A)-C(13)-H(13B)	108.1
C(13)-S(12)-C(14)	102.82(8)
C(13)-S(12)-Cu(11)	98.82(5)
C(14)-S(12)-Cu(11)	96.14(5)
C(11)-C(12)-C(13)	114.98(13)
C(11)-C(12)-H(12A)	108.5
C(13)-C(12)-H(12A)	108.5
C(11)-C(12)-H(12B)	108.5
C(13)-C(12)-H(12B)	108.5
H(12A)-C(12)-H(12B)	107.5
C(18)-S(14)-C(19)	105.28(7)
C(18)-S(14)-Cu(11)	99.46(5)
C(19)-S(14)-Cu(11)	96.27(5)
C(14)-C(15)-S(13)	109.82(11)
C(14)-C(15)-H(15A)	109.7
S(13)-C(15)-H(15A)	109.7
C(14)-C(15)-H(15B)	109.7
S(13)-C(15)-H(15B)	109.7
H(15A)-C(15)-H(15B)	108.2
C(17)-C(16)-S(13)	116.66(11)
C(17)-C(16)-H(16A)	108.1
S(13)-C(16)-H(16A)	108.1
C(17)-C(16)-H(16B)	108.1
S(13)-C(16)-H(16B)	108.1
H(16A)-C(16)-H(16B)	107.3
C(16)-C(17)-C(18)	115.46(13)

C(16)-C(17)-H(17A)	108.4
C(18)-C(17)-H(17A)	108.4
C(16)-C(17)-H(17B)	108.4
C(18)-C(17)-H(17B)	108.4
H(17A)-C(17)-H(17B)	107.5
C(17)-C(18)-S(14)	108.84(10)
C(17)-C(18)-H(18A)	109.9
S(14)-C(18)-H(18A)	109.9
C(17)-C(18)-H(18B)	109.9
S(14)-C(18)-H(18B)	109.9
H(18A)-C(18)-H(18B)	108.3
C(20)-C(19)-S(14)	109.21(10)
C(20)-C(19)-H(19A)	109.8
S(14)-C(19)-H(19A)	109.8
C(20)-C(19)-H(19B)	109.8
S(14)-C(19)-H(19B)	109.8
H(19A)-C(19)-H(19B)	108.3
C(19)-C(20)-S(11)	108.09(10)
C(19)-C(20)-H(20A)	110.1
S(11)-C(20)-H(20A)	110.1
C(19)-C(20)-H(20B)	110.1
S(11)-C(20)-H(20B)	110.1
H(20A)-C(20)-H(20B)	108.4
C(15)-C(14)-S(12)	110.68(11)
C(15)-C(14)-H(14A)	109.5
S(12)-C(14)-H(14A)	109.5
C(15)-C(14)-H(14B)	109.5

S(12)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	108.1
O(22)-S(21)-O(21)	114.96(8)
O(22)-S(21)-O(23)	115.76(8)
O(21)-S(21)-O(23)	114.76(8)
O(22)-S(21)-C(21)	102.77(8)
O(21)-S(21)-C(21)	103.09(8)
O(23)-S(21)-C(21)	102.86(8)
F(21)-C(21)-F(22)	106.90(15)
F(21)-C(21)-F(23)	107.00(15)
F(22)-C(21)-F(23)	107.16(15)
F(21)-C(21)-S(21)	111.78(12)
F(22)-C(21)-S(21)	111.91(12)
F(23)-C(21)-S(21)	111.79(12)
O(31)-S(31)-O(32)	115.17(9)
O(31)-S(31)-O(33)	115.41(9)
O(32)-S(31)-O(33)	114.65(8)
O(31)-S(31)-C(31)	103.13(8)
O(32)-S(31)-C(31)	103.34(8)
O(33)-S(31)-C(31)	102.60(8)
F(33)-C(31)-F(31)	107.14(14)
F(33)-C(31)-F(32)	107.51(14)
F(31)-C(31)-F(32)	107.23(14)
F(33)-C(31)-S(31)	111.42(12)
F(31)-C(31)-S(31)	111.43(12)

Table S4. Anisotropic displacement parameters ($Å^2 \times 10^3$) for [Cu^I(14-S_4)]OTf. The anisotropic displacement factor exponent takes the form: $2\pi^2 [h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cu(1)	10(1)	14(1)	9(1)	0(1)	0(1)	3(1)
S(1)	12(1)	12(1)	13(1)	-1(1)	-1(1)	0(1)
S(2)	13(1)	11(1)	10(1)	0(1)	1(1)	0(1)
S(3)	12(1)	11(1)	12(1)	2(1)	-1(1)	0(1)
S(4)	13(1)	11(1)	11(1)	0(1)	2(1)	0(1)
C(1)	18(1)	19(1)	10(1)	1(1)	-2(1)	2(1)
C(2)	21(1)	15(1)	10(1)	-2(1)	0(1)	1(1)
C(3)	18(1)	20(1)	9(1)	1(1)	2(1)	1(1)
C(4)	12(1)	15(1)	16(1)	0(1)	2(1)	4(1)
C(5)	10(1)	18(1)	14(1)	3(1)	0(1)	2(1)
C(6)	15(1)	16(1)	11(1)	3(1)	-2(1)	-1(1)
C(7)	14(1)	15(1)	10(1)	1(1)	-2(1)	-4(1)
C(8)	16(1)	14(1)	9(1)	0(1)	1(1)	-1(1)
C(9)	11(1)	16(1)	14(1)	0(1)	3(1)	3(1)
C(10)	13(1)	15(1)	15(1)	0(1)	-1(1)	4(1)
Cu(11)	10(1)	15(1)	8(1)	1(1)	0(1)	-3(1)
C(11)	16(1)	16(1)	9(1)	1(1)	-3(1)	-1(1)
S(11)	12(1)	10(1)	11(1)	0(1)	-2(1)	0(1)
S(13)	12(1)	11(1)	13(1)	-1(1)	-1(1)	-1(1)
C(13)	19(1)	21(1)	10(1)	4(1)	2(1)	0(1)
S(12)	13(1)	13(1)	11(1)	0(1)	1(1)	1(1)
C(12)	21(1)	15(1)	11(1)	-3(1)	-1(1)	-1(1)
S(14)	12(1)	11(1)	10(1)	1(1)	1(1)	0(1)

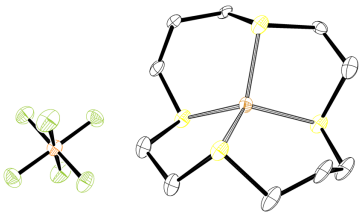
C(15)	10(1)	21(1)	14(1)	-1(1)	1(1)	-3(1)
C(16)	15(1)	18(1)	10(1)	-3(1)	0(1)	-1(1)
C(17)	12(1)	17(1)	10(1)	1(1)	-1(1)	2(1)
C(18)	13(1)	15(1)	9(1)	0(1)	1(1)	1(1)
C(19)	12(1)	14(1)	12(1)	1(1)	2(1)	-2(1)
C(20)	13(1)	14(1)	12(1)	0(1)	-2(1)	-4(1)
C(14)	14(1)	20(1)	15(1)	0(1)	2(1)	-6(1)
S(21)	11(1)	12(1)	10(1)	0(1)	0(1)	-1(1)
F(21)	47(1)	42(1)	21(1)	14(1)	-9(1)	-3(1)
F(22)	61(1)	32(1)	30(1)	-17(1)	22(1)	-9(1)
F(23)	32(1)	39(1)	31(1)	-3(1)	15(1)	-18(1)
O(21)	20(1)	23(1)	32(1)	8(1)	-9(1)	3(1)
O(22)	15(1)	29(1)	20(1)	-1(1)	0(1)	-8(1)
O(23)	37(1)	17(1)	20(1)	-6(1)	6(1)	0(1)
C(21)	24(1)	21(1)	16(1)	-2(1)	5(1)	-6(1)
S(31)	13(1)	12(1)	12(1)	-1(1)	0(1)	1(1)
F(31)	41(1)	32(1)	29(1)	11(1)	21(1)	5(1)
F(32)	34(1)	27(1)	29(1)	-1(1)	10(1)	16(1)
F(33)	37(1)	36(1)	20(1)	-12(1)	-7(1)	3(1)
O(31)	59(1)	15(1)	22(1)	1(1)	18(1)	-6(1)
O(32)	17(1)	32(1)	34(1)	-10(1)	-11(1)	2(1)
O(33)	16(1)	24(1)	22(1)	-4(1)	-1(1)	9(1)
C(31)	21(1)	18(1)	17(1)	1(1)	5(1)	4(1)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for [Cu^I(14-S_4)]OTf.

	x	y	z	U(eq)
H(1A)	9521	7140	9337	19
H(1AB)	10025	8375	9661	19
H(2A)	9069	9377	9985	19
H(2AB)	8980	9985	9236	19
H(3A)	7955	8889	9608	19
H(3AB)	8348	7364	9657	19
H(4A)	7017	9403	8468	17
H(4AB)	7711	10365	8513	17
H(5A)	7096	10403	7407	17
H(5AB)	7283	8710	7337	17
H(6A)	7735	9737	6207	17
H(6AB)	8533	10096	6140	17
H(7A)	8193	7668	5804	16
H(7AB)	8072	7320	6569	16
H(8A)	9418	8290	6354	15
H(8AB)	9227	6723	6040	15
H(9A)	10457	6109	7275	16
H(9AB)	10330	7834	7229	16
H(10A)	10800	7071	8329	17
H(10B)	10100	6176	8414	17
H(11A)	4875	5163	9430	17
H(11B)	5288	6664	9429	17

H(13A)	3252	6272	9704	20
H(13B)	3630	5098	9262	20
H(12A)	4208	7916	9246	19
H(12B)	4307	7119	9955	19
H(15A)	2291	6222	7343	18
H(15B)	2041	4567	7417	18
H(16A)	3465	4621	6118	17
H(16B)	2672	5017	6193	17
H(17A)	3048	7424	6549	16
H(17B)	3128	7059	5779	16
H(18A)	4187	7923	5959	15
H(18B)	4369	6372	6298	15
H(19A)	5340	7028	7115	15
H(19B)	5428	8760	7188	15
H(20A)	5071	8536	8331	16
H(20B)	5803	7778	8227	16
H(14A)	2653	4490	8513	19
H(14B)	2026	5633	8478	19

[Cu^{I}(14-S$_4$)]PF$_6$



The structure of [Cu^{I}(14-S$_4$)]PF$_6$ was solved in the monoclinic space group *C*2/*c* as pseudo-merohedral twin. The twin ratio was refined and converged to 0.365(3). The asymmetric unit contains two half occupied cations disordered at two fold rotation axis, one of them additionally found to be disordered over two positions, one anion of [Cu^{I}(14-S$_4$)]PF$_6$ and one DCM molecule. The disorder was refined with the help of same distance restraints on 1,2- and 1,3-distances, strong similarity restraints on anisotropic displacement parameters[3][Müller, P. *Cryst. Rev.* **2009**, 15(1), 57] and advanced rigid bond restraints.[4][A. Thorn, B. Dittrich, G. M. Sheldrick *Acta Cryst. A* **2012**, 68, 448] Some disordered atoms with similar positions were set to have the same anisotropic displacement parameters. The disorder ratio for the non-symmetry related disorder was allowed to refine freely and converged to 0.929(5).

Table S6. Crystal data and structure refinement for [Cu^{I}(14-S$_4$)]PF$_6$.

CCDC No	2107321	
Empirical formula	C_{11} H_{22} Cl_2 Cu F_6 P S_4	
Formula weight	561.93	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	*C*2/*c*	
Unit cell dimensions	a = 24.959(3) Å	α= 90°.
	b = 9.5840(12) Å	β= 126.366(3)°.
	c = 20.849(4) Å	γ = 90°.
Volume	4016.0(10) Å^3	
Z	8	
Density (calculated)	1.859 Mg/m^3	
Absorption coefficient	1.897 mm^{-1}	
F(000)	2272	
Crystal size	0.231 x 0.062 x 0.056 mm^3	
Theta range for data collection	2.027 to 27.093°.	
Index ranges	-31 ≤ h ≤ 31, -12 ≤ k ≤ 12, -26 ≤ l ≤ 26	

Reflections collected	41006
Independent reflections	4443 [R(int) = 0.0823]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4443 / 1804 / 403
Goodness-of-fit on F^2	1.048
Final R indices [I>2σ(I)]	R1 = 0.0794, wR2 = 0.2029
R indices (all data)	R1 = 0.0927, wR2 = 0.2129
Largest diff. peak and hole	2.088 and -0.985 e.Å^{-3}

Table S7. Atomic coordinates (x 10^2) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for $[Cu^I(14\text{-}S_4)]PF_6$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cu(1)	5000	2587(2)	7500	18(1)
S(1)	5637(7)	1500(14)	7211(7)	23(1)
S(2)	4351(5)	3712(11)	6314(7)	23(1)
S(3)	4318(7)	1551(13)	7741(7)	23(1)
S(4)	5589(6)	3779(12)	8678(7)	23(1)
C(1)	5413(10)	2640(30)	6358(11)	24(4)
C(2)	4650(9)	2780(30)	5800(10)	24(4)
C(3)	3538(9)	3180(30)	5834(12)	22(4)
C(4)	3330(11)	2140(20)	6196(11)	17(4)
C(5)	3554(8)	2470(30)	7046(10)	18(4)
C(6)	4643(9)	2390(20)	8707(10)	17(4)
C(7)	5408(9)	2500(20)	9215(10)	27(5)
C(8)	6454(9)	3380(30)	9128(14)	31(5)
C(9)	6574(12)	2060(30)	8818(12)	29(6)
C(10)	6457(9)	2270(30)	8013(12)	30(5)
Cu(2)	5000	7411(2)	7500	17(1)
S(11)	4139(4)	8552(9)	6427(6)	16(1)
S(12)	4358(6)	6278(14)	7781(7)	16(1)
S(13)	5789(4)	8610(10)	8586(6)	16(1)
S(14)	5684(6)	6335(13)	7281(7)	16(1)
C(11)	3463(8)	7580(20)	6352(11)	19(3)
C(12)	3619(9)	7400(20)	7178(12)	19(3)
C(13)	4656(11)	6620(30)	8753(11)	21(4)

C(14)	5075(11)	7930(30)	9170(16)	19(3)
C(15)	5764(9)	7790(30)	9341(11)	19(2)
C(16)	6512(8)	7860(20)	8678(11)	19(2)
C(17)	6375(9)	7630(20)	7864(12)	19(2)
C(18)	5370(11)	6800(30)	6268(11)	19(4)
C(19)	4838(11)	7900(30)	5827(17)	22(4)
C(20)	4162(9)	7600(20)	5657(11)	19(3)
S(11A)	4420(20)	8530(80)	6310(30)	16(1)
S(12A)	4099(19)	6380(60)	7290(30)	16(1)
S(13A)	5530(20)	8610(80)	8670(30)	16(1)
S(14A)	5909(19)	6250(60)	7800(30)	16(1)
C(11A)	3770(30)	7160(130)	5760(17)	18(4)
C(12A)	3490(20)	6660(120)	6210(30)	18(4)
C(13A)	3860(30)	7420(130)	7740(50)	18(5)
C(14A)	4300(30)	8490(130)	8370(60)	20(6)
C(15A)	5030(30)	8110(160)	8980(30)	19(5)
C(16A)	6270(20)	7450(130)	9248(17)	18(4)
C(17A)	6547(13)	7100(120)	8780(30)	18(4)
C(18A)	6080(30)	7030(120)	7150(40)	19(4)
C(19A)	5690(30)	8360(120)	6730(50)	20(6)
C(20A)	4970(30)	8130(160)	6010(30)	19(5)
P(1)	3147(1)	5315(2)	3747(2)	21(1)
F(1)	3928(3)	5396(7)	4408(4)	32(1)
F(2)	3167(4)	3661(6)	3879(4)	40(2)
F(3)	3278(3)	5065(8)	3083(4)	36(2)
F(4)	3016(3)	5535(8)	4411(4)	34(1)
F(5)	3122(4)	6962(6)	3615(4)	39(2)

F(6)	2369(3)	5224(7)	3082(4)	32(1)
Cl(1)	2854(2)	10162(3)	4349(2)	38(1)
Cl(2)	3870(2)	10366(3)	4077(2)	34(1)
C(31)	3019(5)	10285(10)	3625(5)	20(2)

Table S8. Bond lengths [Å] and angles [°] for $[Cu^{I}(14\text{-}S_4)]PF_6$.

Cu(1)-S(1)	2.263(13)
Cu(1)-S(3)	2.269(14)
Cu(1)-S(2)	2.270(12)
Cu(1)-S(4)	2.284(11)
S(1)-C(10)	1.86(2)
S(1)-C(1)	1.87(2)
S(2)-C(3)	1.723(17)
S(2)-C(2)	1.859(18)
S(3)-C(5)	1.80(2)
S(3)-C(6)	1.852(17)
S(4)-C(8)	1.812(18)
S(4)-C(7)	1.88(2)
C(1)-C(2)	1.538(14)
C(1)-H(1A)	0.9900
C(1)-H(1AB)	0.9900
C(2)-H(2A)	0.9900
C(2)-H(2AB)	0.9900
C(3)-C(4)	1.519(14)
C(3)-H(3A)	0.9900

C(3)-H(3AB)	0.9900
C(4)-C(5)	1.543(13)
C(4)-H(4A)	0.9900
C(4)-H(4AB)	0.9900
C(5)-H(5A)	0.9900
C(5)-H(5AB)	0.9900
C(6)-C(7)	1.542(14)
C(6)-H(6A)	0.9900
C(6)-H(6AB)	0.9900
C(7)-H(7A)	0.9900
C(7)-H(7AB)	0.9900
C(8)-C(9)	1.528(14)
C(8)-H(8A)	0.9900
C(8)-H(8AB)	0.9900
C(9)-C(10)	1.537(15)
C(9)-H(9A)	0.9900
C(9)-H(9AB)	0.9900
C(10)-H(10A)	0.9900
C(10)-H(10B)	0.9900
Cu(2)-S(13)	2.244(10)
Cu(2)-S(12A)	2.25(2)
Cu(2)-S(14A)	2.26(2)
Cu(2)-S(14)	2.262(13)
Cu(2)-S(11)	2.263(9)
Cu(2)-S(11A)	2.27(2)
Cu(2)-S(13A)	2.27(2)
Cu(2)-S(12)	2.280(13)

S(11)-C(11)	1.851(18)
S(11)-C(20)	1.875(19)
S(12)-C(13)	1.727(18)
S(12)-C(12)	1.839(18)
S(13)-C(15)	1.794(19)
S(13)-C(16)	1.845(17)
S(14)-C(18)	1.819(18)
S(14)-C(17)	1.87(2)
C(11)-C(12)	1.533(14)
C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900
C(12)-H(12A)	0.9900
C(12)-H(12B)	0.9900
C(13)-C(14)	1.526(14)
C(13)-H(13A)	0.9900
C(13)-H(13B)	0.9900
C(14)-C(15)	1.541(14)
C(14)-H(14A)	0.9900
C(14)-H(14B)	0.9900
C(15)-H(15A)	0.9900
C(15)-H(15B)	0.9900
C(16)-C(17)	1.536(14)
C(16)-H(16A)	0.9900
C(16)-H(16B)	0.9900
C(17)-H(17A)	0.9900
C(17)-H(17B)	0.9900
C(18)-C(19)	1.512(14)

C(18)-H(18A)	0.9900
C(18)-H(18B)	0.9900
C(19)-C(20)	1.532(14)
C(19)-H(19A)	0.9900
C(19)-H(19B)	0.9900
C(20)-H(20A)	0.9900
C(20)-H(20B)	0.9900
S(11A)-C(11A)	1.86(2)
S(11A)-C(20A)	1.87(2)
S(12A)-C(13A)	1.71(2)
S(12A)-C(12A)	1.85(2)
S(13A)-C(15A)	1.80(3)
S(13A)-C(16A)	1.85(2)
S(14A)-C(18A)	1.80(2)
S(14A)-C(17A)	1.87(2)
C(11A)-C(12A)	1.521(16)
C(11A)-H(11C)	0.9900
C(11A)-H(11D)	0.9900
C(12A)-H(12C)	0.9900
C(12A)-H(12D)	0.9900
C(13A)-C(14A)	1.515(16)
C(13A)-H(13C)	0.9900
C(13A)-H(13D)	0.9900
C(14A)-C(15A)	1.529(17)
C(14A)-H(14C)	0.9900
C(14A)-H(14D)	0.9900
C(15A)-H(15C)	0.9900

C(15A)-H(15D)	0.9900
C(16A)-C(17A)	1.529(17)
C(16A)-H(16C)	0.9900
C(16A)-H(16D)	0.9900
C(17A)-H(17C)	0.9900
C(17A)-H(17D)	0.9900
C(18A)-C(19A)	1.522(16)
C(18A)-H(18C)	0.9900
C(18A)-H(18D)	0.9900
C(19A)-C(20A)	1.533(17)
C(19A)-H(19C)	0.9900
C(19A)-H(19D)	0.9900
C(20A)-H(20C)	0.9900
C(20A)-H(20D)	0.9900
P(1)-F(6)	1.585(7)
P(1)-F(1)	1.587(7)
P(1)-F(5)	1.597(6)
P(1)-F(2)	1.605(6)
P(1)-F(4)	1.616(7)
P(1)-F(3)	1.617(7)
Cl(1)-C(31)	1.788(10)
Cl(2)-C(31)	1.740(11)
C(31)-H(31A)	0.9900
C(31)-H(31B)	0.9900

S(1)-Cu(1)-S(3)	126.61(16)
S(1)-Cu(1)-S(2)	95.1(4)

S(3)-Cu(1)-S(2)	107.7(4)
S(1)-Cu(1)-S(4)	114.3(5)
S(3)-Cu(1)-S(4)	94.0(4)
S(2)-Cu(1)-S(4)	121.48(15)
C(10)-S(1)-C(1)	99.8(12)
C(10)-S(1)-Cu(1)	98.6(8)
C(1)-S(1)-Cu(1)	97.0(8)
C(3)-S(2)-C(2)	105.1(11)
C(3)-S(2)-Cu(1)	109.0(8)
C(2)-S(2)-Cu(1)	97.4(7)
C(5)-S(3)-C(6)	103.6(11)
C(5)-S(3)-Cu(1)	100.6(8)
C(6)-S(3)-Cu(1)	98.5(7)
C(8)-S(4)-C(7)	100.9(12)
C(8)-S(4)-Cu(1)	105.2(7)
C(7)-S(4)-Cu(1)	95.0(7)
C(2)-C(1)-S(1)	108.0(13)
C(2)-C(1)-H(1A)	110.1
S(1)-C(1)-H(1A)	110.1
C(2)-C(1)-H(1AB)	110.1
S(1)-C(1)-H(1AB)	110.1
H(1A)-C(1)-H(1AB)	108.4
C(1)-C(2)-S(2)	110.2(12)
C(1)-C(2)-H(2A)	109.6
S(2)-C(2)-H(2A)	109.6
C(1)-C(2)-H(2AB)	109.6
S(2)-C(2)-H(2AB)	109.6

H(2A)-C(2)-H(2AB)	108.1
C(4)-C(3)-S(2)	122.5(14)
C(4)-C(3)-H(3A)	106.7
S(2)-C(3)-H(3A)	106.7
C(4)-C(3)-H(3AB)	106.7
S(2)-C(3)-H(3AB)	106.7
H(3A)-C(3)-H(3AB)	106.6
C(3)-C(4)-C(5)	115.9(15)
C(3)-C(4)-H(4A)	108.3
C(5)-C(4)-H(4A)	108.3
C(3)-C(4)-H(4AB)	108.3
C(5)-C(4)-H(4AB)	108.3
H(4A)-C(4)-H(4AB)	107.4
C(4)-C(5)-S(3)	108.3(13)
C(4)-C(5)-H(5A)	110.0
S(3)-C(5)-H(5A)	110.0
C(4)-C(5)-H(5AB)	110.0
S(3)-C(5)-H(5AB)	110.0
H(5A)-C(5)-H(5AB)	108.4
C(7)-C(6)-S(3)	110.0(11)
C(7)-C(6)-H(6A)	109.7
S(3)-C(6)-H(6A)	109.7
C(7)-C(6)-H(6AB)	109.7
S(3)-C(6)-H(6AB)	109.7
H(6A)-C(6)-H(6AB)	108.2
C(6)-C(7)-S(4)	105.8(11)
C(6)-C(7)-H(7A)	110.6

S(4)-C(7)-H(7A)	110.6
C(6)-C(7)-H(7AB)	110.6
S(4)-C(7)-H(7AB)	110.6
H(7A)-C(7)-H(7AB)	108.7
C(9)-C(8)-S(4)	115.2(14)
C(9)-C(8)-H(8A)	108.5
S(4)-C(8)-H(8A)	108.5
C(9)-C(8)-H(8AB)	108.5
S(4)-C(8)-H(8AB)	108.5
H(8A)-C(8)-H(8AB)	107.5
C(8)-C(9)-C(10)	113.3(18)
C(8)-C(9)-H(9A)	108.9
C(10)-C(9)-H(9A)	108.9
C(8)-C(9)-H(9AB)	108.9
C(10)-C(9)-H(9AB)	108.9
H(9A)-C(9)-H(9AB)	107.7
C(9)-C(10)-S(1)	108.9(15)
C(9)-C(10)-H(10A)	109.9
S(1)-C(10)-H(10A)	109.9
C(9)-C(10)-H(10B)	109.9
S(1)-C(10)-H(10B)	109.9
H(10A)-C(10)-H(10B)	108.3
S(12A)-Cu(2)-S(14A)	124.2(12)
S(13)-Cu(2)-S(14)	97.0(3)
S(13)-Cu(2)-S(11)	120.06(16)
S(14)-Cu(2)-S(11)	114.1(4)
S(12A)-Cu(2)-S(11A)	94.3(9)

S(14A)-Cu(2)-S(11A)	115.3(12)
S(12A)-Cu(2)-S(13A)	108.4(13)
S(14A)-Cu(2)-S(13A)	95.5(9)
S(11A)-Cu(2)-S(13A)	121.3(12)
S(13)-Cu(2)-S(12)	108.3(5)
S(14)-Cu(2)-S(12)	124.39(14)
S(11)-Cu(2)-S(12)	94.8(3)
C(11)-S(11)-C(20)	100.0(10)
C(11)-S(11)-Cu(2)	97.2(6)
C(20)-S(11)-Cu(2)	96.8(7)
C(13)-S(12)-C(12)	104.5(12)
C(13)-S(12)-Cu(2)	109.3(8)
C(12)-S(12)-Cu(2)	96.8(7)
C(15)-S(13)-C(16)	106.2(10)
C(15)-S(13)-Cu(2)	101.2(8)
C(16)-S(13)-Cu(2)	97.1(6)
C(18)-S(14)-C(17)	101.0(11)
C(18)-S(14)-Cu(2)	105.4(8)
C(17)-S(14)-Cu(2)	94.8(7)
C(12)-C(11)-S(11)	110.6(12)
C(12)-C(11)-H(11A)	109.5
S(11)-C(11)-H(11A)	109.5
C(12)-C(11)-H(11B)	109.5
S(11)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	108.1
C(11)-C(12)-S(12)	108.7(12)
C(11)-C(12)-H(12A)	110.0

S(12)-C(12)-H(12A)	110.0
C(11)-C(12)-H(12B)	110.0
S(12)-C(12)-H(12B)	110.0
H(12A)-C(12)-H(12B)	108.3
C(14)-C(13)-S(12)	119.9(14)
C(14)-C(13)-H(13A)	107.3
S(12)-C(13)-H(13A)	107.3
C(14)-C(13)-H(13B)	107.3
S(12)-C(13)-H(13B)	107.3
H(13A)-C(13)-H(13B)	106.9
C(13)-C(14)-C(15)	110.8(16)
C(13)-C(14)-H(14A)	109.5
C(15)-C(14)-H(14A)	109.5
C(13)-C(14)-H(14B)	109.5
C(15)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	108.1
C(14)-C(15)-S(13)	112.0(14)
C(14)-C(15)-H(15A)	109.2
S(13)-C(15)-H(15A)	109.2
C(14)-C(15)-H(15B)	109.2
S(13)-C(15)-H(15B)	109.2
H(15A)-C(15)-H(15B)	107.9
C(17)-C(16)-S(13)	112.2(12)
C(17)-C(16)-H(16A)	109.2
S(13)-C(16)-H(16A)	109.2
C(17)-C(16)-H(16B)	109.2
S(13)-C(16)-H(16B)	109.2

H(16A)-C(16)-H(16B)	107.9
C(16)-C(17)-S(14)	109.2(13)
C(16)-C(17)-H(17A)	109.8
S(14)-C(17)-H(17A)	109.8
C(16)-C(17)-H(17B)	109.8
S(14)-C(17)-H(17B)	109.8
H(17A)-C(17)-H(17B)	108.3
C(19)-C(18)-S(14)	119.7(15)
C(19)-C(18)-H(18A)	107.4
S(14)-C(18)-H(18A)	107.4
C(19)-C(18)-H(18B)	107.4
S(14)-C(18)-H(18B)	107.4
H(18A)-C(18)-H(18B)	106.9
C(18)-C(19)-C(20)	117.2(17)
C(18)-C(19)-H(19A)	108.0
C(20)-C(19)-H(19A)	108.0
C(18)-C(19)-H(19B)	108.0
C(20)-C(19)-H(19B)	108.0
H(19A)-C(19)-H(19B)	107.2
C(19)-C(20)-S(11)	107.3(15)
C(19)-C(20)-H(20A)	110.2
S(11)-C(20)-H(20A)	110.2
C(19)-C(20)-H(20B)	110.2
S(11)-C(20)-H(20B)	110.2
H(20A)-C(20)-H(20B)	108.5
C(11A)-S(11A)-C(20A)	101.0(19)
C(11A)-S(11A)-Cu(2)	95.6(14)

C(20A)-S(11A)-Cu(2)	98.3(14)
C(13A)-S(12A)-C(12A)	107(2)
C(13A)-S(12A)-Cu(2)	106.1(15)
C(12A)-S(12A)-Cu(2)	99.9(11)
C(15A)-S(13A)-C(16A)	104(2)
C(15A)-S(13A)-Cu(2)	99.5(16)
C(16A)-S(13A)-Cu(2)	97.2(13)
C(18A)-S(14A)-C(17A)	102(2)
C(18A)-S(14A)-Cu(2)	103.2(13)
C(17A)-S(14A)-Cu(2)	98.8(12)
C(12A)-C(11A)-S(11A)	113(2)
C(12A)-C(11A)-H(11C)	109.1
S(11A)-C(11A)-H(11C)	109.1
C(12A)-C(11A)-H(11D)	109.1
S(11A)-C(11A)-H(11D)	109.1
H(11C)-C(11A)-H(11D)	107.8
C(11A)-C(12A)-S(12A)	117.2(19)
C(11A)-C(12A)-H(12C)	108.0
S(12A)-C(12A)-H(12C)	108.0
C(11A)-C(12A)-H(12D)	108.0
S(12A)-C(12A)-H(12D)	108.0
H(12C)-C(12A)-H(12D)	107.2
C(14A)-C(13A)-S(12A)	124(2)
C(14A)-C(13A)-H(13C)	106.3
S(12A)-C(13A)-H(13C)	106.2
C(14A)-C(13A)-H(13D)	106.2
S(12A)-C(13A)-H(13D)	106.2

H(13C)-C(13A)-H(13D)	106.4
C(13A)-C(14A)-C(15A)	117(3)
C(13A)-C(14A)-H(14C)	108.0
C(15A)-C(14A)-H(14C)	108.0
C(13A)-C(14A)-H(14D)	108.0
C(15A)-C(14A)-H(14D)	108.0
H(14C)-C(14A)-H(14D)	107.3
C(14A)-C(15A)-S(13A)	113(2)
C(14A)-C(15A)-H(15C)	109.1
S(13A)-C(15A)-H(15C)	109.1
C(14A)-C(15A)-H(15D)	109.1
S(13A)-C(15A)-H(15D)	109.1
H(15C)-C(15A)-H(15D)	107.8
C(17A)-C(16A)-S(13A)	111(2)
C(17A)-C(16A)-H(16C)	109.4
S(13A)-C(16A)-H(16C)	109.4
C(17A)-C(16A)-H(16D)	109.4
S(13A)-C(16A)-H(16D)	109.4
H(16C)-C(16A)-H(16D)	108.0
C(16A)-C(17A)-S(14A)	112(2)
C(16A)-C(17A)-H(17C)	109.2
S(14A)-C(17A)-H(17C)	109.2
C(16A)-C(17A)-H(17D)	109.2
S(14A)-C(17A)-H(17D)	109.2
H(17C)-C(17A)-H(17D)	107.9
C(19A)-C(18A)-S(14A)	116(2)
C(19A)-C(18A)-H(18C)	108.2

S(14A)-C(18A)-H(18C)	108.2
C(19A)-C(18A)-H(18D)	108.2
S(14A)-C(18A)-H(18D)	108.2
H(18C)-C(18A)-H(18D)	107.3
C(18A)-C(19A)-C(20A)	114(3)
C(18A)-C(19A)-H(19C)	108.6
C(20A)-C(19A)-H(19C)	108.6
C(18A)-C(19A)-H(19D)	108.6
C(20A)-C(19A)-H(19D)	108.6
H(19C)-C(19A)-H(19D)	107.6
C(19A)-C(20A)-S(11A)	109(2)
C(19A)-C(20A)-H(20C)	109.9
S(11A)-C(20A)-H(20C)	109.9
C(19A)-C(20A)-H(20D)	109.9
S(11A)-C(20A)-H(20D)	109.9
H(20C)-C(20A)-H(20D)	108.3
F(6)-P(1)-F(1)	179.4(4)
F(6)-P(1)-F(5)	90.1(4)
F(1)-P(1)-F(5)	90.2(4)
F(6)-P(1)-F(2)	89.6(4)
F(1)-P(1)-F(2)	90.1(4)
F(5)-P(1)-F(2)	179.5(5)
F(6)-P(1)-F(4)	89.5(4)
F(1)-P(1)-F(4)	91.0(3)
F(5)-P(1)-F(4)	90.7(4)
F(2)-P(1)-F(4)	89.0(4)
F(6)-P(1)-F(3)	90.5(3)

F(1)-P(1)-F(3)	89.0(4)
F(5)-P(1)-F(3)	90.4(4)
F(2)-P(1)-F(3)	89.9(4)
F(4)-P(1)-F(3)	178.9(4)
Cl(2)-C(31)-Cl(1)	111.3(5)
Cl(2)-C(31)-H(31A)	109.4
Cl(1)-C(31)-H(31A)	109.4
Cl(2)-C(31)-H(31B)	109.4
Cl(1)-C(31)-H(31B)	109.4

Table S9. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $[Cu^{I}(14\text{-}S_4)]PF_6$. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [\ h^2\ a^*2U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cu(1)	18(1)	19(1)	15(1)	0	8(1)	0
S(1)	22(1)	16(1)	25(1)	-6(3)	12(1)	1(2)
S(2)	22(1)	16(1)	25(1)	-6(3)	12(1)	1(2)
S(3)	22(1)	16(1)	25(1)	-6(3)	12(1)	1(2)
S(4)	22(1)	16(1)	25(1)	-6(3)	12(1)	1(2)
C(1)	28(5)	16(5)	23(5)	-9(4)	12(4)	3(4)
C(2)	28(5)	16(5)	23(5)	-9(4)	12(4)	3(4)
C(3)	19(6)	19(7)	23(6)	-11(6)	10(5)	-5(6)
C(4)	12(6)	20(7)	23(6)	-13(6)	13(5)	-3(6)
C(5)	17(6)	16(7)	24(6)	-14(5)	14(5)	-8(6)
C(6)	26(6)	13(7)	21(6)	-2(6)	18(5)	-3(6)
C(7)	32(6)	14(7)	22(6)	-3(6)	8(5)	1(6)
C(8)	24(7)	17(7)	30(7)	-11(6)	4(5)	-6(6)
C(9)	21(8)	16(7)	28(7)	-11(7)	2(6)	-6(7)

C(10)	26(7)	14(7)	30(6)	-9(6)	5(6)	-3(6)
Cu(2)	16(1)	16(1)	16(1)	0	8(1)	0
S(11)	16(1)	12(1)	22(1)	7(2)	12(1)	4(2)
S(12)	16(1)	12(1)	22(1)	7(2)	12(1)	4(2)
S(13)	16(1)	12(1)	22(1)	7(2)	12(1)	4(2)
S(14)	16(1)	12(1)	22(1)	7(2)	12(1)	4(2)
C(11)	17(4)	12(5)	26(4)	12(4)	11(4)	3(4)
C(12)	18(4)	12(5)	24(4)	10(4)	11(4)	5(4)
C(13)	21(5)	17(6)	26(5)	9(5)	13(4)	3(5)
C(14)	19(5)	18(5)	25(5)	8(5)	16(4)	4(5)
C(15)	17(3)	13(3)	25(3)	6(3)	12(2)	8(3)
C(16)	17(3)	13(3)	25(3)	6(3)	12(2)	8(3)
C(17)	17(3)	13(3)	25(3)	6(3)	12(2)	8(3)
C(18)	22(5)	12(5)	23(5)	10(5)	13(4)	1(5)
C(19)	24(5)	14(5)	24(5)	7(5)	11(4)	3(5)
C(20)	23(4)	10(5)	19(4)	6(4)	10(4)	2(4)
S(11A)	16(1)	12(1)	22(1)	7(2)	12(1)	4(2)
S(12A)	16(1)	12(1)	22(1)	7(2)	12(1)	4(2)
S(13A)	16(1)	12(1)	22(1)	7(2)	12(1)	4(2)
S(14A)	16(1)	12(1)	22(1)	7(2)	12(1)	4(2)
C(11A)	18(5)	12(5)	23(5)	8(5)	11(4)	4(5)
C(12A)	17(6)	12(6)	24(5)	9(6)	11(5)	4(6)
C(13A)	17(5)	13(6)	24(5)	8(6)	12(5)	5(6)
C(14A)	19(6)	16(6)	25(6)	8(6)	13(6)	4(6)
C(15A)	18(5)	15(6)	24(5)	7(5)	13(5)	5(5)
C(16A)	17(5)	13(5)	24(5)	6(5)	12(4)	6(5)
C(17A)	17(5)	13(6)	24(5)	6(6)	12(5)	6(6)

C(18A)	19(5)	13(5)	24(5)	8(5)	12(5)	4(5)
C(19A)	21(6)	13(6)	24(6)	8(6)	12(6)	3(6)
C(20A)	21(5)	12(6)	23(5)	8(5)	12(5)	3(5)
P(1)	23(1)	14(1)	24(1)	0(1)	12(1)	2(1)
F(1)	22(3)	31(3)	28(3)	-1(3)	6(3)	5(3)
F(2)	47(4)	14(3)	48(4)	3(2)	22(3)	1(3)
F(3)	30(3)	53(4)	28(3)	2(3)	19(3)	7(3)
F(4)	32(3)	43(4)	33(3)	-1(3)	24(3)	3(3)
F(5)	39(4)	17(3)	43(4)	5(3)	15(3)	2(3)
F(6)	22(3)	32(3)	31(3)	1(3)	10(2)	1(2)
Cl(1)	35(2)	40(2)	43(2)	5(1)	24(1)	10(1)
Cl(2)	33(1)	26(1)	50(2)	-1(1)	28(1)	1(1)
C(31)	26(5)	17(4)	15(4)	-2(3)	11(4)	4(4)

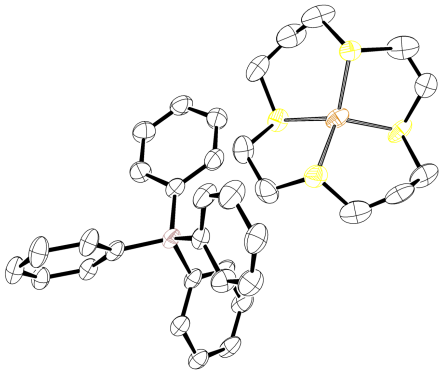
Table S10. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for [Cu^I(tetrathiacyclam)]PF_6.

	x	y	z	U(eq)
H(1A)	5620	3573	6556	29
H(1AB)	5575	2226	6068	29
H(2A)	4446	1842	5635	29
H(2AB)	4515	3302	5315	29
H(3A)	3271	4035	5718	26
H(3AB)	3392	2795	5313	26
H(4A)	3510	1211	6204	20
H(4AB)	2839	2065	5843	20

H(5A)	3208	2171	7110	21
H(5AB)	3624	3486	7145	21
H(6A)	4448	3336	8614	21
H(6AB)	4514	1837	8996	21
H(7A)	5607	1583	9260	33
H(7AB)	5591	2847	9756	33
H(8A)	6653	4185	9039	37
H(8AB)	6691	3287	9710	37
H(9A)	6274	1318	8762	35
H(9AB)	7038	1749	9215	35
H(10A)	6817	1814	8021	36
H(10B)	6461	3281	7911	36
H(11A)	3039	8099	6002	23
H(11B)	3409	6656	6111	23
H(12A)	3236	6962	7126	23
H(12B)	3705	8317	7438	23
H(13A)	4268	6668	8769	26
H(13B)	4925	5809	9078	26
H(14A)	5130	8065	9677	23
H(14B)	4842	8753	8829	23
H(15A)	5876	6790	9374	22
H(15B)	6103	8224	9863	22
H(16A)	6898	8489	9000	22
H(16B)	6629	6952	8961	22
H(17A)	6781	7272	7938	22
H(17B)	6250	8521	7570	22
H(18A)	5755	7100	6279	23

H(18B)	5195	5935	5945	23
H(19A)	4764	8078	5312	27
H(19B)	5013	8780	6139	27
H(20A)	4108	6586	5689	23
H(20B)	3797	7929	5117	23
H(11C)	3397	7528	5235	22
H(11D)	3961	6352	5666	22
H(12C)	3254	5774	5964	21
H(12D)	3164	7354	6122	21
H(13C)	3455	7922	7305	22
H(13D)	3704	6778	7976	22
H(14C)	4106	8703	8664	23
H(14D)	4274	9361	8100	23
H(15C)	5067	7093	9075	22
H(15D)	5200	8581	9493	22
H(16C)	6619	7922	9753	21
H(16D)	6145	6581	9382	21
H(17C)	6934	6472	9103	22
H(17D)	6705	7972	8685	22
H(18C)	6557	7241	7470	22
H(18D)	5975	6335	6745	22
H(19C)	5929	8859	6543	24
H(19D)	5700	8976	7113	24
H(20C)	4906	7146	5830	23
H(20D)	4858	8739	5563	23
H(31A)	2829	9462	3269	24
H(31B)	2801	11129	3296	24

[Cu^{I}(14-S$_4$)]BPh$_4$



The structure of [Cu^{I}(14-S$_4$)]BPh$_4$ was solved in the hexagonal space group *P*6$_1$ and the asymmetric unit contains one full anion and cation, which was found to be disordered over three positions, of [Cu^{I}(14-S$_4$)]BPh$_4$. The disorder was refined using same distance restraints on 1,2- and 1,3-distances, similarity restraints on anisotropic displacement parameters, by setting some atoms to have the same anisotropic displacement parameters and by using advanced rigid bond restraints. The disorder ratio refined to 0.484(4): 0.261(4):0.254(4).

Table S11. Crystal data and structure refinement for [Cu^{I}(14-S$_4$)]BPh$_4$.

CCDC No	2107327
Empirical formula	C_{34} H_{40} B Cu S_4
Formula weight	651.25
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Hexagonal
Space group	*P*6$_1$

Unit cell dimensions	a = 10.7164(11) Å	α= 90°.
	b = 10.7164(11) Å	β= 90°.
	c = 47.139(7) Å	γ = 120°.
Volume	4688.3(12) $Å^3$	
Z	6	
Density (calculated)	1.384 Mg/m^3	
Absorption coefficient	0.989 mm^{-1}	
F(000)	2052	
Crystal size	0.309 x 0.224 x 0.108 mm^3	
Theta range for data collection	2.194 to 27.868°.	
Index ranges	-14 ≤ h ≤ 14, -14 ≤ k ≤ 14, -62 ≤ l ≤ 62	
Reflections collected	151798	
Independent reflections	7451 [R(int) = 0.0566]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7451 / 1803 / 605	
Goodness-of-fit on F^2	1.037	
Final R indices [I>2σ(I)]	R1 = 0.0400, wR2 = 0.0994	
R indices (all data)	R1 = 0.0507, wR2 = 0.1076	
Absolute structure parameter	0.006(4)	
Extinction coefficient	0.0038(5)	
Largest diff. peak and hole	0.548 and -0.548 e.$Å^{-3}$	

Table S12. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for $[Cu^I(14\text{-}S_4)]BPh_4$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)

Cu(1)	10414(1)	0(1)	4497(1)	45(1)
S(1)	8811(14)	-136(12)	4845(2)	53(2)
S(2)	10962(16)	-1764(16)	4558(3)	53(3)
S(3)	12645(15)	1796(17)	4419(3)	41(3)
S(4)	8959(13)	-21(11)	4152(2)	46(2)
C(1)	8455(15)	-1662(15)	5020(3)	66(3)
C(2)	9786(14)	-1666(13)	5106(2)	57(3)
C(3)	10412(18)	-2370(19)	4939(3)	63(3)
C(4)	12860(20)	-550(20)	4593(3)	52(3)
C(5)	13490(20)	640(20)	4409(5)	70(5)
C(6)	12843(19)	2470(20)	4074(4)	73(5)
C(7)	11571(18)	1710(30)	3880(4)	73(4)
C(8)	10134(15)	1668(14)	3971(3)	62(3)
C(9)	7844(18)	530(20)	4351(3)	55(3)
C(10)	7240(20)	-490(20)	4612(4)	61(3)
S(1A)	9542(16)	417(16)	4100(3)	87(4)
S(2A)	9090(20)	-362(18)	4880(4)	100(5)
S(3A)	10870(20)	-1930(20)	4614(4)	35(3)
S(4A)	12660(30)	1830(20)	4406(5)	43(4)
C(1A)	8980(30)	1500(20)	4270(5)	69(5)
C(2A)	7720(30)	560(40)	4456(6)	81(7)
C(3A)	7470(40)	-610(40)	4646(9)	72(6)
C(4A)	8450(30)	-2280(30)	4893(6)	66(5)
C(5A)	9730(30)	-2410(30)	4941(6)	62(6)
C(6A)	12640(30)	-840(40)	4726(5)	54(5)
C(7A)	13740(20)	-70(30)	4495(5)	56(4)

C(8A)	13460(30)	800(30)	4270(4)	43(4)
C(9A)	12380(30)	2590(30)	4089(6)	50(5)
C(10A)	11180(30)	1640(40)	3896(6)	70(6)
S(1B)	9030(20)	20(20)	4859(4)	57(4)
S(2B)	10780(20)	-1790(20)	4565(5)	24(2)
S(3B)	12870(30)	1830(30)	4436(6)	59(5)
S(4B)	8970(30)	230(20)	4132(4)	47(4)
C(1B)	7910(30)	-2080(30)	4858(6)	66(5)
C(2B)	8830(30)	-2590(30)	5024(5)	71(5)
C(3B)	9940(40)	-2610(40)	4870(6)	63(3)
C(4B)	12730(50)	-620(40)	4664(9)	52(3)
C(5B)	13330(30)	500(40)	4362(8)	46(6)
C(6B)	12290(30)	1930(30)	4017(5)	65(5)
C(7B)	11590(30)	2560(30)	3998(6)	79(5)
C(8B)	10190(30)	2140(20)	4140(5)	58(4)
C(9B)	7480(30)	-130(30)	4354(6)	53(5)
C(10B)	7640(30)	190(30)	4645(5)	59(5)
C(11)	5107(5)	3789(4)	5307(1)	30(1)
C(12)	5431(6)	5093(5)	5432(1)	39(1)
C(13)	4565(6)	5707(5)	5404(1)	46(1)
C(14)	3317(6)	5025(5)	5244(1)	42(1)
C(15)	2943(5)	3720(5)	5116(1)	35(1)
C(16)	3816(5)	3124(4)	5150(1)	32(1)
C(21)	7150(5)	3486(4)	5042(1)	32(1)
C(22)	8480(6)	3551(6)	5036(1)	45(1)
C(23)	9331(6)	3897(7)	4792(1)	54(1)
C(24)	8853(6)	4179(5)	4540(1)	47(1)

C(25)	7529(6)	4091(6)	4534(1)	46(1)
C(26)	6702(5)	3758(5)	4780(1)	41(1)
C(31)	7148(5)	3665(5)	5618(1)	32(1)
C(32)	8479(6)	4929(5)	5624(1)	45(1)
C(33)	9322(6)	5434(6)	5870(1)	53(1)
C(34)	8855(6)	4676(5)	6120(1)	47(1)
C(35)	7528(6)	3442(5)	6126(1)	45(1)
C(36)	6699(6)	2944(5)	5879(1)	41(1)
C(41)	5111(4)	1321(4)	5353(1)	30(1)
C(42)	5438(6)	343(5)	5229(1)	40(1)
C(43)	4573(6)	-1141(5)	5257(1)	45(1)
C(44)	3321(6)	-1706(5)	5418(1)	42(1)
C(45)	2944(5)	-778(5)	5543(1)	35(1)
C(46)	3821(5)	695(4)	5510(1)	32(1)
B(11)	6145(5)	3074(5)	5329(1)	30(1)

Table S13. Bond lengths [Å] and angles [°] for $[Cu^{I}(14\text{-}S_4)]BPh_4$.

Cu(1)-S(2B)	2.17(2)	Cu(1)-S(3B)	2.38(3)	S(4)-C(8)	1.818(16)
Cu(1)-S(2A)	2.211(16)	Cu(1)-S(4B)	2.41(2)	S(4)-C(9)	1.830(19)
Cu(1)-S(3)	2.226(15)	Cu(1)-S(3A)	2.42(2)	C(1)-C(2)	1.485(19)
Cu(1)-S(1A)	2.233(15)	S(1)-C(1)	1.696(16)	C(1)-H(1A)	0.9900
Cu(1)-S(4)	2.245(11)	S(1)-C(10)	1.885(18)	C(1)-H(1B)	0.9900
Cu(1)-S(4A)	2.26(3)	S(2)-C(4)	1.79(2)	C(2)-C(3)	1.47(2)
Cu(1)-S(2)	2.260(17)	S(2)-C(3)	1.90(2)	C(2)-H(2A)	0.9900
Cu(1)-S(1B)	2.267(19)	S(3)-C(6)	1.75(2)	C(2)-H(2B)	0.9900
Cu(1)-S(1)	2.327(12)	S(3)-C(5)	1.87(3)	C(3)-H(3A)	0.9900

C(3)-H(3B)	0.9900	C(1A)-C(2A)	1.50(3)	S(1B)-C(1B)	1.95(4)
C(4)-C(5)	1.40(2)	C(1A)-H(1AA)	0.9900	S(2B)-C(3B)	1.69(4)
C(4)-H(4A)	0.9900	C(1A)-H(1AB)	0.9900	S(2B)-C(4B)	1.88(5)
C(4)-H(4B)	0.9900	C(2A)-C(3A)	1.45(3)	S(3B)-C(5B)	1.76(5)
C(5)-H(5A)	0.9900	C(2A)-H(2AA)	0.9900	S(3B)-C(6B)	2.09(4)
C(5)-H(5B)	0.9900	C(2A)-H(2AB)	0.9900	S(4B)-C(9B)	1.78(4)
C(6)-C(7)	1.50(2)	C(3A)-H(3AA)	0.9900	S(4B)-C(8B)	1.80(3)
C(6)-H(6A)	0.9900	C(3A)-H(3AB)	0.9900	C(1B)-C(2B)	1.56(4)
C(6)-H(6B)	0.9900	C(4A)-C(5A)	1.46(3)	C(1B)-H(1BA)	0.9900
C(7)-C(8)	1.58(2)	C(4A)-H(4AA)	0.9900	C(1B)-H(1BB)	0.9900
C(7)-H(7A)	0.9900	C(4A)-H(4AB)	0.9900	C(2B)-C(3B)	1.40(4)
C(7)-H(7B)	0.9900	C(5A)-H(5AA)	0.9900	C(2B)-H(2BA)	0.9900
C(8)-H(8A)	0.9900	C(5A)-H(5AB)	0.9900	C(2B)-H(2BB)	0.9900
C(8)-H(8B)	0.9900	C(6A)-C(7A)	1.51(2)	C(3B)-H(3BA)	0.9900
C(9)-C(10)	1.56(2)	C(6A)-H(6AA)	0.9900	C(3B)-H(3BB)	0.9900
C(9)-H(9A)	0.9900	C(6A)-H(6AB)	0.9900	C(4B)-C(5B)	1.77(5)
C(9)-H(9B)	0.9900	C(7A)-C(8A)	1.54(2)	C(4B)-H(4BA)	0.9900
C(10)-H(10A)	0.9900	C(7A)-H(7AA)	0.9900	C(4B)-H(4BB)	0.9900
C(10)-H(10B)	0.9900	C(7A)-H(7AB)	0.9900	C(5B)-H(5BA)	0.9900
S(1A)-C(1A)	1.74(2)	C(8A)-H(8AA)	0.9900	C(5B)-H(5BB)	0.9900
S(1A)-C(10A)	1.85(2)	C(8A)-H(8AB)	0.9900	C(6B)-C(7B)	1.25(4)
S(2A)-C(4A)	1.81(3)	C(9A)-C(10A)	1.49(3)	C(6B)-H(6BA)	0.9900
S(2A)-C(3A)	1.95(3)	C(9A)-H(9AA)	0.9900	C(6B)-H(6BB)	0.9900
S(3A)-C(6A)	1.73(3)	C(9A)-H(9AB)	0.9900	C(7B)-C(8B)	1.49(4)
S(3A)-C(5A)	1.87(3)	C(10A)-H(10C)	0.9900	C(7B)-H(7BA)	0.9900
S(4A)-C(9A)	1.80(3)	C(10A)-H(10D)	0.9900	C(7B)-H(7BB)	0.9900
S(4A)-C(8A)	1.81(2)	S(1B)-C(10B)	1.88(2)	C(8B)-H(8BA)	0.9900

C(8B)-H(8BB)	0.9900	C(25)-C(26)	1.394(7)	S(2A)-Cu(1)-S(1A)	115.0(6)
C(9B)-C(10B)	1.40(3)	C(25)-H(25)	0.9500	S(3)-Cu(1)-S(4)	109.3(5)
C(9B)-H(9BA)	0.9900	C(26)-H(26)	0.9500	S(2A)-Cu(1)-S(4A)	128.4(8)
C(9B)-H(9BB)	0.9900	C(31)-C(32)	1.392(7)	S(1A)-Cu(1)-S(4A)	92.3(7)
C(10B)-H(10E)	0.9900	C(31)-C(36)	1.403(6)	S(3)-Cu(1)-S(2)	97.4(6)
C(10B)-H(10F)	0.9900	C(31)-B(11)	1.652(7)	S(4)-Cu(1)-S(2)	123.6(5)
C(11)-C(12)	1.392(6)	C(32)-C(33)	1.400(7)	S(2B)-Cu(1)-S(1B)	107.8(7)
C(11)-C(16)	1.408(6)	C(32)-H(32)	0.9500	S(3)-Cu(1)-S(1)	127.6(6)
C(11)-B(11)	1.640(7)	C(33)-C(34)	1.377(8)	S(4)-Cu(1)-S(1)	91.3(3)
C(12)-C(13)	1.387(7)	C(33)-H(33)	0.9500	S(2)-Cu(1)-S(1)	110.5(4)
C(12)-H(12)	0.9500	C(34)-C(35)	1.375(8)	S(2B)-Cu(1)-S(3B)	97.5(9)
C(13)-C(14)	1.383(7)	C(34)-H(34)	0.9500	S(1B)-Cu(1)-S(3B)	122.6(10)
C(13)-H(13)	0.9500	C(35)-C(36)	1.398(7)	S(2B)-Cu(1)-S(4B)	127.4(8)
C(14)-C(15)	1.387(6)	C(35)-H(35)	0.9500	S(1B)-Cu(1)-S(4B)	94.7(8)
C(14)-H(14)	0.9500	C(36)-H(36)	0.9500	S(3B)-Cu(1)-S(4B)	109.3(8)
C(15)-C(16)	1.381(6)	C(41)-C(42)	1.389(6)	S(2A)-Cu(1)-S(3A)	93.0(7)
C(15)-H(15)	0.9500	C(41)-C(46)	1.408(6)	S(1A)-Cu(1)-S(3A)	130.3(6)
C(16)-H(16)	0.9500	C(41)-B(11)	1.639(7)	S(4A)-Cu(1)-S(3A)	101.5(7)
C(21)-C(22)	1.392(7)	C(42)-C(43)	1.390(7)	C(1)-S(1)-C(10)	109.9(10)
C(21)-C(26)	1.405(6)	C(42)-H(42)	0.9500	C(1)-S(1)-Cu(1)	102.0(7)
C(21)-B(11)	1.648(7)	C(43)-C(44)	1.390(7)	C(10)-S(1)-Cu(1)	99.2(7)
C(22)-C(23)	1.397(7)	C(43)-H(43)	0.9500	C(4)-S(2)-C(3)	101.8(11)
C(22)-H(22)	0.9500	C(44)-C(45)	1.380(6)	C(4)-S(2)-Cu(1)	94.5(9)
C(23)-C(24)	1.389(8)	C(44)-H(44)	0.9500	C(3)-S(2)-Cu(1)	103.9(9)
C(23)-H(23)	0.9500	C(45)-C(46)	1.384(6)	C(6)-S(3)-C(5)	104.4(13)
C(24)-C(25)	1.374(8)	C(45)-H(45)	0.9500	C(6)-S(3)-Cu(1)	111.5(8)
C(24)-H(24)	0.9500	C(46)-H(46)	0.9500	C(5)-S(3)-Cu(1)	95.7(9)

C(8)-S(4)-C(9)	99.2(9)	C(4)-C(5)-S(3)	114.0(17)	C(10)-C(9)-H(9B)	110.3
C(8)-S(4)-Cu(1)	101.3(7)	C(4)-C(5)-H(5A)	108.8	S(4)-C(9)-H(9B)	110.3
C(9)-S(4)-Cu(1)	100.7(6)	S(3)-C(5)-H(5A)	108.8	H(9A)-C(9)-H(9B)	108.6
C(2)-C(1)-S(1)	112.5(10)	C(4)-C(5)-H(5B)	108.8	C(9)-C(10)-S(1)	107.5(12)
C(2)-C(1)-H(1A)	109.1	S(3)-C(5)-H(5B)	108.8	C(9)-C(10)-H(10A)	110.2
S(1)-C(1)-H(1A)	109.1	H(5A)-C(5)-H(5B)	107.7	S(1)-C(10)-H(10A)	110.2
C(2)-C(1)-H(1B)	109.1	C(7)-C(6)-S(3)	117.0(14)	C(9)-C(10)-H(10B)	110.2
S(1)-C(1)-H(1B)	109.1	C(7)-C(6)-H(6A)	108.0	S(1)-C(10)-H(10B)	110.2
H(1A)-C(1)-H(1B)	107.8	S(3)-C(6)-H(6A)	108.0	H(10A)-C(10)-H(10B)	108.5
C(3)-C(2)-C(1)	122.9(12)	C(7)-C(6)-H(6B)	108.0	C(1A)-S(1A)-C(10A)	106.7(17)
C(3)-C(2)-H(2A)	106.6	S(3)-C(6)-H(6B)	108.0	C(1A)-S(1A)-Cu(1)	93.7(9)
C(1)-C(2)-H(2A)	106.6	H(6A)-C(6)-H(6B)	107.3	C(10A)-S(1A)-Cu(1)	103.6(12)
C(3)-C(2)-H(2B)	106.6	C(6)-C(7)-C(8)	117.6(17)	C(4A)-S(2A)-C(3A)	93.4(15)
C(1)-C(2)-H(2B)	106.6	C(6)-C(7)-H(7A)	107.9	C(4A)-S(2A)-Cu(1)	94.1(10)
H(2A)-C(2)-H(2B)	106.6	C(8)-C(7)-H(7A)	107.9	C(3A)-S(2A)-Cu(1)	90.5(14)
C(2)-C(3)-S(2)	118.4(12)	C(6)-C(7)-H(7B)	107.9	C(6A)-S(3A)-C(5A)	106.2(15)
C(2)-C(3)-H(3A)	107.7	C(8)-C(7)-H(7B)	107.9	C(6A)-S(3A)-Cu(1)	96.4(14)
S(2)-C(3)-H(3A)	107.7	H(7A)-C(7)-H(7B)	107.2	C(5A)-S(3A)-Cu(1)	91.9(12)
C(2)-C(3)-H(3B)	107.7	C(7)-C(8)-S(4)	109.7(12)	C(9A)-S(4A)-C(8A)	102.6(15)
S(2)-C(3)-H(3B)	107.7	C(7)-C(8)-H(8A)	109.7	C(9A)-S(4A)-Cu(1)	101.7(14)
H(3A)-C(3)-H(3B)	107.1	S(4)-C(8)-H(8A)	109.7	C(8A)-S(4A)-Cu(1)	99.5(12)
C(5)-C(4)-S(2)	117.5(16)	C(7)-C(8)-H(8B)	109.7	C(2A)-C(1A)-S(1A)	108.8(18)
C(5)-C(4)-H(4A)	107.9	S(4)-C(8)-H(8B)	109.7	C(2A)-C(1A)-H(1AA)	109.9
S(2)-C(4)-H(4A)	107.9	H(8A)-C(8)-H(8B)	108.2	S(1A)-C(1A)-H(1AA)	109.9
C(5)-C(4)-H(4B)	107.9	C(10)-C(9)-S(4)	106.9(12)	C(2A)-C(1A)-H(1AB)	109.9
S(2)-C(4)-H(4B)	107.9	C(10)-C(9)-H(9A)	110.3	S(1A)-C(1A)-H(1AB)	109.9
H(4A)-C(4)-H(4B)	107.2	S(4)-C(9)-H(9A)	110.3	H(1AA)-C(1A)-H(1AB)	108.3

C(3A)-C(2A)-C(1A)	131(3)	C(7A)-C(6A)-H(6AB)	108.3	C(10B)-S(1B)-C(1B)	92.7(15)
C(3A)-C(2A)-H(2AA)	104.6	S(3A)-C(6A)-H(6AB)	108.3	C(10B)-S(1B)-Cu(1)	98.7(11)
C(1A)-C(2A)-H(2AA)	104.6	H(6AA)-C(6A)-H(6AB)	107.4	C(1B)-S(1B)-Cu(1)	90.9(12)
C(3A)-C(2A)-H(2AB)	104.6	C(6A)-C(7A)-C(8A)	119.4(17)	C(3B)-S(2B)-C(4B)	105(2)
C(1A)-C(2A)-H(2AB)	104.6	C(6A)-C(7A)-H(7AA)	107.5	C(3B)-S(2B)-Cu(1)	107.5(14)
H(2AA)-C(2A)-H(2AB)	105.7	C(8A)-C(7A)-H(7AA)	107.5	C(4B)-S(2B)-Cu(1)	94.6(16)
C(2A)-C(3A)-S(2A)	118(2)	C(6A)-C(7A)-H(7AB)	107.5	C(5B)-S(3B)-C(6B)	94(2)
C(2A)-C(3A)-H(3AA)	107.9	C(8A)-C(7A)-H(7AB)	107.5	C(5B)-S(3B)-Cu(1)	89.9(17)
S(2A)-C(3A)-H(3AA)	107.9	H(7AA)-C(7A)-H(7AB)	107.0	C(6B)-S(3B)-Cu(1)	85.6(12)
C(2A)-C(3A)-H(3AB)	107.9	C(7A)-C(8A)-S(4A)	114.8(16)	C(9B)-S(4B)-C(8B)	107.2(17)
S(2A)-C(3A)-H(3AB)	107.9	C(7A)-C(8A)-H(8AA)	108.6	C(9B)-S(4B)-Cu(1)	96.3(11)
H(3AA)-C(3A)-H(3AB)	107.2	S(4A)-C(8A)-H(8AA)	108.6	C(8B)-S(4B)-Cu(1)	87.9(12)
C(5A)-C(4A)-S(2A)	105.8(19)	C(7A)-C(8A)-H(8AB)	108.6	C(2B)-C(1B)-S(1B)	106(2)
C(5A)-C(4A)-H(4AA)	110.6	S(4A)-C(8A)-H(8AB)	108.6	C(2B)-C(1B)-H(1BA)	110.6
S(2A)-C(4A)-H(4AA)	110.6	H(8AA)-C(8A)-H(8AB)	107.5	S(1B)-C(1B)-H(1BA)	110.6
C(5A)-C(4A)-H(4AB)	110.6	C(10A)-C(9A)-S(4A)	119(2)	C(2B)-C(1B)-H(1BB)	110.6
S(2A)-C(4A)-H(4AB)	110.6	C(10A)-C(9A)-H(9AA)	107.6	S(1B)-C(1B)-H(1BB)	110.6
H(4AA)-C(4A)-H(4AB)	108.7	S(4A)-C(9A)-H(9AA)	107.6	H(1BA)-C(1B)-H(1BB)	108.7
C(4A)-C(5A)-S(3A)	111.5(19)	C(10A)-C(9A)-H(9AB)	107.6	C(3B)-C(2B)-C(1B)	116(2)
C(4A)-C(5A)-H(5AA)	109.3	S(4A)-C(9A)-H(9AB)	107.6	C(3B)-C(2B)-H(2BA)	108.3
S(3A)-C(5A)-H(5AA)	109.3	H(9AA)-C(9A)-H(9AB)	107.0	C(1B)-C(2B)-H(2BA)	108.3
C(4A)-C(5A)-H(5AB)	109.3	C(9A)-C(10A)-S(1A)	110.9(19)	C(3B)-C(2B)-H(2BB)	108.3
S(3A)-C(5A)-H(5AB)	109.3	C(9A)-C(10A)-H(10C)	109.5	C(1B)-C(2B)-H(2BB)	108.3
H(5AA)-C(5A)-H(5AB)	108.0	S(1A)-C(10A)-H(10C)	109.5	H(2BA)-C(2B)-H(2BB)	107.4
C(7A)-C(6A)-S(3A)	116.0(18)	C(9A)-C(10A)-H(10D)	109.5	C(2B)-C(3B)-S(2B)	132(3)
C(7A)-C(6A)-H(6AA)	108.3	S(1A)-C(10A)-H(10D)	109.5	C(2B)-C(3B)-H(3BA)	104.2
S(3A)-C(6A)-H(6AA)	108.3	H(10C)-C(10A)-H(10D)	108.0	S(2B)-C(3B)-H(3BA)	104.2

C(2B)-C(3B)-H(3BB)	104.2	C(7B)-C(8B)-S(4B)	113(2)	C(13)-C(14)-C(15)	119.1(4)
S(2B)-C(3B)-H(3BB)	104.2	C(7B)-C(8B)-H(8BA)	109.1	C(13)-C(14)-H(14)	120.5
H(3BA)-C(3B)-H(3BB)	105.5	S(4B)-C(8B)-H(8BA)	109.1	C(15)-C(14)-H(14)	120.5
C(5B)-C(4B)-S(2B)	99(2)	C(7B)-C(8B)-H(8BB)	109.1	C(16)-C(15)-C(14)	119.6(4)
C(5B)-C(4B)-H(4BA)	112.0	S(4B)-C(8B)-H(8BB)	109.1	C(16)-C(15)-H(15)	120.2
S(2B)-C(4B)-H(4BA)	112.0	H(8BA)-C(8B)-H(8BB)	107.8	C(14)-C(15)-H(15)	120.2
C(5B)-C(4B)-H(4BB)	112.0	C(10B)-C(9B)-S(4B)	122(2)	C(15)-C(16)-C(11)	123.3(4)
S(2B)-C(4B)-H(4BB)	112.0	C(10B)-C(9B)-H(9BA)	106.7	C(15)-C(16)-H(16)	118.4
H(4BA)-C(4B)-H(4BB)	109.6	S(4B)-C(9B)-H(9BA)	106.7	C(11)-C(16)-H(16)	118.4
S(3B)-C(5B)-C(4B)	104(3)	C(10B)-C(9B)-H(9BB)	106.7	C(22)-C(21)-C(26)	114.8(4)
S(3B)-C(5B)-H(5BA)	111.0	S(4B)-C(9B)-H(9BB)	106.7	C(22)-C(21)-B(11)	123.0(4)
C(4B)-C(5B)-H(5BA)	111.0	H(9BA)-C(9B)-H(9BB)	106.6	C(26)-C(21)-B(11)	122.1(4)
S(3B)-C(5B)-H(5BB)	111.0	C(9B)-C(10B)-S(1B)	120(2)	C(21)-C(22)-C(23)	123.0(5)
C(4B)-C(5B)-H(5BB)	111.0	C(9B)-C(10B)-H(10E)	107.3	C(21)-C(22)-H(22)	118.5
H(5BA)-C(5B)-H(5BB)	109.0	S(1B)-C(10B)-H(10E)	107.3	C(23)-C(22)-H(22)	118.5
C(7B)-C(6B)-S(3B)	112(2)	C(9B)-C(10B)-H(10F)	107.3	C(24)-C(23)-C(22)	120.1(5)
C(7B)-C(6B)-H(6BA)	109.2	S(1B)-C(10B)-H(10F)	107.3	C(24)-C(23)-H(23)	120.0
S(3B)-C(6B)-H(6BA)	109.2	H(10E)-C(10B)-H(10F)	106.9	C(22)-C(23)-H(23)	120.0
C(7B)-C(6B)-H(6BB)	109.2	C(12)-C(11)-C(16)	114.9(4)	C(25)-C(24)-C(23)	118.8(5)
S(3B)-C(6B)-H(6BB)	109.2	C(12)-C(11)-B(11)	123.6(4)	C(25)-C(24)-H(24)	120.6
H(6BA)-C(6B)-H(6BB)	107.9	C(16)-C(11)-B(11)	121.5(4)	C(23)-C(24)-H(24)	120.6
C(6B)-C(7B)-C(8B)	126(2)	C(13)-C(12)-C(11)	123.0(4)	C(24)-C(25)-C(26)	120.3(5)
C(6B)-C(7B)-H(7BA)	105.7	C(13)-C(12)-H(12)	118.5	C(24)-C(25)-H(25)	119.9
C(8B)-C(7B)-H(7BA)	105.7	C(11)-C(12)-H(12)	118.5	C(26)-C(25)-H(25)	119.9
C(6B)-C(7B)-H(7BB)	105.7	C(14)-C(13)-C(12)	120.2(4)	C(25)-C(26)-C(21)	123.0(5)
C(8B)-C(7B)-H(7BB)	105.7	C(14)-C(13)-H(13)	119.9	C(25)-C(26)-H(26)	118.5
H(7BA)-C(7B)-H(7BB)	106.2	C(12)-C(13)-H(13)	119.9	C(21)-C(26)-H(26)	118.5

C(32)-C(31)-C(36)	114.9(4)	C(36)-C(35)-H(35)	119.9	C(45)-C(44)-H(44)	120.4
C(32)-C(31)-B(11)	122.9(4)	C(35)-C(36)-C(31)	122.8(5)	C(43)-C(44)-H(44)	120.4
C(36)-C(31)-B(11)	122.2(4)	C(35)-C(36)-H(36)	118.6	C(44)-C(45)-C(46)	119.8(4)
C(31)-C(32)-C(33)	122.8(5)	C(31)-C(36)-H(36)	118.6	C(44)-C(45)-H(45)	120.1
C(31)-C(32)-H(32)	118.6	C(42)-C(41)-C(46)	114.8(4)	C(46)-C(45)-H(45)	120.1
C(33)-C(32)-H(32)	118.6	C(42)-C(41)-B(11)	123.7(4)	C(45)-C(46)-C(41)	123.2(4)
C(34)-C(33)-C(32)	120.4(5)	C(46)-C(41)-B(11)	121.5(4)	C(45)-C(46)-H(46)	118.4
C(34)-C(33)-H(33)	119.8	C(41)-C(42)-C(43)	123.3(4)	C(41)-C(46)-H(46)	118.4
C(32)-C(33)-H(33)	119.8	C(41)-C(42)-H(42)	118.4	C(41)-B(11)-C(11)	108.2(3)
C(35)-C(34)-C(33)	118.8(5)	C(43)-C(42)-H(42)	118.4	C(41)-B(11)-C(21)	109.8(4)
C(35)-C(34)-H(34)	120.6	C(44)-C(43)-C(42)	119.7(4)	C(11)-B(11)-C(21)	109.0(4)
C(33)-C(34)-H(34)	120.6	C(44)-C(43)-H(43)	120.1	C(41)-B(11)-C(31)	108.7(4)
C(34)-C(35)-C(36)	120.2(5)	C(42)-C(43)-H(43)	120.1	C(11)-B(11)-C(31)	109.8(4)
C(34)-C(35)-H(35)	119.9	C(45)-C(44)-C(43)	119.1(4)	C(21)-B(11)-C(31)	111.2(3)

Table S14. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $[Cu^I(14\text{-}S_4)]BPh_4$. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2\ a^* 2U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cu(1)	60(1)	35(1)	31(1)	1(1)	1(1)	18(1)
S(1)	56(4)	63(4)	34(2)	5(2)	-3(2)	26(3)
S(2)	84(6)	41(4)	25(4)	3(3)	-8(3)	25(4)
S(3)	41(4)	43(4)	27(3)	-4(3)	-9(3)	12(3)
S(4)	62(3)	53(4)	26(2)	-6(3)	-6(2)	32(3)
C(1)	77(6)	53(6)	49(6)	-7(5)	11(5)	18(5)
C(2)	84(7)	42(5)	32(5)	9(4)	17(5)	22(5)

C(3)	87(7)	65(5)	21(5)	2(4)	-4(5)	25(5)
C(4)	65(5)	53(4)	42(7)	-6(4)	-3(5)	34(4)
C(5)	79(8)	58(7)	57(9)	-11(6)	16(7)	21(6)
C(6)	83(8)	53(7)	34(6)	-3(5)	-10(6)	-2(7)
C(7)	79(8)	60(7)	51(7)	0(6)	-11(6)	12(7)
C(8)	88(7)	46(5)	49(6)	4(5)	-13(5)	32(5)
C(9)	68(7)	73(7)	37(5)	-13(6)	-19(5)	44(6)
C(10)	61(8)	76(7)	60(8)	-6(6)	10(6)	45(6)
S(1A)	146(9)	57(6)	50(5)	-6(4)	-32(7)	43(7)
S(2A)	109(9)	74(8)	39(5)	-20(5)	35(6)	-14(6)
S(3A)	55(5)	28(4)	21(6)	9(3)	-7(4)	19(3)
S(4A)	51(7)	24(5)	47(8)	-3(5)	3(6)	14(5)
C(1A)	88(9)	66(8)	51(8)	17(7)	-14(7)	35(7)
C(2A)	74(10)	92(11)	49(11)	-12(9)	-2(9)	20(9)
C(3A)	58(10)	91(10)	48(9)	-13(8)	-9(8)	23(8)
C(4A)	80(10)	68(9)	27(8)	-8(8)	4(8)	20(8)
C(5A)	76(9)	64(9)	25(9)	24(8)	18(8)	20(8)
C(6A)	58(8)	66(10)	33(9)	8(7)	1(7)	28(7)
C(7A)	58(8)	84(10)	28(7)	19(7)	4(7)	38(8)
C(8A)	47(8)	59(8)	27(8)	6(7)	6(7)	30(6)
C(9A)	71(10)	35(8)	39(9)	14(7)	-2(8)	24(7)
C(10A)	90(10)	52(9)	45(9)	5(8)	-17(8)	18(9)
S(1B)	47(5)	73(7)	47(5)	-40(5)	-9(4)	26(5)
S(2B)	41(4)	26(4)	16(5)	2(4)	3(4)	25(3)
S(3B)	71(9)	42(6)	34(7)	-6(5)	12(6)	7(7)
S(4B)	66(6)	37(5)	41(5)	19(3)	1(4)	29(4)
C(1B)	79(10)	69(10)	33(9)	5(8)	-2(9)	24(8)

C(2B)	94(10)	73(10)	34(8)	12(8)	0(8)	33(8)
C(3B)	87(7)	65(5)	21(5)	2(4)	-4(5)	25(5)
C(4B)	65(5)	53(4)	42(7)	-6(4)	-3(5)	34(4)
C(5B)	35(8)	49(9)	38(9)	-19(7)	-12(7)	9(7)
C(6B)	65(9)	61(10)	23(8)	-4(8)	-3(7)	-4(8)
C(7B)	92(10)	51(9)	47(9)	-12(8)	-3(8)	1(7)
C(8B)	98(9)	37(8)	33(8)	2(7)	-15(7)	29(7)
C(9B)	60(9)	60(9)	49(7)	-2(8)	-9(7)	38(8)
C(10B)	64(9)	68(10)	45(7)	-8(8)	-5(8)	33(9)
C(11)	47(2)	30(2)	19(2)	3(1)	2(2)	23(2)
C(12)	60(3)	34(2)	30(2)	-4(2)	-13(2)	29(2)
C(13)	73(3)	42(2)	38(3)	-12(2)	-15(2)	41(2)
C(14)	67(3)	44(2)	32(2)	-1(2)	-6(2)	40(2)
C(15)	48(2)	38(2)	27(2)	0(2)	-2(2)	28(2)
C(16)	48(2)	30(2)	24(2)	-2(1)	-2(2)	23(2)
C(21)	42(2)	27(2)	27(2)	2(1)	2(2)	18(2)
C(22)	53(3)	51(3)	39(3)	16(2)	8(2)	33(2)
C(23)	54(3)	68(3)	54(3)	24(3)	21(2)	42(3)
C(24)	58(3)	48(3)	39(3)	15(2)	19(2)	30(2)
C(25)	56(3)	56(3)	29(2)	6(2)	7(2)	31(2)
C(26)	46(2)	54(3)	25(2)	4(2)	3(2)	28(2)
C(31)	42(2)	31(2)	28(2)	0(2)	-2(2)	23(2)
C(32)	53(3)	36(2)	40(3)	7(2)	-9(2)	18(2)
C(33)	56(3)	39(3)	53(3)	2(2)	-18(2)	15(2)
C(34)	60(3)	44(2)	39(3)	-4(2)	-18(2)	28(2)
C(35)	58(3)	50(3)	26(2)	-2(2)	-7(2)	27(2)
C(36)	47(3)	46(3)	25(2)	-1(2)	-5(2)	19(2)

C(41)	46(2)	29(2)	19(2)	1(1)	-2(2)	22(2)
C(42)	59(3)	36(2)	34(2)	9(2)	13(2)	31(2)
C(43)	71(3)	34(2)	40(3)	6(2)	17(2)	34(2)
C(44)	68(3)	29(2)	31(2)	5(2)	7(2)	26(2)
C(45)	48(2)	33(2)	25(2)	2(2)	2(2)	22(2)
C(46)	48(2)	30(2)	23(2)	0(1)	2(2)	23(2)
B(11)	42(2)	29(2)	23(2)	3(1)	1(2)	21(2)

Table S15. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for $[Cu^I(14\text{-}S_4)]BPh_4$.

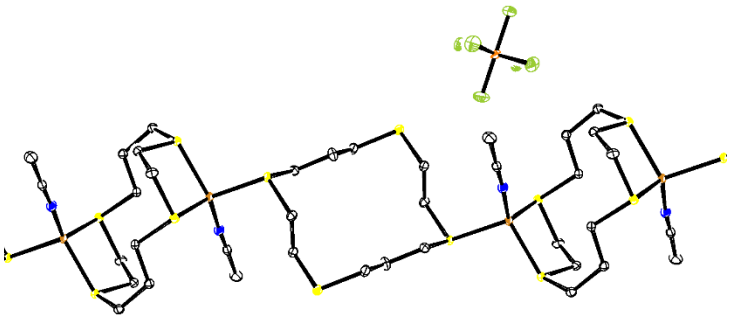
	x	y	z	U(eq)
H(1A)	7877	-1760	5191	79
H(1B)	7871	-2504	4897	79
H(2A)	10548	-645	5127	68
H(2B)	9605	-2096	5298	68
H(3A)	9708	-3416	4936	76
H(3B)	11276	-2242	5041	76
H(4A)	13041	-177	4790	62
H(4B)	13354	-1109	4568	62
H(5A)	13435	280	4212	84
H(5B)	14527	1235	4458	84
H(6A)	13102	3490	4086	88
H(6B)	13665	2439	3985	88
H(7A)	11357	706	3857	88
H(7B)	11854	2178	3692	88
H(8A)	9642	1758	3801	74
H(8B)	10360	2487	4099	74
H(9A)	8430	1540	4414	67
H(9B)	7046	439	4231	67
H(10A)	6724	-1513	4550	73
H(10B)	6552	-303	4718	73
H(1AA)	9779	2237	4386	83
H(1AB)	8702	1989	4128	83

H(2AA)	7601	1250	4578	98
H(2AB)	6883	140	4327	98
H(3AA)	7150	-1485	4529	86
H(3AB)	6669	-785	4774	86
H(4AA)	7748	-2739	5049	79
H(4AB)	7975	-2746	4712	79
H(5AA)	9426	-3409	4997	74
H(5AB)	10299	-1761	5098	74
H(6AA)	12662	-104	4857	65
H(6AB)	12931	-1437	4836	65
H(7AA)	13873	-806	4393	67
H(7AB)	14668	589	4588	67
H(8AA)	12820	135	4122	51
H(8AB)	14390	1480	4178	51
H(9AA)	12236	3395	4147	59
H(9AB)	13285	3011	3977	59
H(10C)	11468	1066	3778	84
H(10D)	10963	2243	3768	84
H(1BA)	6970	-2419	4953	80
H(1BB)	7734	-2453	4662	80
H(2BA)	9266	-1958	5191	85
H(2BB)	8183	-3579	5096	85
H(3BA)	9582	-3647	4834	76
H(3BB)	10734	-2310	5009	76
H(4BA)	12850	-69	4840	62
H(4BB)	13228	-1187	4684	62
H(5BA)	14379	933	4336	55

H(5BB)	12829	-47	4189	55
H(6BA)	13172	2438	3900	78
H(6BB)	11707	939	3942	78
H(7BA)	11414	2605	3793	95
H(7BB)	12252	3570	4057	95
H(8BA)	9731	2636	4044	70
H(8BB)	10375	2472	4339	70
H(9BA)	7016	383	4270	64
H(9BB)	6779	-1173	4337	64
H(10E)	6693	-436	4736	70
H(10F)	7842	1196	4666	70
H(12)	6285	5584	5543	47
H(13)	4830	6597	5495	55
H(14)	2724	5446	5223	50
H(15)	2091	3239	5004	42
H(16)	3531	2220	5063	39
H(22)	8825	3350	5206	54
H(23)	10238	3941	4799	65
H(24)	9430	4428	4373	56
H(25)	7176	4259	4362	55
H(26)	5795	3712	4771	49
H(32)	8830	5471	5454	54
H(33)	10222	6306	5863	64
H(34)	9438	5000	6285	56
H(35)	7174	2926	6299	54
H(36)	5792	2081	5888	49
H(42)	6297	707	5121	48

H(43)	4836	-1767	5166	54
H(44)	2732	-2718	5441	51
H(45)	2084	-1149	5652	42
H(46)	3539	1314	5598	38

{[Cu^{I}(14-S$_4$)(MeCN)PF$_6$]}$_n$



The structure of {[Cu^{I}(14-S$_4$)(MeCN)PF$_6$]}$_n$ was solved in the triclinic space group $P\bar{1}$ and the asymmetric unit contains as part of the 1-dimensional coordination polymer {[Cu^{I}(14-S$_4$)(MeCN)PF$_6$]}$_n$ two half ligands coordinating the copper ion, an acetonitrile molecule coordinating the copper ion and one anion.

Table S16. Crystal data and structure refinement for {[Cu^{I}(14-S$_4$)(MeCN)PF$_6$]}$_n$.

CCDC No	2107320	
Empirical formula	C_{12} H_{23} Cu F_6 N P S_4	
Formula weight	518.06	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 8.9013(13) Å	α= 71.697(5)°.
	b = 10.1583(15) Å	β= 70.925(5)°.
	c = 12.8933(18) Å	γ = 67.975(5)°.
Volume	996.7(3) Å^3	
Z	2	
Density (calculated)	1.726 Mg/m^3	

Absorption coefficient	1.645 mm^{-1}
F(000)	528
Crystal size	0.420 x 0.207 x 0.030 mm^3
Theta range for data collection	2.216 to 27.877°.
Index ranges	-11 ≤ h ≤ 11, -13 ≤ k ≤ 13, -16 ≤ l ≤ 16
Reflections collected	30842
Independent reflections	4751 [R(int) = 0.0612]
Completeness to theta = 25.242°	99.9 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4751 / 0 / 228
Goodness-of-fit on F^2	1.063
Final R indices [I>2σ(I)]	R1 = 0.0266, wR2 = 0.0625
R indices (all data)	R1 = 0.0330, wR2 = 0.0654
Largest diff. peak and hole	0.369 and -0.499 e.$Å^{-3}$

Table S17. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for $\{[Cu^{I}(14\text{-}S_4)(MeCN)PF_6]\}_n$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cu(1)	8626(1)	2741(1)	1354(1)	12(1)
S(1)	11148(1)	1572(1)	260(1)	11(1)
S(2)	7515(1)	3988(1)	-191(1)	12(1)
C(1)	10872(2)	2618(2)	-1131(1)	13(1)
C(2)	9082(2)	2960(2)	-1200(2)	14(1)
C(3)	7972(2)	5716(2)	-667(1)	11(1)
C(4)	6697(2)	6738(2)	79(1)	12(1)
C(5)	6880(2)	8263(2)	-260(2)	13(1)

S(11)	7522(1)	820(1)	2269(1)	11(1)
S(12)	7650(1)	-3398(1)	6277(1)	14(1)
C(11)	8144(2)	126(2)	3598(2)	13(1)
C(12)	7625(2)	-1220(2)	4296(2)	17(1)
C(13)	8211(2)	-1788(2)	5384(2)	15(1)
C(14)	5387(2)	-2735(2)	6662(2)	13(1)
C(15)	4740(2)	-1526(2)	7302(2)	13(1)
N(21)	8398(2)	3726(2)	2502(1)	15(1)
C(21)	8117(2)	4292(2)	3207(2)	14(1)
C(22)	7756(3)	5062(2)	4086(2)	20(1)
P(1)	3517(1)	7902(1)	3014(1)	13(1)
F(1)	3471(1)	8072(1)	1750(1)	22(1)
F(2)	5232(1)	8308(1)	2566(1)	25(1)
F(3)	3563(2)	7750(1)	4284(1)	29(1)
F(4)	1807(1)	7494(1)	3468(1)	22(1)
F(5)	4551(2)	6216(1)	3092(1)	27(1)
F(6)	2480(2)	9595(1)	2937(1)	23(1)

Table S18. Bond lengths [Å] and angles [°] for $\{[Cu^{I}(14\text{-}S_4)(MeCN)PF_6]\}_n$.

Cu(1)-N(21)	1.9529(15)	C(11)-C(12)	1.524(2)	P(1)-F(2)	1.6068(12)
Cu(1)-S(2)	2.3050(5)	C(11)-H(11A)	0.9900	P(1)-F(3)	1.6080(12)
Cu(1)-S(11)	2.3237(5)	C(11)-H(11B)	0.9900	N(21)-Cu(1)-S(2)	121.18(5)
Cu(1)-S(1)	2.3284(5)	C(12)-C(13)	1.522(2)	N(21)-Cu(1)-S(11)	106.85(5)
S(1)-C(1)	1.8176(18)	C(12)-H(12A)	0.9900	S(2)-Cu(1)-S(11)	107.876(19)
S(1)-C(5)#1	1.8251(18)	C(12)-H(12B)	0.9900	N(21)-Cu(1)-S(1)	125.11(5)
S(2)-C(2)	1.8179(18)	C(13)-H(13A)	0.9900	S(2)-Cu(1)-S(1)	92.49(2)
S(2)-C(3)	1.8222(17)	C(13)-H(13B)	0.9900	S(11)-Cu(1)-S(1)	100.800(19)
C(1)-C(2)	1.525(2)	C(14)-C(15)	1.521(2)	C(1)-S(1)-C(5)#1	102.01(8)
C(1)-H(1A)	0.9900	C(14)-H(14A)	0.9900	C(1)-S(1)-Cu(1)	99.73(6)
C(1)-H(1AB)	0.9900	C(14)-H(14B)	0.9900	C(5)#1-S(1)-Cu(1)	121.45(6)
C(2)-H(2A)	0.9900	C(15)-H(15A)	0.9900	C(2)-S(2)-C(3)	101.78(8)
C(2)-H(2AB)	0.9900	C(15)-H(15B)	0.9900	C(2)-S(2)-Cu(1)	98.07(6)
C(3)-C(4)	1.523(2)	N(21)-C(21)	1.137(2)	C(3)-S(2)-Cu(1)	106.29(6)
C(3)-H(3A)	0.9900	C(21)-C(22)	1.459(2)	C(2)-C(1)-S(1)	110.45(12)
C(3)-H(3AB)	0.9900	C(22)-H(22A)	0.9800	C(2)-C(1)-H(1A)	109.6
C(4)-C(5)	1.528(2)	C(22)-H(22B)	0.9800	S(1)-C(1)-H(1A)	109.6
C(4)-H(4A)	0.9900	C(22)-H(22C)	0.9800	C(2)-C(1)-H(1AB)	109.6
C(4)-H(4AB)	0.9900	C(22)-H(22D)	0.9800	S(1)-C(1)-H(1AB)	109.6
C(5)-H(5A)	0.9900	C(22)-H(22E)	0.9800	H(1A)-C(1)-H(1AB)	108.1
C(5)-H(5AB)	0.9900	C(22)-H(22F)	0.9800	C(1)-C(2)-S(2)	114.25(12)
S(11)-C(11)	1.8187(18)	P(1)-F(1)	1.5969(12)	C(1)-C(2)-H(2A)	108.7
S(11)-C(15)#2	1.8204(18)	P(1)-F(5)	1.6002(12)	S(2)-C(2)-H(2A)	108.7
S(12)-C(14)	1.8160(18)	P(1)-F(4)	1.6030(12)	C(1)-C(2)-H(2AB)	108.7
S(12)-C(13)	1.8180(19)	P(1)-F(6)	1.6065(12)	S(2)-C(2)-H(2AB)	108.7

H(2A)-C(2)-H(2AB)	107.6	S(11)-C(11)-H(11B)	109.1	N(21)-C(21)-C(22)	178.23(19)
C(4)-C(3)-S(2)	108.19(12)	H(11A)-C(11)-H(11B)	107.8	C(21)-C(22)-H(22A)	109.5
C(4)-C(3)-H(3A)	110.1	C(13)-C(12)-C(11)	110.67(15)	C(21)-C(22)-H(22B)	109.5
S(2)-C(3)-H(3A)	110.1	C(13)-C(12)-H(12A)	109.5	H(22A)-C(22)-H(22B)	109.5
C(4)-C(3)-H(3AB)	110.1	C(11)-C(12)-H(12A)	109.5	C(21)-C(22)-H(22C)	109.5
S(2)-C(3)-H(3AB)	110.1	C(13)-C(12)-H(12B)	109.5	H(22A)-C(22)-H(22C)	109.5
H(3A)-C(3)-H(3AB)	108.4	C(11)-C(12)-H(12B)	109.5	H(22B)-C(22)-H(22C)	109.5
C(3)-C(4)-C(5)	113.95(14)	H(12A)-C(12)-H(12B)	108.1	C(21)-C(22)-H(22D)	109.5
C(3)-C(4)-H(4A)	108.8	C(12)-C(13)-S(12)	113.98(13)	C(21)-C(22)-H(22E)	109.5
C(5)-C(4)-H(4A)	108.8	C(12)-C(13)-H(13A)	108.8	H(22D)-C(22)-H(22E)	109.5
C(3)-C(4)-H(4AB)	108.8	S(12)-C(13)-H(13A)	108.8	C(21)-C(22)-H(22F)	109.5
C(5)-C(4)-H(4AB)	108.8	C(12)-C(13)-H(13B)	108.8	H(22D)-C(22)-H(22F)	109.5
H(4A)-C(4)-H(4AB)	107.7	S(12)-C(13)-H(13B)	108.8	H(22E)-C(22)-H(22F)	109.5
C(4)-C(5)-S(1)#1	117.86(12)	H(13A)-C(13)-H(13B)	107.7	F(1)-P(1)-F(5)	90.48(7)
C(4)-C(5)-H(5A)	107.8	C(15)-C(14)-S(12)	112.38(12)	F(1)-P(1)-F(4)	90.20(6)
S(1)#1-C(5)-H(5A)	107.8	C(15)-C(14)-H(14A)	109.1	F(5)-P(1)-F(4)	89.99(7)
C(4)-C(5)-H(5AB)	107.8	S(12)-C(14)-H(14A)	109.1	F(1)-P(1)-F(6)	89.56(6)
S(1)#1-C(5)-H(5AB)	107.8	C(15)-C(14)-H(14B)	109.1	F(5)-P(1)-F(6)	179.93(8)
H(5A)-C(5)-H(5AB)	107.2	S(12)-C(14)-H(14B)	109.1	F(4)-P(1)-F(6)	90.07(6)
C(11)-S(11)-C(15)#2	103.17(8)	H(14A)-C(14)-H(14B)	107.9	F(1)-P(1)-F(2)	90.11(6)
C(11)-S(11)-Cu(1)	104.54(6)	C(14)-C(15)-S(11)#2	114.92(12)	F(5)-P(1)-F(2)	89.94(7)
C(15)#2-S(11)-Cu(1)	109.52(6)	C(14)-C(15)-H(15A)	108.5	F(4)-P(1)-F(2)	179.69(7)
C(14)-S(12)-C(13)	102.88(8)	S(11)#2-C(15)-H(15A)	108.5	F(6)-P(1)-F(2)	90.00(7)
C(12)-C(11)-S(11)	112.46(12)	C(14)-C(15)-H(15B)	108.5	F(1)-P(1)-F(3)	179.29(7)
C(12)-C(11)-H(11A)	109.1	S(11)#2-C(15)-H(15B)	108.5	F(5)-P(1)-F(3)	90.12(7)
S(11)-C(11)-H(11A)	109.1	H(15A)-C(15)-H(15B)	107.5	F(4)-P(1)-F(3)	90.18(7)
C(12)-C(11)-H(11B)	109.1	C(21)-N(21)-Cu(1)	173.64(15)	F(6)-P(1)-F(3)	89.84(7)

F(2)-P(1)-F(3) 89.51(7)

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y+1,-z #2 -x+1,-y,-z+1

Table S19. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $\{[Cu^I(14\text{-}S_4)(MeCN)PF_6]\}_n$. The anisotropic displacement factor exponent takes the form: $-2\pi^2\ [h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cu(1)	14(1)	11(1)	10(1)	-2(1)	1(1)	-6(1)
S(1)	11(1)	10(1)	11(1)	-2(1)	-1(1)	-4(1)
S(2)	10(1)	12(1)	14(1)	-4(1)	-2(1)	-4(1)
C(1)	13(1)	12(1)	11(1)	-4(1)	-1(1)	-3(1)
C(2)	17(1)	16(1)	14(1)	-8(1)	-4(1)	-4(1)
C(3)	12(1)	11(1)	10(1)	-2(1)	-1(1)	-4(1)
C(4)	10(1)	13(1)	12(1)	-2(1)	-3(1)	-4(1)
C(5)	11(1)	12(1)	15(1)	-3(1)	-4(1)	-2(1)
S(11)	12(1)	11(1)	10(1)	-2(1)	1(1)	-5(1)
S(12)	12(1)	14(1)	10(1)	0(1)	-2(1)	-2(1)
C(11)	12(1)	12(1)	13(1)	-2(1)	-3(1)	-3(1)
C(12)	23(1)	16(1)	14(1)	1(1)	-6(1)	-10(1)
C(13)	13(1)	18(1)	12(1)	-2(1)	-1(1)	-5(1)
C(14)	12(1)	14(1)	13(1)	-3(1)	0(1)	-5(1)
C(15)	11(1)	16(1)	14(1)	-4(1)	-2(1)	-5(1)
N(21)	15(1)	15(1)	15(1)	-4(1)	-1(1)	-7(1)
C(21)	14(1)	12(1)	13(1)	1(1)	-4(1)	-5(1)
C(22)	29(1)	17(1)	16(1)	-7(1)	-6(1)	-5(1)

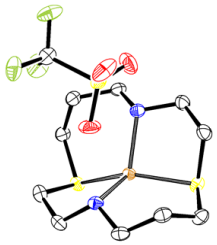
P(1)	11(1)	14(1)	14(1)	-6(1)	-1(1)	-3(1)
F(1)	21(1)	34(1)	16(1)	-10(1)	-1(1)	-11(1)
F(2)	16(1)	32(1)	33(1)	-11(1)	-3(1)	-12(1)
F(3)	38(1)	34(1)	16(1)	-8(1)	-10(1)	-9(1)
F(4)	14(1)	24(1)	23(1)	-3(1)	2(1)	-9(1)
F(5)	21(1)	16(1)	41(1)	-11(1)	-9(1)	1(1)
F(6)	24(1)	14(1)	29(1)	-7(1)	-4(1)	-2(1)

Table S20. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for {[Cu^I(14-S_4)(MeCN)PF_6]}$_n$.

	x	y	z	U(eq)
H(1A)	11136	3538	-1294	15
H(1AB)	11650	2058	-1703	15
H(2A)	8857	2033	-1080	17
H(2AB)	8972	3519	-1968	17
H(3A)	9113	5565	-616	14
H(3AB)	7905	6142	-1461	14
H(4A)	6805	6304	865	14
H(4AB)	5563	6819	57	14
H(5A)	5977	8850	253	16
H(5AB)	6688	8708	-1025	16
H(11A)	9371	-118	3446	15
H(11B)	7632	896	4035	15
H(12A)	6395	-974	4473	21
H(12B)	8113	-1987	3857	21

H(13A)	7727	-1007	5811	18
H(13B)	9440	-2018	5196	18
H(14A)	4962	-2367	5972	16
H(14B)	4951	-3552	7134	16
H(15A)	5179	-713	6823	16
H(15B)	5191	-1898	7982	16
H(22A)	8653	5477	3949	30
H(22B)	7675	4381	4820	30
H(22C)	6696	5845	4080	30
H(22D)	8782	4854	4317	30
H(22E)	6925	4737	4735	30
H(22F)	7318	6111	3798	30

[Cu^{I}(14-N_2S_2)]OTf



The structure of [Cu^{I}(14-N_2S_2)]OTf was solved in the monoclinic space group $P2_1/n$ and the asymmetric unit contains one full molecule of [Cu^{I}(14-N_2S_2)]OTf.

Table S21. Crystal data and structure refinement for [Cu^{I}(14-N_2S_2)]OTf.

CCDC No	2107326	
Empirical formula	C_{11} H_{22} Cu F_3 N_2 O_3 S_3	
Formula weight	447.02	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 8.7939(6) Å	α= 90°.
	b = 14.9481(11) Å	β= 102.586(4)°.
	c = 13.6317(10) Å	γ = 90°.
Volume	1748.9(2) Å^3	
Z	4	
Density (calculated)	1.698 Mg/m^3	
Absorption coefficient	1.648 mm^{-1}	
F(000)	920	
Crystal size	0.472 x 0.297 x 0.236 mm^3	

Theta range for data collection	2.049 to 30.507°.
Index ranges	-12 ≤ h ≤ 12, -21 ≤ k ≤ 21, -19 ≤ l ≤ 19
Reflections collected	60945
Independent reflections	5347 [R(int) = 0.0546]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5347 / 2 / 214
Goodness-of-fit on F^2	1.035
Final R indices [I>2σ(I)]	R1 = 0.0345, wR2 = 0.0801
R indices (all data)	R1 = 0.0462, wR2 = 0.0858
Largest diff. peak and hole	1.306 and -0.701 e.Å^{-3}

Table S22. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for [Cu^I(14-N_2S_2)]OTf. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cu(1)	4315(1)	6245(1)	1053(1)	17(1)
S(1)	6273(1)	5228(1)	1284(1)	21(1)
S(2)	2702(1)	7129(1)	-51(1)	23(1)
N(1)	2410(2)	5597(1)	1426(1)	22(1)
N(2)	5641(2)	7099(1)	2128(1)	21(1)
C(1)	5448(2)	4209(1)	1704(2)	25(1)
C(2)	4027(2)	4306(1)	2163(2)	25(1)
C(3)	2538(2)	4615(1)	1448(2)	24(1)
C(4)	987(2)	5906(1)	710(2)	27(1)
C(5)	1059(2)	6904(1)	533(2)	28(1)
C(6)	3192(3)	8274(1)	372(2)	26(1)
C(7)	3938(3)	8406(1)	1478(2)	26(1)
C(8)	5596(3)	8050(1)	1838(2)	26(1)
C(9)	7249(2)	6746(1)	2371(2)	25(1)
C(10)	7236(2)	5733(2)	2485(2)	28(1)
S(11)	2105(1)	6796(1)	3900(1)	21(1)
F(11)	1657(2)	5514(1)	5124(1)	42(1)
F(12)	3823(2)	6210(1)	5596(1)	44(1)
F(13)	3524(2)	5272(1)	4366(1)	46(1)
O(11)	1435(2)	7422(1)	4481(1)	42(1)
O(12)	3489(2)	7091(1)	3601(1)	37(1)
O(13)	1024(2)	6336(1)	3120(1)	42(1)
C(11)	2812(3)	5905(1)	4792(2)	26(1)

Table S23. Bond lengths [Å] and angles [°] for [Cu^{I}(14-N_2S_2)]OTf.

Cu(1)-N(1)	2.0914(17)	C(4)-H(4B)	0.9900	N(1)-Cu(1)-N(2)	117.71(7)
Cu(1)-N(2)	2.0959(17)	C(5)-H(5A)	0.9900	N(1)-Cu(1)-S(2)	90.77(5)
Cu(1)-S(2)	2.2574(6)	C(5)-H(5B)	0.9900	N(2)-Cu(1)-S(2)	106.40(5)
Cu(1)-S(1)	2.2664(5)	C(6)-C(7)	1.521(3)	N(1)-Cu(1)-S(1)	106.29(5)
S(1)-C(1)	1.832(2)	C(6)-H(6A)	0.9900	N(2)-Cu(1)-S(1)	91.22(5)
S(1)-C(10)	1.834(2)	C(6)-H(6B)	0.9900	S(2)-Cu(1)-S(1)	146.42(2)
S(2)-C(5)	1.827(2)	C(7)-C(8)	1.528(3)	C(1)-S(1)-C(10)	101.54(10)
S(2)-C(6)	1.827(2)	C(7)-H(7A)	0.9900	C(1)-S(1)-Cu(1)	105.08(7)
N(1)-C(3)	1.472(3)	C(7)-H(7B)	0.9900	C(10)-S(1)-Cu(1)	92.13(7)
N(1)-C(4)	1.484(3)	C(8)-H(8A)	0.9900	C(5)-S(2)-C(6)	100.91(10)
N(1)-H(1)	0.889(16)	C(8)-H(8B)	0.9900	C(5)-S(2)-Cu(1)	92.46(7)
N(2)-C(8)	1.475(3)	C(9)-C(10)	1.523(3)	C(6)-S(2)-Cu(1)	105.53(7)
N(2)-C(9)	1.477(3)	C(9)-H(9A)	0.9900	C(3)-N(1)-C(4)	111.92(16)
N(2)-H(2)	0.883(16)	C(9)-H(9B)	0.9900	C(3)-N(1)-Cu(1)	113.88(12)
C(1)-C(2)	1.522(3)	C(10)-H(10A)	0.9900	C(4)-N(1)-Cu(1)	107.54(12)
C(1)-H(1A)	0.9900	C(10)-H(10B)	0.9900	C(3)-N(1)-H(1)	106.0(17)
C(1)-H(1B)	0.9900	S(11)-O(11)	1.4335(16)	C(4)-N(1)-H(1)	108.8(17)
C(2)-C(3)	1.523(3)	S(11)-O(12)	1.4348(16)	Cu(1)-N(1)-H(1)	108.5(17)
C(2)-H(2A)	0.9900	S(11)-O(13)	1.4366(18)	C(8)-N(2)-C(9)	111.87(16)
C(2)-H(2B)	0.9900	S(11)-C(11)	1.819(2)	C(8)-N(2)-Cu(1)	114.92(13)
C(3)-H(3A)	0.9900	F(11)-C(11)	1.333(3)	C(9)-N(2)-Cu(1)	107.39(12)
C(3)-H(3B)	0.9900	F(12)-C(11)	1.332(3)	C(8)-N(2)-H(2)	108.7(17)
C(4)-C(5)	1.516(3)	F(13)-C(11)	1.336(2)	C(9)-N(2)-H(2)	107.4(17)
C(4)-H(4A)	0.9900			Cu(1)-N(2)-H(2)	106.2(17)

C(2)-C(1)-S(1)	117.80(14)	C(4)-C(5)-S(2)	108.37(15)	N(2)-C(9)-C(10)	110.47(17)
C(2)-C(1)-H(1A)	107.9	C(4)-C(5)-H(5A)	110.0	N(2)-C(9)-H(9A)	109.6
S(1)-C(1)-H(1A)	107.9	S(2)-C(5)-H(5A)	110.0	C(10)-C(9)-H(9A)	109.6
C(2)-C(1)-H(1B)	107.9	C(4)-C(5)-H(5B)	110.0	N(2)-C(9)-H(9B)	109.6
S(1)-C(1)-H(1B)	107.9	S(2)-C(5)-H(5B)	110.0	C(10)-C(9)-H(9B)	109.6
H(1A)-C(1)-H(1B)	107.2	H(5A)-C(5)-H(5B)	108.4	H(9A)-C(9)-H(9B)	108.1
C(1)-C(2)-C(3)	115.73(17)	C(7)-C(6)-S(2)	117.07(15)	C(9)-C(10)-S(1)	109.28(15)
C(1)-C(2)-H(2A)	108.3	C(7)-C(6)-H(6A)	108.0	C(9)-C(10)-H(10A)	109.8
C(3)-C(2)-H(2A)	108.3	S(2)-C(6)-H(6A)	108.0	S(1)-C(10)-H(10A)	109.8
C(1)-C(2)-H(2B)	108.3	C(7)-C(6)-H(6B)	108.0	C(9)-C(10)-H(10B)	109.8
C(3)-C(2)-H(2B)	108.3	S(2)-C(6)-H(6B)	108.0	S(1)-C(10)-H(10B)	109.8
H(2A)-C(2)-H(2B)	107.4	H(6A)-C(6)-H(6B)	107.3	H(10A)-C(10)-H(10B)	108.3
N(1)-C(3)-C(2)	111.49(17)	C(6)-C(7)-C(8)	116.65(18)	O(11)-S(11)-O(12)	115.59(12)
N(1)-C(3)-H(3A)	109.3	C(6)-C(7)-H(7A)	108.1	O(11)-S(11)-O(13)	115.86(12)
C(2)-C(3)-H(3A)	109.3	C(8)-C(7)-H(7A)	108.1	O(12)-S(11)-O(13)	113.73(11)
N(1)-C(3)-H(3B)	109.3	C(6)-C(7)-H(7B)	108.1	O(11)-S(11)-C(11)	103.29(10)
C(2)-C(3)-H(3B)	109.3	C(8)-C(7)-H(7B)	108.1	O(12)-S(11)-C(11)	103.15(11)
H(3A)-C(3)-H(3B)	108.0	H(7A)-C(7)-H(7B)	107.3	O(13)-S(11)-C(11)	102.69(11)
N(1)-C(4)-C(5)	110.64(17)	N(2)-C(8)-C(7)	112.93(17)	F(12)-C(11)-F(11)	107.06(18)
N(1)-C(4)-H(4A)	109.5	N(2)-C(8)-H(8A)	109.0	F(12)-C(11)-F(13)	107.94(18)
C(5)-C(4)-H(4A)	109.5	C(7)-C(8)-H(8A)	109.0	F(11)-C(11)-F(13)	107.49(18)
N(1)-C(4)-H(4B)	109.5	N(2)-C(8)-H(8B)	109.0	F(12)-C(11)-S(11)	111.65(15)
C(5)-C(4)-H(4B)	109.5	C(7)-C(8)-H(8B)	109.0	F(11)-C(11)-S(11)	111.91(15)
H(4A)-C(4)-H(4B)	108.1	H(8A)-C(8)-H(8B)	107.8	F(13)-C(11)-S(11)	110.58(15)

Table S24. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for [Cu^I(14-N_2S_2)]OTf. The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [$h^2\ a^{*2}U^{11}$ + ... + 2 h k a* b* U^{12}].

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cu(1)	17(1)	18(1)	17(1)	-1(1)	5(1)	-1(1)
S(1)	18(1)	26(1)	20(1)	-5(1)	7(1)	2(1)
S(2)	29(1)	22(1)	20(1)	2(1)	6(1)	3(1)
N(1)	23(1)	22(1)	22(1)	-1(1)	7(1)	-1(1)
N(2)	22(1)	23(1)	19(1)	-2(1)	8(1)	-2(1)
C(1)	26(1)	22(1)	28(1)	1(1)	9(1)	4(1)
C(2)	27(1)	24(1)	26(1)	2(1)	10(1)	4(1)
C(3)	25(1)	20(1)	27(1)	2(1)	9(1)	-2(1)
C(4)	23(1)	23(1)	32(1)	2(1)	1(1)	-2(1)
C(5)	21(1)	25(1)	37(1)	2(1)	4(1)	3(1)
C(6)	34(1)	18(1)	27(1)	1(1)	7(1)	-1(1)
C(7)	31(1)	20(1)	29(1)	-1(1)	11(1)	-2(1)
C(8)	30(1)	24(1)	26(1)	-4(1)	11(1)	-8(1)
C(9)	18(1)	31(1)	27(1)	-4(1)	4(1)	-2(1)
C(10)	24(1)	32(1)	25(1)	-3(1)	1(1)	2(1)
S(11)	23(1)	23(1)	18(1)	1(1)	10(1)	3(1)
F(11)	60(1)	23(1)	50(1)	6(1)	31(1)	-4(1)
F(12)	48(1)	55(1)	24(1)	3(1)	-4(1)	6(1)
F(13)	57(1)	34(1)	51(1)	-1(1)	22(1)	23(1)
O(11)	71(1)	26(1)	38(1)	8(1)	34(1)	21(1)
O(12)	36(1)	50(1)	30(1)	1(1)	19(1)	-13(1)
O(13)	27(1)	66(1)	30(1)	-7(1)	-1(1)	-2(1)
C(11)	32(1)	21(1)	26(1)	-2(1)	11(1)	6(1)

Table S25. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for [Cu^I(dithiacyclam)]OTf.

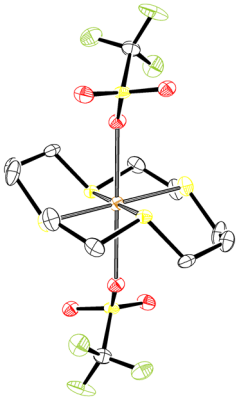
	x	y	z	U(eq)
H(1)	2350(30)	5761(17)	2043(13)	26
H(2)	5260(30)	7045(17)	2674(15)	25
H(1A)	5169	3801	1121	29
H(1B)	6278	3912	2206	29
H(2A)	4279	4737	2726	30
H(2B)	3821	3721	2449	30
H(3A)	2529	4392	763	29
H(3B)	1626	4357	1663	29
H(4A)	58	5766	982	32
H(4B)	886	5585	64	32
H(5A)	1197	7229	1180	34
H(5B)	77	7110	88	34
H(6A)	3908	8521	-29	32
H(6B)	2225	8635	214	32
H(7A)	3267	8114	1880	31
H(7B)	3947	9054	1626	31
H(8A)	6170	8128	1294	31
H(8B)	6134	8409	2421	31
H(9A)	7829	7020	3004	30
H(9B)	7786	6908	1829	30
H(10A)	6673	5567	3013	33

H(10B)	8318	5508	2689	33

Table S26. Hydrogen bonds for [Cu^{I}(14-N_2S_2)]OTf [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1)...O(13)	0.889(16)	2.236(19)	3.043(3)	151(2)
N(2)-H(2)...O(12)	0.883(16)	2.210(18)	3.044(2)	157(2)

$[Cu^{II}(14\text{-}S_4)]OTf_2$



The structure of $[Cu^{II}(14\text{-}S_4)]OTf_2$ was solved in the monoclinic space group $P2_1/n$ and the asymmetric unit contains one half cation $[Cu^{II}(14\text{-}S_4)]$, a disordered triflate anion and a disordered DCM molecule. The disorder was refined with the help of same distance restraints on 1,2- and 1,3-distances, similarity restraints on anisotropic displacement parameters, advanced rigid bond restraints and by setting some disordered atoms with very similar positions to have the same values. The disorder ratios were allowed to refine freely and converged to 0.492(4) and 0.64(4).

Table S27. Crystal data and structure refinement for $[Cu^{II}(14\text{-}S_4)]OTf_2$.

CCDC No	2107323	
Empirical formula	$C_{14}\ H_{24}\ Cl_4\ Cu\ F_6\ O_6\ S_6$	
Formula weight	800.03	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 9.4758(15) Å	α= 90°.
	b = 10.1782(17) Å	β= 99.132(10)°.
	c = 15.084(3) Å	γ = 90°.
Volume	1436.4(4) $Å^3$	
Z	2	
Density (calculated)	1.850 Mg/m^3	
Absorption coefficient	1.638 mm^{-1}	
F(000)	806	
Crystal size	0.102 x 0.047 x 0.035 mm^3	
Theta range for data collection	2.380 to 25.346°.	

Index ranges	$-11 \leq h \leq 11, -12 \leq k \leq 12, -18 \leq l \leq 18$
Reflections collected	15105
Independent reflections	2633 [R(int) = 0.0767]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2633 / 484 / 246
Goodness-of-fit on F^2	1.039
Final R indices [I>2σ(I)]	R1 = 0.0395, wR2 = 0.0807
R indices (all data)	R1 = 0.0638, wR2 = 0.0911
Largest diff. peak and hole	0.479 and -0.449 e.Å^{-3}

Table S28. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for $[Cu^{II}(14\text{-}S_4)]OTf_2$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cu(1)	5000	5000	5000	18(1)
S(1)	6029(1)	6032(1)	6299(1)	19(1)
S(2)	6079(1)	6475(1)	4171(1)	26(1)
C(1)	6617(4)	7545(4)	5829(3)	28(1)
C(2)	7385(4)	7175(4)	5053(3)	29(1)
C(3)	7155(4)	5489(5)	3535(3)	34(1)
C(4)	6195(4)	4665(4)	2835(3)	28(1)
C(5)	5499(4)	3474(4)	3187(3)	24(1)
S(11)	3147(10)	1931(9)	811(6)	20(1)
F(11)	1679(5)	4066(5)	409(3)	38(1)
F(12)	3796(7)	4494(5)	1087(4)	49(2)
F(13)	3487(10)	3780(12)	-287(6)	38(2)
O(11)	3105(7)	2132(9)	1749(5)	24(1)
O(12)	4213(6)	1029(6)	612(4)	28(1)
O(13)	1788(6)	1826(6)	208(4)	24(1)
C(11)	3053(9)	3668(9)	510(5)	25(2)
S(11A)	3230(10)	1991(8)	901(6)	20(1)
F(11A)	2983(7)	4511(6)	597(4)	42(2)
F(12A)	5138(5)	3772(5)	886(3)	36(1)
F(13A)	3917(10)	3514(11)	-428(5)	36(2)
O(11A)	2655(6)	2052(8)	1740(5)	24(1)
O(12A)	4725(6)	1698(7)	1009(4)	34(2)
O(13A)	2324(6)	1288(6)	211(4)	24(1)

C(11A)	3812(8)	3522(8)	436(5)	25(2)
Cl(1)	-109(15)	3210(7)	3005(6)	34(2)
Cl(2)	-869(10)	4850(10)	1402(10)	31(2)
C(21)	547(13)	4171(13)	2202(13)	31(3)
Cl(1A)	-500(16)	3078(9)	3155(8)	20(2)
Cl(2A)	-820(17)	4928(17)	1643(11)	21(2)
C(21A)	401(19)	4110(20)	2506(18)	19(4)

Table S29. Bond lengths [Å] and angles [°] for $[Cu^{II}(14\text{-}S_4)]OTf_2$.

Cu(1)-S(2)	2.2951(10)	F(11)-C(11)	1.349(9)	C(5)#1-S(1)-C(1)	104.22(19)
Cu(1)-S(2)#1	2.2952(10)	F(12)-C(11)	1.329(9)	C(5)#1-S(1)-Cu(1)	103.35(13)
Cu(1)-S(1)#1	2.2989(10)	F(13)-C(11)	1.336(9)	C(1)-S(1)-Cu(1)	99.76(14)
Cu(1)-S(1)	2.2989(10)	S(11A)-O(12A)	1.431(9)	C(2)-S(2)-C(3)	103.3(2)
S(1)-C(5)#1	1.818(4)	S(11A)-O(13A)	1.432(9)	C(2)-S(2)-Cu(1)	99.73(14)
S(1)-C(1)	1.819(4)	S(11A)-O(11A)	1.456(9)	C(3)-S(2)-Cu(1)	105.25(16)
S(2)-C(2)	1.812(4)	S(11A)-C(11A)	1.830(10)	C(2)-C(1)-S(1)	107.7(3)
S(2)-C(3)	1.812(4)	F(11A)-C(11A)	1.323(8)	C(2)-C(1)-H(1A)	110.2
C(1)-C(2)	1.521(6)	F(12A)-C(11A)	1.355(8)	S(1)-C(1)-H(1A)	110.2
C(1)-H(1A)	0.9900	F(13A)-C(11A)	1.322(9)	C(2)-C(1)-H(1AB)	110.2
C(1)-H(1AB)	0.9900	Cl(1)-C(21)	1.745(8)	S(1)-C(1)-H(1AB)	110.2
C(2)-H(2A)	0.9900	Cl(2)-C(21)	1.795(8)	H(1A)-C(1)-H(1AB)	108.5
C(2)-H(2AB)	0.9900	C(21)-H(21A)	0.9900	C(1)-C(2)-S(2)	107.9(3)
C(3)-C(4)	1.530(6)	C(21)-H(21B)	0.9900	C(1)-C(2)-H(2A)	110.1
C(3)-H(3A)	0.9900	Cl(1A)-C(21A)	1.748(13)	S(2)-C(2)-H(2A)	110.1
C(3)-H(3AB)	0.9900	Cl(2A)-C(21A)	1.803(13)	C(1)-C(2)-H(2AB)	110.1
C(4)-C(5)	1.516(6)	C(21A)-H(21C)	0.9900	S(2)-C(2)-H(2AB)	110.1
C(4)-H(4A)	0.9900	C(21A)-H(21D)	0.9900	H(2A)-C(2)-H(2AB)	108.4
C(4)-H(4AB)	0.9900			C(4)-C(3)-S(2)	110.2(3)
C(5)-H(5A)	0.9900	S(2)-Cu(1)-S(2)#1	180.0	C(4)-C(3)-H(3A)	109.6
C(5)-H(5AB)	0.9900	S(2)-Cu(1)-S(1)#1	90.02(4)	S(2)-C(3)-H(3A)	109.6
S(11)-O(12)	1.431(9)	S(2)#1-Cu(1)-S(1)#1	89.98(4)	C(4)-C(3)-H(3AB)	109.6
S(11)-O(11)	1.437(9)	S(2)-Cu(1)-S(1)	89.99(4)	S(2)-C(3)-H(3AB)	109.6
S(11)-O(13)	1.458(9)	S(2)#1-Cu(1)-S(1)	90.01(4)	H(3A)-C(3)-H(3AB)	108.1
S(11)-C(11)	1.824(11)	S(1)#1-Cu(1)-S(1)	180.00(3)	C(5)-C(4)-C(3)	116.1(3)

C(5)-C(4)-H(4A)	108.3	O(13)-S(11)-C(11)	85.0(5)	F(13A)-C(11A)-S(11A)	116.6(7)
C(3)-C(4)-H(4A)	108.3	F(12)-C(11)-F(13)	109.2(8)	F(11A)-C(11A)-S(11A)	110.7(6)
C(5)-C(4)-H(4AB)	108.3	F(12)-C(11)-F(11)	106.5(8)	F(12A)-C(11A)-S(11A)	106.2(6)
C(3)-C(4)-H(4AB)	108.3	F(13)-C(11)-F(11)	107.6(7)	Cl(1)-C(21)-Cl(2)	111.8(6)
H(4A)-C(4)-H(4AB)	107.4	F(12)-C(11)-S(11)	116.8(7)	Cl(1)-C(21)-H(21A)	109.3
C(4)-C(5)-S(1)#1	110.4(3)	F(13)-C(11)-S(11)	107.3(8)	Cl(2)-C(21)-H(21A)	109.3
C(4)-C(5)-H(5A)	109.6	F(11)-C(11)-S(11)	109.1(6)	Cl(1)-C(21)-H(21B)	109.3
S(1)#1-C(5)-H(5A)	109.6	O(12A)-S(11A)-O(13A)	116.5(7)	Cl(2)-C(21)-H(21B)	109.3
C(4)-C(5)-H(5AB)	109.6	O(12A)-S(11A)-O(11A)	114.2(7)	H(21A)-C(21)-H(21B)	107.9
S(1)#1-C(5)-H(5AB)	109.6	O(13A)-S(11A)-O(11A)	112.9(7)	Cl(1A)-C(21A)-Cl(2A)	111.6(10)
H(5A)-C(5)-H(5AB)	108.1	O(12A)-S(11A)-C(11A)	82.4(6)	Cl(1A)-C(21A)-H(21C)	109.3
O(12)-S(11)-O(11)	115.4(7)	O(13A)-S(11A)-C(11A)	109.2(6)	Cl(2A)-C(21A)-H(21C)	109.3
O(12)-S(11)-O(13)	113.9(7)	O(11A)-S(11A)-C(11A)	118.3(7)	Cl(1A)-C(21A)-H(21D)	109.3
O(11)-S(11)-O(13)	117.7(7)	F(13A)-C(11A)-F(11A)	109.0(7)	Cl(2A)-C(21A)-H(21D)	109.3
O(12)-S(11)-C(11)	125.3(7)	F(13A)-C(11A)-F(12A)	106.6(7)	H(21C)-C(21A)-H(21D)	108.0
O(11)-S(11)-C(11)	95.7(6)	F(11A)-C(11A)-F(12A)	107.2(6)		

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1

Table S30. Anisotropic displacement parameters ($Å^2$ x 10^3) for $[Cu^{II}(14\text{-}S_4)](OTf)_2$. The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [h^2 a*2U^{11} + ... + 2 h k a* b* U^{12}].

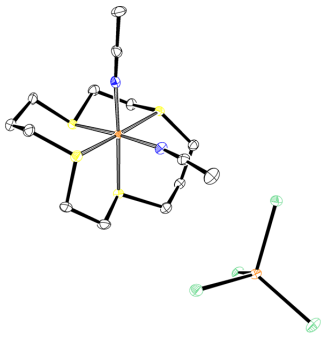
	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cu(1)	15(1)	18(1)	21(1)	-2(1)	3(1)	-3(1)
S(1)	16(1)	17(1)	23(1)	-1(1)	1(1)	0(1)
S(2)	25(1)	27(1)	24(1)	1(1)	1(1)	-11(1)

C(1)	27(2)	19(2)	35(2)	0(2)	-2(2)	-9(2)
C(2)	29(2)	29(2)	26(2)	0(2)	-2(2)	-18(2)
C(3)	20(2)	62(3)	22(2)	-2(2)	6(2)	-13(2)
C(4)	17(2)	42(3)	23(2)	-2(2)	3(2)	-8(2)
C(5)	21(2)	26(2)	24(2)	-4(2)	4(2)	8(2)
S(11)	12(1)	17(1)	29(1)	0(1)	1(1)	-2(1)
F(11)	34(3)	33(3)	45(3)	7(2)	4(2)	15(2)
F(12)	65(4)	21(3)	50(4)	0(3)	-19(3)	-16(3)
F(13)	37(5)	37(5)	39(4)	12(3)	7(3)	-3(4)
O(11)	16(2)	29(2)	24(1)	1(1)	-1(1)	-2(2)
O(12)	19(3)	22(3)	44(4)	-4(3)	2(3)	4(3)
O(13)	16(2)	29(2)	24(1)	1(1)	-1(1)	-2(2)
C(11)	25(4)	24(4)	25(4)	1(4)	-3(3)	-2(4)
S(11A)	12(1)	17(1)	29(1)	0(1)	1(1)	-2(1)
F(11A)	50(4)	18(3)	62(4)	4(3)	22(3)	8(3)
F(12A)	26(2)	47(3)	34(3)	-5(2)	5(2)	-22(2)
F(13A)	42(5)	39(5)	28(3)	6(3)	8(3)	-12(4)
O(11A)	16(2)	29(2)	24(1)	1(1)	-1(1)	-2(2)
O(12A)	10(3)	49(4)	43(4)	11(3)	1(2)	3(3)
O(13A)	16(2)	29(2)	24(1)	1(1)	-1(1)	-2(2)
C(11A)	18(4)	25(4)	30(4)	-7(3)	2(3)	0(3)
Cl(1)	33(3)	39(2)	28(2)	0(1)	2(2)	10(2)
Cl(2)	27(1)	22(2)	39(4)	6(3)	-6(2)	-1(1)
C(21)	22(4)	40(5)	29(7)	7(5)	-2(4)	-1(3)
Cl(1A)	17(3)	22(2)	23(3)	1(2)	9(2)	4(2)
Cl(2A)	19(3)	24(2)	18(4)	-2(3)	0(3)	-2(2)
C(21A)	13(6)	24(7)	21(10)	-7(6)	2(5)	-1(5)

Table S31. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for $[Cu^{II}(14\text{-}S_4)](OTf)_2$.

	x	y	z	U(eq)
H(1A)	5785	8113	5613	33
H(1AB)	7271	8032	6292	33
H(2A)	8148	6527	5254	34
H(2AB)	7828	7963	4827	34
H(3A)	7767	6069	3230	41
H(3AB)	7785	4902	3946	41
H(4A)	5430	5241	2524	33
H(4AB)	6772	4364	2381	33
H(5A)	6203	3014	3636	29
H(5AB)	5183	2858	2687	29
H(21A)	1172	3626	1883	37
H(21B)	1133	4894	2507	37
H(21C)	1090	3585	2224	23
H(21D)	947	4775	2899	23

$[Fe^{II}(14\text{-}S_4)(MeCN)_2]FeI_4$



The structure of $[Fe^{II}(14\text{-}S_4)(MeCN)_2]FeI_4$ was solved in the orthorhombic space group *Pbca* and the asymmetric unit contains one full molecule of $[Fe^{II}(14\text{-}S_4)(MeCN)_2]FeI_4$ and one additional acetonitrile molecule.

Table S32. Crystal data and structure refinement for $[Fe^{II}(14\text{-}S_4)(MeCN)_2]FeI_4$.

Identification code	D20409	
Empirical formula	$C_{16}\ H_{29}\ Fe_2\ I_4\ N_3\ S_4$	
Formula weight	1010.96	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	*Pbca*	
Unit cell dimensions	a = 13.5519(8) Å	α= 90°.
	b = 19.3693(10) Å	β= 90°.
	c = 22.7518(13) Å	γ = 90°.
Volume	5972.1(6) $Å^3$	
Z	8	
Density (calculated)	2.249 Mg/m^3	
Absorption coefficient	5.397 mm^{-1}	
F(000)	3792	
Crystal size	0.356 x 0.213 x 0.155 mm^3	
Theta range for data collection	2.041 to 27.876°.	
Index ranges	-17 ≤ h ≤ 17, -25 ≤ k ≤ 24, -29 ≤ l ≤ 29	
Reflections collected	122024	

Independent reflections	7113 [R(int) = 0.0701]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7113 / 0 / 265
Goodness-of-fit on F^2	1.066
Final R indices [I>2σ(I)]	R1 = 0.0259, wR2 = 0.0507
R indices (all data)	R1 = 0.0381, wR2 = 0.0541
Largest diff. peak and hole	1.006 and -0.742 e.Å^{-3}

Table S33. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for [Fe^{II}(14-S_4)$(MeCN)_2$]FeI_4. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Fe(1)	6221(1)	4931(1)	3620(1)	11(1)
S(1)	4988(1)	4614(1)	4227(1)	12(1)
S(2)	5811(1)	4049(1)	3036(1)	13(1)
S(3)	7530(1)	5250(1)	3076(1)	16(1)
S(4)	5268(1)	5558(1)	3018(1)	14(1)
C(1)	4363(2)	3922(2)	3836(2)	16(1)
C(2)	5126(3)	3484(2)	3524(2)	17(1)
C(3)	6880(2)	3541(2)	2851(2)	16(1)
C(4)	7546(3)	3965(2)	2449(2)	20(1)
C(5)	8155(3)	4519(2)	2750(2)	19(1)
C(6)	6996(3)	5726(2)	2464(2)	20(1)
C(7)	6154(3)	6158(2)	2703(2)	19(1)
C(8)	4432(2)	6092(2)	3436(2)	17(1)
C(9)	3682(2)	5631(2)	3744(2)	15(1)

C(10)	4042(3)	5274(2)	4299(2)	16(1)
N(11)	7117(2)	4390(1)	4111(1)	13(1)
C(11)	7640(3)	4126(2)	4428(1)	16(1)
C(12)	8324(3)	3804(2)	4839(2)	23(1)
N(21)	6496(2)	5742(1)	4097(1)	15(1)
C(21)	6734(2)	6242(2)	4315(2)	15(1)
C(22)	7057(3)	6898(2)	4559(2)	24(1)
I(11)	4411(1)	7232(1)	4942(1)	19(1)
I(12)	2262(1)	7382(1)	3622(1)	17(1)
I(13)	5396(1)	7967(1)	3291(1)	20(1)
I(14)	3569(1)	9304(1)	4309(1)	24(1)
Fe(11)	3885(1)	7992(1)	4018(1)	15(1)
N(31)	6192(4)	1842(2)	3168(2)	57(1)
C(31)	5780(3)	1525(2)	3505(2)	34(1)
C(32)	5259(4)	1112(3)	3930(2)	43(1)

Table S34. Bond lengths [Å] and angles [°] for $[Fe^{II}(14\text{-}S_4)(MeCN)_2]FeI_4$.

Fe(1)-N(21)	1.945(3)	S(2)-C(2)	1.814(3)	C(2)-H(2AB)	0.9900
Fe(1)-N(11)	1.955(3)	S(3)-C(5)	1.809(3)	C(3)-C(4)	1.524(5)
Fe(1)-S(2)	2.2330(9)	S(3)-C(6)	1.820(4)	C(3)-H(3A)	0.9900
Fe(1)-S(4)	2.2401(9)	S(4)-C(8)	1.806(3)	C(3)-H(3AB)	0.9900
Fe(1)-S(3)	2.2493(10)	S(4)-C(7)	1.819(3)	C(4)-C(5)	1.517(5)
Fe(1)-S(1)	2.2523(9)	C(1)-C(2)	1.514(5)	C(4)-H(4A)	0.9900
S(1)-C(1)	1.818(3)	C(1)-H(1A)	0.9900	C(4)-H(4AB)	0.9900
S(1)-C(10)	1.819(3)	C(1)-H(1AB)	0.9900	C(5)-H(5A)	0.9900
S(2)-C(3)	1.803(3)	C(2)-H(2A)	0.9900	C(5)-H(5AB)	0.9900

C(6)-C(7)	1.515(5)	N(31)-C(31)	1.130(6)	C(5)-S(3)-C(6)	105.63(17)
C(6)-H(6A)	0.9900	C(31)-C(32)	1.440(6)	C(5)-S(3)-Fe(1)	112.33(12)
C(6)-H(6AB)	0.9900	C(32)-H(32A)	0.9800	C(6)-S(3)-Fe(1)	104.23(12)
C(7)-H(7A)	0.9900	C(32)-H(32B)	0.9800	C(8)-S(4)-C(7)	104.77(16)
C(7)-H(7AB)	0.9900	C(32)-H(32C)	0.9800	C(8)-S(4)-Fe(1)	110.49(12)
C(8)-C(9)	1.524(5)			C(7)-S(4)-Fe(1)	101.98(12)
C(8)-H(8A)	0.9900	N(21)-Fe(1)-N(11)	89.72(11)	C(2)-C(1)-S(1)	108.8(2)
C(8)-H(8AB)	0.9900	N(21)-Fe(1)-S(2)	175.39(9)	C(2)-C(1)-H(1A)	109.9
C(9)-C(10)	1.521(5)	N(11)-Fe(1)-S(2)	94.84(8)	S(1)-C(1)-H(1A)	109.9
C(9)-H(9A)	0.9900	N(21)-Fe(1)-S(4)	90.82(9)	C(2)-C(1)-H(1AB)	109.9
C(9)-H(9AB)	0.9900	N(11)-Fe(1)-S(4)	176.54(9)	S(1)-C(1)-H(1AB)	109.9
C(10)-H(10A)	0.9900	S(2)-Fe(1)-S(4)	84.67(3)	H(1A)-C(1)-H(1AB)	108.3
C(10)-H(10B)	0.9900	N(21)-Fe(1)-S(3)	86.22(9)	C(1)-C(2)-S(2)	107.4(2)
N(11)-C(11)	1.133(4)	N(11)-Fe(1)-S(3)	88.38(8)	C(1)-C(2)-H(2A)	110.2
C(11)-C(12)	1.457(5)	S(2)-Fe(1)-S(3)	94.55(4)	S(2)-C(2)-H(2A)	110.2
C(12)-H(12A)	0.9800	S(4)-Fe(1)-S(3)	88.24(3)	C(1)-C(2)-H(2AB)	110.2
C(12)-H(12B)	0.9800	N(21)-Fe(1)-S(1)	91.16(9)	S(2)-C(2)-H(2AB)	110.2
C(12)-H(12C)	0.9800	N(11)-Fe(1)-S(1)	87.94(8)	H(2A)-C(2)-H(2AB)	108.5
N(21)-C(21)	1.135(4)	S(2)-Fe(1)-S(1)	88.36(3)	C(4)-C(3)-S(2)	108.8(2)
C(21)-C(22)	1.455(5)	S(4)-Fe(1)-S(1)	95.47(3)	C(4)-C(3)-H(3A)	109.9
C(22)-H(22A)	0.9800	S(3)-Fe(1)-S(1)	175.49(4)	S(2)-C(3)-H(3A)	109.9
C(22)-H(22B)	0.9800	C(1)-S(1)-C(10)	103.52(16)	C(4)-C(3)-H(3AB)	109.9
C(22)-H(22C)	0.9800	C(1)-S(1)-Fe(1)	104.34(11)	S(2)-C(3)-H(3AB)	109.9
I(11)-Fe(11)	2.6635(5)	C(10)-S(1)-Fe(1)	112.78(12)	H(3A)-C(3)-H(3AB)	108.3
I(12)-Fe(11)	2.6546(5)	C(3)-S(2)-C(2)	103.00(16)	C(5)-C(4)-C(3)	115.6(3)
I(13)-Fe(11)	2.6331(6)	C(3)-S(2)-Fe(1)	110.92(12)	C(5)-C(4)-H(4A)	108.4
I(14)-Fe(11)	2.6613(5)	C(2)-S(2)-Fe(1)	102.98(11)	C(3)-C(4)-H(4A)	108.4

C(5)-C(4)-H(4AB)	108.4	S(4)-C(8)-H(8A)	109.9	H(12B)-C(12)-H(12C)	109.5
C(3)-C(4)-H(4AB)	108.4	C(9)-C(8)-H(8AB)	109.9	C(21)-N(21)-Fe(1)	170.9(3)
H(4A)-C(4)-H(4AB)	107.4	S(4)-C(8)-H(8AB)	109.9	N(21)-C(21)-C(22)	176.4(4)
C(4)-C(5)-S(3)	118.9(3)	H(8A)-C(8)-H(8AB)	108.3	C(21)-C(22)-H(22A)	109.5
C(4)-C(5)-H(5A)	107.6	C(10)-C(9)-C(8)	115.8(3)	C(21)-C(22)-H(22B)	109.5
S(3)-C(5)-H(5A)	107.6	C(10)-C(9)-H(9A)	108.3	H(22A)-C(22)-H(22B)	109.5
C(4)-C(5)-H(5AB)	107.6	C(8)-C(9)-H(9A)	108.3	C(21)-C(22)-H(22C)	109.5
S(3)-C(5)-H(5AB)	107.6	C(10)-C(9)-H(9AB)	108.3	H(22A)-C(22)-H(22C)	109.5
H(5A)-C(5)-H(5AB)	107.0	C(8)-C(9)-H(9AB)	108.3	H(22B)-C(22)-H(22C)	109.5
C(7)-C(6)-S(3)	107.8(2)	H(9A)-C(9)-H(9AB)	107.4	I(13)-Fe(11)-I(12)	115.06(2)
C(7)-C(6)-H(6A)	110.1	C(9)-C(10)-S(1)	118.1(2)	I(13)-Fe(11)-I(14)	107.415(18)
S(3)-C(6)-H(6A)	110.1	C(9)-C(10)-H(10A)	107.8	I(12)-Fe(11)-I(14)	112.103(19)
C(7)-C(6)-H(6AB)	110.1	S(1)-C(10)-H(10A)	107.8	I(13)-Fe(11)-I(11)	106.097(18)
S(3)-C(6)-H(6AB)	110.1	C(9)-C(10)-H(10B)	107.8	I(12)-Fe(11)-I(11)	104.065(18)
H(6A)-C(6)-H(6AB)	108.5	S(1)-C(10)-H(10B)	107.8	I(14)-Fe(11)-I(11)	111.996(19)
C(6)-C(7)-S(4)	106.5(2)	H(10A)-C(10)-H(10B)	107.1	N(31)-C(31)-C(32)	179.2(5)
C(6)-C(7)-H(7A)	110.4	C(11)-N(11)-Fe(1)	173.8(3)	C(31)-C(32)-H(32A)	109.5
S(4)-C(7)-H(7A)	110.4	N(11)-C(11)-C(12)	178.6(4)	C(31)-C(32)-H(32B)	109.5
C(6)-C(7)-H(7AB)	110.4	C(11)-C(12)-H(12A)	109.5	H(32A)-C(32)-H(32B)	109.5
S(4)-C(7)-H(7AB)	110.4	C(11)-C(12)-H(12B)	109.5	C(31)-C(32)-H(32C)	109.5
H(7A)-C(7)-H(7AB)	108.6	H(12A)-C(12)-H(12B)	109.5	H(32A)-C(32)-H(32C)	109.5
C(9)-C(8)-S(4)	109.0(2)	C(11)-C(12)-H(12C)	109.5	H(32B)-C(32)-H(32C)	109.5
C(9)-C(8)-H(8A)	109.9	H(12A)-C(12)-H(12C)	109.5		

Table S35. Anisotropic displacement parameters ($Å^2$ x 10^3) for $[Fe^{II}(14\text{-}S_4)(MeCN)_2]FeI_4$. The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [h^2 a^*2U^{11} + ... + 2 h k a^* b^* U^{12}].

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Fe(1)	12(1)	9(1)	11(1)	0(1)	-1(1)	0(1)
S(1)	13(1)	12(1)	12(1)	1(1)	-1(1)	-1(1)
S(2)	16(1)	11(1)	12(1)	0(1)	0(1)	-1(1)
S(3)	16(1)	13(1)	19(1)	1(1)	3(1)	0(1)
S(4)	16(1)	13(1)	13(1)	1(1)	0(1)	2(1)
C(1)	17(2)	13(2)	17(2)	-3(1)	0(1)	-4(1)
C(2)	20(2)	11(2)	20(2)	-1(1)	-1(1)	-2(1)
C(3)	18(2)	14(2)	16(2)	-3(1)	3(1)	2(1)
C(4)	22(2)	19(2)	18(2)	0(1)	3(2)	6(1)
C(5)	18(2)	17(2)	22(2)	3(1)	8(2)	3(1)
C(6)	26(2)	16(2)	19(2)	7(1)	6(2)	2(1)
C(7)	18(2)	16(2)	22(2)	8(1)	4(2)	2(1)
C(8)	15(2)	15(2)	20(2)	0(1)	0(1)	2(1)
C(9)	14(2)	14(2)	18(2)	-1(1)	-1(1)	1(1)
C(10)	17(2)	14(2)	17(2)	-1(1)	-1(1)	1(1)
N(11)	16(1)	11(1)	12(1)	-2(1)	2(1)	-4(1)
C(11)	22(2)	14(2)	12(2)	-2(1)	0(1)	-1(1)
C(12)	28(2)	18(2)	23(2)	3(2)	-6(2)	8(2)
N(21)	14(1)	14(1)	19(2)	-1(1)	-1(1)	0(1)
C(21)	10(2)	16(2)	18(2)	2(1)	-1(1)	3(1)
C(22)	21(2)	18(2)	33(2)	-6(2)	-4(2)	-4(2)
I(11)	21(1)	19(1)	16(1)	3(1)	0(1)	5(1)
I(12)	15(1)	13(1)	24(1)	-2(1)	-3(1)	2(1)

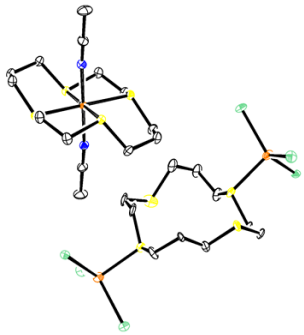
I(13)	20(1)	17(1)	23(1)	3(1)	5(1)	-2(1)
I(14)	25(1)	13(1)	34(1)	-5(1)	-4(1)	3(1)
Fe(11)	15(1)	12(1)	18(1)	1(1)	-1(1)	1(1)
N(31)	74(3)	29(2)	68(3)	14(2)	29(3)	18(2)
C(31)	37(2)	26(2)	39(3)	-1(2)	4(2)	8(2)
C(32)	40(3)	47(3)	42(3)	2(2)	11(2)	-1(2)

Table S36. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for $[Fe^{II}(14\text{-}S_4)(MeCN)_2]FeI_4$.

	x	y	z	U(eq)
H(1A)	3985	3634	4117	19
H(1AB)	3895	4118	3547	19
H(2A)	4800	3114	3297	21
H(2AB)	5577	3269	3814	21
H(3A)	7242	3412	3212	20
H(3AB)	6674	3112	2648	20
H(4A)	8001	3646	2244	23
H(4AB)	7130	4188	2146	23
H(5A)	8631	4700	2458	23
H(5AB)	8545	4292	3063	23
H(6A)	7501	6027	2282	24
H(6AB)	6749	5402	2162	24
H(7A)	5845	6429	2383	22
H(7AB)	6397	6482	3007	22
H(8A)	4805	6363	3730	20
H(8AB)	4088	6418	3170	20
H(9A)	3099	5915	3846	18
H(9AB)	3461	5273	3463	18
H(10A)	3463	5061	4493	19
H(10B)	4296	5634	4569	19
H(12A)	7962	3486	5096	35
H(12B)	8643	4161	5078	35

H(12C)	8828	3547	4620	35
H(22A)	6810	6944	4962	36
H(22B)	6800	7277	4318	36
H(22C)	7780	6916	4561	36
H(32A)	5653	1076	4290	65
H(32B)	5145	650	3769	65
H(32C)	4624	1329	4021	65

$[Fe^{II}(14\text{-}S_4)(MeCN)_2][(FeI_3)_2(14\text{-}S_4)]$



The structure of $[Fe^{II}(14\text{-}S_4)(MeCN)_2][(FeI_3)_2(14\text{-}S_4)]$ was solved in the monoclinic space group $P2_1/c$ and the asymmetric unit contains one full molecule of $[Fe^{II}(14\text{-}S_4)(MeCN)_2][(FeI_3)_2(14\text{-}S_4)]$. One ligand was found to be disordered over two positions. The disorder was refined using same distance restraints on 1,2- and 1,3-distances, similarity restraints on anisotropic displacement parameters, advanced rigid bond restraints and by setting some anisotropic displacement parameters to the same values. The refined disorder ratio converged to 0.716(4).

Table S37. Crystal data and structure refinement for $[Fe^{II}(14\text{-}S_4)(MeCN)_2][(FeI_3)_2(14\text{-}S_4)]$.

CCDC No	2107319	
Empirical formula	$C_{28}\ H_{52}\ Fe_3\ I_6\ N_4\ S_8$	
Formula weight	1630.16	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 17.8349(13) Å	α= 90°.
	b = 19.1835(12) Å	β= 101.373(2)°.
	c = 15.1569(11) Å	γ = 90°.
Volume	5083.9(6) $Å^3$	
Z	4	
Density (calculated)	2.130 Mg/m^3	
Absorption coefficient	4.842 mm^{-1}	
F(000)	3088	
Crystal size	0.439 x 0.279 x 0.203 mm^3	
Theta range for data collection	1.576 to 28.699°.	

Index ranges	$-24 \leq h \leq 24, -25 \leq k \leq 25, -20 \leq l \leq 20$
Reflections collected	124242
Independent reflections	13139 [R(int) = 0.0556]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	13139 / 830 / 495
Goodness-of-fit on F^2	1.015
Final R indices [I>2σ(I)]	R1 = 0.0395, wR2 = 0.0867
R indices (all data)	R1 = 0.0581, wR2 = 0.0951
Largest diff. peak and hole	2.898 and -2.157 e.Å^{-3}

Table S38. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for [Fe^{II}(14-S_4)$(MeCN)_2$][$(FeI_3)_2$(14-S_4)]. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
I(1)	4952(1)	2992(1)	2502(1)	16(1)
I(2)	10710(1)	1541(1)	6580(1)	39(1)
I(3)	5542(1)	978(1)	1367(1)	29(1)
I(4)	4121(1)	933(1)	3436(1)	29(1)
I(5)	9391(1)	1501(1)	8710(1)	27(1)
I(6)	10032(1)	-504(1)	7476(1)	18(1)
Fe(1)	5092(1)	1637(1)	2686(1)	21(1)
Fe(2)	9756(1)	838(1)	7343(1)	24(1)
S(1)	6153(2)	1598(2)	3996(2)	18(1)
S(2)	7237(1)	1410(1)	7203(1)	22(1)
S(3)	8523(2)	808(2)	6234(2)	18(1)
S(4)	7836(1)	1066(1)	3487(2)	38(1)
C(1)	5809(4)	2063(5)	4913(4)	22(2)
C(2)	6373(4)	2065(4)	5796(4)	17(1)
C(3)	6563(4)	1335(4)	6146(5)	24(1)
C(4)	7560(5)	516(4)	7396(5)	26(1)
C(5)	7880(5)	209(4)	6662(5)	26(1)
C(6)	8705(5)	268(4)	5305(4)	29(1)
C(7)	9143(4)	668(4)	4685(4)	29(1)
C(8)	8822(5)	1385(5)	4321(5)	29(1)
C(9)	7363(4)	1872(4)	3197(5)	33(1)
C(10)	6935(4)	2154(4)	3866(5)	33(1)
S(1A)	6241(7)	1577(7)	3770(8)	53(3)

S(2A)	8579(6)	1456(6)	4128(7)	95(3)
S(3A)	8704(5)	842(6)	6160(7)	18(1)
S(4A)	6290(5)	1035(4)	5869(5)	69(2)
C(1A)	6899(11)	2291(9)	3646(13)	33(1)
C(2A)	7347(10)	2085(10)	2969(12)	33(1)
C(3A)	7725(9)	1365(9)	3020(10)	33(1)
C(4A)	8467(10)	526(7)	4352(9)	29(1)
C(5A)	8977(10)	371(9)	5217(9)	29(1)
C(6A)	7952(11)	270(10)	6450(14)	26(1)
C(7A)	7554(10)	613(11)	7165(12)	26(1)
C(8A)	7053(9)	1271(8)	6853(11)	26(1)
C(9A)	6210(17)	1984(8)	5542(12)	46(4)
C(10A)	5802(14)	2039(13)	4637(11)	37(4)
Fe(11)	7524(1)	6244(1)	4974(1)	11(1)
S(11)	8109(1)	5889(1)	3869(1)	14(1)
S(12)	6714(1)	6903(1)	3986(1)	15(1)
S(13)	6950(1)	6598(1)	6088(1)	14(1)
S(14)	8330(1)	5591(1)	5969(1)	15(1)
C(11)	8443(2)	6658(2)	3365(3)	17(1)
C(12)	7749(2)	7070(2)	2857(3)	17(1)
C(13)	7284(2)	7481(2)	3430(3)	17(1)
C(14)	6339(3)	7476(2)	4756(3)	20(1)
C(15)	6088(2)	7018(2)	5463(3)	21(1)
C(16)	6609(2)	5831(2)	6580(3)	19(1)
C(17)	7294(3)	5406(2)	7087(3)	20(1)
C(18)	7758(3)	5003(2)	6503(3)	20(1)
C(19)	8731(3)	5023(2)	5209(3)	18(1)

C(20)	8974(2)	5487(2)	4504(3)	18(1)
N(11)	6839(2)	5474(2)	4617(2)	16(1)
C(21)	6464(3)	5020(2)	4312(3)	20(1)
C(22)	6009(3)	4431(3)	3913(4)	31(1)
N(12)	8217(2)	7010(2)	5314(2)	16(1)
C(23)	9096(3)	8037(3)	5966(4)	31(1)
C(24)	8610(3)	7457(2)	5595(3)	21(1)
N(31)	7269(4)	9044(3)	4589(4)	56(2)
C(31)	5969(4)	9645(3)	4001(4)	53(2)
C(32)	6697(4)	9311(3)	4331(4)	45(1)
N(41)	7657(4)	3488(3)	5285(5)	59(2)
C(41)	8745(5)	2853(4)	6325(7)	89(3)
C(42)	8141(5)	3213(3)	5755(5)	50(2)

Table S3964. Bond lengths [Å] and angles [°] for [Fe^{II}(14-S_4)$(MeCN)_2$][$(FeI_3)_2$(14-S_4)].

I(1)-Fe(1)	2.6210(7)	S(1)-C(10)	1.798(7)	C(1)-H(1AB)	0.9900
I(2)-Fe(2)	2.6130(7)	S(1)-C(1)	1.855(7)	C(2)-C(3)	1.511(9)
I(3)-Fe(1)	2.6205(7)	S(2)-C(3)	1.809(6)	C(2)-H(2A)	0.9900
I(4)-Fe(1)	2.6249(7)	S(2)-C(4)	1.816(7)	C(2)-H(2AB)	0.9900
I(5)-Fe(2)	2.6216(8)	S(3)-C(6)	1.828(7)	C(3)-H(3A)	0.9900
I(6)-Fe(2)	2.6199(8)	S(3)-C(5)	1.831(6)	C(3)-H(3AB)	0.9900
Fe(1)-S(1A)	2.363(13)	S(4)-C(9)	1.776(7)	C(4)-C(5)	1.470(10)
Fe(1)-S(1)	2.460(4)	S(4)-C(8)	2.046(8)	C(4)-H(4A)	0.9900
Fe(2)-S(3A)	2.327(11)	C(1)-C(2)	1.508(8)	C(4)-H(4AB)	0.9900
Fe(2)-S(3)	2.492(3)	C(1)-H(1A)	0.9900	C(5)-H(5A)	0.9900

C(5)-H(5AB)	0.9900	C(2A)-H(2AC)	0.9900	S(11)-C(11)	1.815(4)
C(6)-C(7)	1.540(9)	C(3A)-H(3AA)	0.9900	S(11)-C(20)	1.821(4)
C(6)-H(6A)	0.9900	C(3A)-H(3AC)	0.9900	S(12)-C(13)	1.819(4)
C(6)-H(6AB)	0.9900	C(4A)-C(5A)	1.472(16)	S(12)-C(14)	1.824(4)
C(7)-C(8)	1.550(11)	C(4A)-H(4AA)	0.9900	S(13)-C(16)	1.810(4)
C(7)-H(7A)	0.9900	C(4A)-H(4AC)	0.9900	S(13)-C(15)	1.827(4)
C(7)-H(7AB)	0.9900	C(5A)-H(5AA)	0.9900	S(14)-C(18)	1.815(4)
C(8)-H(8A)	0.9900	C(5A)-H(5AC)	0.9900	S(14)-C(19)	1.830(4)
C(8)-H(8AB)	0.9900	C(6A)-C(7A)	1.554(16)	C(11)-C(12)	1.540(6)
C(9)-C(10)	1.486(10)	C(6A)-H(6AA)	0.9900	C(11)-H(11A)	0.9900
C(9)-H(9A)	0.9900	C(6A)-H(6AC)	0.9900	C(11)-H(11B)	0.9900
C(9)-H(9AB)	0.9900	C(7A)-C(8A)	1.564(17)	C(12)-C(13)	1.531(6)
C(10)-H(10A)	0.9900	C(7A)-H(7AA)	0.9900	C(12)-H(12A)	0.9900
C(10)-H(10B)	0.9900	C(7A)-H(7AC)	0.9900	C(12)-H(12B)	0.9900
S(1A)-C(1A)	1.837(13)	C(8A)-H(8AA)	0.9900	C(13)-H(13A)	0.9900
S(1A)-C(10A)	1.880(13)	C(8A)-H(8AC)	0.9900	C(13)-H(13B)	0.9900
S(2A)-C(4A)	1.834(12)	C(9A)-C(10A)	1.424(17)	C(14)-C(15)	1.520(6)
S(2A)-C(3A)	2.040(12)	C(9A)-H(9AA)	0.9900	C(14)-H(14A)	0.9900
S(3A)-C(5A)	1.836(12)	C(9A)-H(9AC)	0.9900	C(14)-H(14B)	0.9900
S(3A)-C(6A)	1.852(12)	C(10A)-H(10C)	0.9900	C(15)-H(15A)	0.9900
S(4A)-C(8A)	1.866(13)	C(10A)-H(10D)	0.9900	C(15)-H(15B)	0.9900
S(4A)-C(9A)	1.886(14)	Fe(11)-N(12)	1.923(4)	C(16)-C(17)	1.542(6)
C(1A)-C(2A)	1.473(16)	Fe(11)-N(11)	1.926(4)	C(16)-H(16A)	0.9900
C(1A)-H(1AA)	0.9900	Fe(11)-S(11)	2.2455(11)	C(16)-H(16B)	0.9900
C(1A)-H(1AC)	0.9900	Fe(11)-S(13)	2.2457(11)	C(17)-C(18)	1.535(6)
C(2A)-C(3A)	1.533(17)	Fe(11)-S(14)	2.2487(11)	C(17)-H(17A)	0.9900
C(2A)-H(2AA)	0.9900	Fe(11)-S(12)	2.2528(11)	C(17)-H(17B)	0.9900

C(18)-H(18A)	0.9900			C(2)-C(1)-S(1)	113.9(5)
C(18)-H(18B)	0.9900	S(1A)-Fe(1)-I(3)	98.8(3)	C(2)-C(1)-H(1A)	108.8
C(19)-C(20)	1.518(6)	S(1)-Fe(1)-I(3)	107.39(7)	S(1)-C(1)-H(1A)	108.8
C(19)-H(19A)	0.9900	S(1A)-Fe(1)-I(1)	100.0(3)	C(2)-C(1)-H(1AB)	108.8
C(19)-H(19B)	0.9900	S(1)-Fe(1)-I(1)	99.12(10)	S(1)-C(1)-H(1AB)	108.8
C(20)-H(20A)	0.9900	I(3)-Fe(1)-I(1)	115.74(3)	H(1A)-C(1)-H(1AB)	107.7
C(20)-H(20B)	0.9900	S(1A)-Fe(1)-I(4)	103.2(3)	C(1)-C(2)-C(3)	111.9(6)
N(11)-C(21)	1.139(6)	S(1)-Fe(1)-I(4)	95.88(8)	C(1)-C(2)-H(2A)	109.2
C(21)-C(22)	1.452(6)	I(3)-Fe(1)-I(4)	114.16(3)	C(3)-C(2)-H(2A)	109.2
C(22)-H(22A)	0.9800	I(1)-Fe(1)-I(4)	119.95(3)	C(1)-C(2)-H(2AB)	109.2
C(22)-H(22B)	0.9800	S(3A)-Fe(2)-I(2)	98.8(2)	C(3)-C(2)-H(2AB)	109.2
C(22)-H(22C)	0.9800	S(3)-Fe(2)-I(2)	106.14(7)	H(2A)-C(2)-H(2AB)	107.9
N(12)-C(24)	1.136(6)	S(3A)-Fe(2)-I(6)	100.0(3)	C(2)-C(3)-S(2)	107.5(5)
C(23)-C(24)	1.454(6)	S(3)-Fe(2)-I(6)	99.00(9)	C(2)-C(3)-H(3A)	110.2
C(23)-H(23A)	0.9800	I(2)-Fe(2)-I(6)	114.38(3)	S(2)-C(3)-H(3A)	110.2
C(23)-H(23B)	0.9800	S(3A)-Fe(2)-I(5)	108.6(2)	C(2)-C(3)-H(3AB)	110.2
C(23)-H(23C)	0.9800	S(3)-Fe(2)-I(5)	102.76(7)	S(2)-C(3)-H(3AB)	110.2
N(31)-C(32)	1.139(9)	I(2)-Fe(2)-I(5)	112.58(3)	H(3A)-C(3)-H(3AB)	108.5
C(31)-C(32)	1.447(10)	I(6)-Fe(2)-I(5)	119.23(3)	C(5)-C(4)-S(2)	114.5(4)
C(31)-H(31A)	0.9800	C(10)-S(1)-C(1)	100.1(4)	C(5)-C(4)-H(4A)	108.6
C(31)-H(31B)	0.9800	C(10)-S(1)-Fe(1)	112.5(3)	S(2)-C(4)-H(4A)	108.6
C(31)-H(31C)	0.9800	C(1)-S(1)-Fe(1)	105.9(3)	C(5)-C(4)-H(4AB)	108.6
N(41)-C(42)	1.135(9)	C(3)-S(2)-C(4)	101.7(4)	S(2)-C(4)-H(4AB)	108.6
C(41)-C(42)	1.419(11)	C(6)-S(3)-C(5)	97.8(4)	H(4A)-C(4)-H(4AB)	107.6
C(41)-H(41A)	0.9800	C(6)-S(3)-Fe(2)	105.4(3)	C(4)-C(5)-S(3)	112.4(5)
C(41)-H(41B)	0.9800	C(5)-S(3)-Fe(2)	107.9(3)	C(4)-C(5)-H(5A)	109.1
C(41)-H(41C)	0.9800	C(9)-S(4)-C(8)	101.5(4)	S(3)-C(5)-H(5A)	109.1

C(4)-C(5)-H(5AB)	109.1	C(9)-C(10)-S(1)	111.9(6)	C(2A)-C(3A)-H(3AA)	111.3
S(3)-C(5)-H(5AB)	109.1	C(9)-C(10)-H(10A)	109.2	S(2A)-C(3A)-H(3AA)	111.3
H(5A)-C(5)-H(5AB)	107.9	S(1)-C(10)-H(10A)	109.2	C(2A)-C(3A)-H(3AC)	111.3
C(7)-C(6)-S(3)	112.1(5)	C(9)-C(10)-H(10B)	109.2	S(2A)-C(3A)-H(3AC)	111.3
C(7)-C(6)-H(6A)	109.2	S(1)-C(10)-H(10B)	109.2	H(3AA)-C(3A)-H(3AC)	109.2
S(3)-C(6)-H(6A)	109.2	H(10A)-C(10)-H(10B)	107.9	C(5A)-C(4A)-S(2A)	106.9(11)
C(7)-C(6)-H(6AB)	109.2	C(1A)-S(1A)-C(10A)	94.7(10)	C(5A)-C(4A)-H(4AA)	110.3
S(3)-C(6)-H(6AB)	109.2	C(1A)-S(1A)-Fe(1)	112.1(9)	S(2A)-C(4A)-H(4AA)	110.3
H(6A)-C(6)-H(6AB)	107.9	C(10A)-S(1A)-Fe(1)	92.3(8)	C(5A)-C(4A)-H(4AC)	110.3
C(6)-C(7)-C(8)	117.6(6)	C(4A)-S(2A)-C(3A)	88.7(8)	S(2A)-C(4A)-H(4AC)	110.3
C(6)-C(7)-H(7A)	107.9	C(5A)-S(3A)-C(6A)	102.1(9)	H(4AA)-C(4A)-H(4AC)	108.6
C(8)-C(7)-H(7A)	107.9	C(5A)-S(3A)-Fe(2)	107.5(7)	C(4A)-C(5A)-S(3A)	112.4(11)
C(6)-C(7)-H(7AB)	107.9	C(6A)-S(3A)-Fe(2)	109.1(9)	C(4A)-C(5A)-H(5AA)	109.1
C(8)-C(7)-H(7AB)	107.9	C(8A)-S(4A)-C(9A)	88.9(8)	S(3A)-C(5A)-H(5AA)	109.1
H(7A)-C(7)-H(7AB)	107.2	C(2A)-C(1A)-S(1A)	108.4(12)	C(4A)-C(5A)-H(5AC)	109.1
C(7)-C(8)-S(4)	99.6(5)	C(2A)-C(1A)-H(1AA)	110.0	S(3A)-C(5A)-H(5AC)	109.1
C(7)-C(8)-H(8A)	111.9	S(1A)-C(1A)-H(1AA)	110.0	H(5AA)-C(5A)-H(5AC)	107.9
S(4)-C(8)-H(8A)	111.9	C(2A)-C(1A)-H(1AC)	110.0	C(7A)-C(6A)-S(3A)	111.5(11)
C(7)-C(8)-H(8AB)	111.9	S(1A)-C(1A)-H(1AC)	110.0	C(7A)-C(6A)-H(6AA)	109.3
S(4)-C(8)-H(8AB)	111.9	H(1AA)-C(1A)-H(1AC)	108.4	S(3A)-C(6A)-H(6AA)	109.3
H(8A)-C(8)-H(8AB)	109.6	C(1A)-C(2A)-C(3A)	120.1(13)	C(7A)-C(6A)-H(6AC)	109.3
C(10)-C(9)-S(4)	115.5(5)	C(1A)-C(2A)-H(2AA)	107.3	S(3A)-C(6A)-H(6AC)	109.3
C(10)-C(9)-H(9A)	108.4	C(3A)-C(2A)-H(2AA)	107.3	H(6AA)-C(6A)-H(6AC)	108.0
S(4)-C(9)-H(9A)	108.4	C(1A)-C(2A)-H(2AC)	107.3	C(6A)-C(7A)-C(8A)	116.3(12)
C(10)-C(9)-H(9AB)	108.4	C(3A)-C(2A)-H(2AC)	107.3	C(6A)-C(7A)-H(7AA)	108.2
S(4)-C(9)-H(9AB)	108.4	H(2AA)-C(2A)-H(2AC)	106.9	C(8A)-C(7A)-H(7AA)	108.2
H(9A)-C(9)-H(9AB)	107.5	C(2A)-C(3A)-S(2A)	102.3(11)	C(6A)-C(7A)-H(7AC)	108.2

C(8A)-C(7A)-H(7AC)	108.2	N(11)-Fe(11)-S(14)	92.68(11)	C(13)-C(12)-H(12A)	108.1
H(7AA)-C(7A)-H(7AC)	107.4	S(11)-Fe(11)-S(14)	90.10(4)	C(11)-C(12)-H(12A)	108.1
C(7A)-C(8A)-S(4A)	109.2(11)	S(13)-Fe(11)-S(14)	89.45(4)	C(13)-C(12)-H(12B)	108.1
C(7A)-C(8A)-H(8AA)	109.8	N(12)-Fe(11)-S(12)	92.47(11)	C(11)-C(12)-H(12B)	108.1
S(4A)-C(8A)-H(8AA)	109.8	N(11)-Fe(11)-S(12)	87.47(11)	H(12A)-C(12)-H(12B)	107.3
C(7A)-C(8A)-H(8AC)	109.8	S(11)-Fe(11)-S(12)	90.32(4)	C(12)-C(13)-S(12)	111.3(3)
S(4A)-C(8A)-H(8AC)	109.8	S(13)-Fe(11)-S(12)	90.13(4)	C(12)-C(13)-H(13A)	109.4
H(8AA)-C(8A)-H(8AC)	108.3	S(14)-Fe(11)-S(12)	179.56(5)	S(12)-C(13)-H(13A)	109.4
C(10A)-C(9A)-S(4A)	108.8(14)	C(11)-S(11)-C(20)	104.6(2)	C(12)-C(13)-H(13B)	109.4
C(10A)-C(9A)-H(9AA)	109.9	C(11)-S(11)-Fe(11)	107.86(14)	S(12)-C(13)-H(13B)	109.4
S(4A)-C(9A)-H(9AA)	109.9	C(20)-S(11)-Fe(11)	101.76(14)	H(13A)-C(13)-H(13B)	108.0
C(10A)-C(9A)-H(9AC)	109.9	C(13)-S(12)-C(14)	103.8(2)	C(15)-C(14)-S(12)	107.4(3)
S(4A)-C(9A)-H(9AC)	109.9	C(13)-S(12)-Fe(11)	107.82(14)	C(15)-C(14)-H(14A)	110.2
H(9AA)-C(9A)-H(9AC)	108.3	C(14)-S(12)-Fe(11)	100.41(14)	S(12)-C(14)-H(14A)	110.2
C(9A)-C(10A)-S(1A)	115.8(15)	C(16)-S(13)-C(15)	104.8(2)	C(15)-C(14)-H(14B)	110.2
C(9A)-C(10A)-H(10C)	108.3	C(16)-S(13)-Fe(11)	107.71(15)	S(12)-C(14)-H(14B)	110.2
S(1A)-C(10A)-H(10C)	108.3	C(15)-S(13)-Fe(11)	101.84(14)	H(14A)-C(14)-H(14B)	108.5
C(9A)-C(10A)-H(10D)	108.3	C(18)-S(14)-C(19)	103.6(2)	C(14)-C(15)-S(13)	106.6(3)
S(1A)-C(10A)-H(10D)	108.3	C(18)-S(14)-Fe(11)	107.70(15)	C(14)-C(15)-H(15A)	110.4
H(10C)-C(10A)-H(10D)	107.4	C(19)-S(14)-Fe(11)	100.76(14)	S(13)-C(15)-H(15A)	110.4
N(12)-Fe(11)-N(11)	179.07(15)	C(12)-C(11)-S(11)	109.2(3)	C(14)-C(15)-H(15B)	110.4
N(12)-Fe(11)-S(11)	93.62(11)	C(12)-C(11)-H(11A)	109.8	S(13)-C(15)-H(15B)	110.4
N(11)-Fe(11)-S(11)	85.45(11)	S(11)-C(11)-H(11A)	109.8	H(15A)-C(15)-H(15B)	108.6
N(12)-Fe(11)-S(13)	86.05(11)	C(12)-C(11)-H(11B)	109.8	C(17)-C(16)-S(13)	109.7(3)
N(11)-Fe(11)-S(13)	94.88(11)	S(11)-C(11)-H(11B)	109.8	C(17)-C(16)-H(16A)	109.7
S(11)-Fe(11)-S(13)	179.45(5)	H(11A)-C(11)-H(11B)	108.3	S(13)-C(16)-H(16A)	109.7
N(12)-Fe(11)-S(14)	87.39(11)	C(13)-C(12)-C(11)	116.9(3)	C(17)-C(16)-H(16B)	109.7

S(13)-C(16)-H(16B)	109.7	H(19A)-C(19)-H(19B)	108.5	C(24)-C(23)-H(23C)	109.5
H(16A)-C(16)-H(16B)	108.2	C(19)-C(20)-S(11)	106.9(3)	H(23A)-C(23)-H(23C)	109.5
C(18)-C(17)-C(16)	116.3(4)	C(19)-C(20)-H(20A)	110.3	H(23B)-C(23)-H(23C)	109.5
C(18)-C(17)-H(17A)	108.2	S(11)-C(20)-H(20A)	110.3	N(12)-C(24)-C(23)	178.3(5)
C(16)-C(17)-H(17A)	108.2	C(19)-C(20)-H(20B)	110.3	C(32)-C(31)-H(31A)	109.5
C(18)-C(17)-H(17B)	108.2	S(11)-C(20)-H(20B)	110.3	C(32)-C(31)-H(31B)	109.5
C(16)-C(17)-H(17B)	108.2	H(20A)-C(20)-H(20B)	108.6	H(31A)-C(31)-H(31B)	109.5
H(17A)-C(17)-H(17B)	107.4	C(21)-N(11)-Fe(11)	171.8(4)	C(32)-C(31)-H(31C)	109.5
C(17)-C(18)-S(14)	111.1(3)	N(11)-C(21)-C(22)	177.9(5)	H(31A)-C(31)-H(31C)	109.5
C(17)-C(18)-H(18A)	109.4	C(21)-C(22)-H(22A)	109.5	H(31B)-C(31)-H(31C)	109.5
S(14)-C(18)-H(18A)	109.4	C(21)-C(22)-H(22B)	109.5	N(31)-C(32)-C(31)	179.6(7)
C(17)-C(18)-H(18B)	109.4	H(22A)-C(22)-H(22B)	109.5	C(42)-C(41)-H(41A)	109.5
S(14)-C(18)-H(18B)	109.4	C(21)-C(22)-H(22C)	109.5	C(42)-C(41)-H(41B)	109.5
H(18A)-C(18)-H(18B)	108.0	H(22A)-C(22)-H(22C)	109.5	H(41A)-C(41)-H(41B)	109.5
C(20)-C(19)-S(14)	107.2(3)	H(22B)-C(22)-H(22C)	109.5	C(42)-C(41)-H(41C)	109.5
C(20)-C(19)-H(19A)	110.3	C(24)-N(12)-Fe(11)	173.4(4)	H(41A)-C(41)-H(41C)	109.5
S(14)-C(19)-H(19A)	110.3	C(24)-C(23)-H(23A)	109.5	H(41B)-C(41)-H(41C)	109.5
C(20)-C(19)-H(19B)	110.3	C(24)-C(23)-H(23B)	109.5	N(41)-C(42)-C(41)	178.4(8)
S(14)-C(19)-H(19B)	110.3	H(23A)-C(23)-H(23B)	109.5		

Table S40. Anisotropic displacement parameters ($Å^2$ x 10^3) for $[Fe^{II}(14\text{-}S_4)(MeCN)_2][(FeI_3)_2(14\text{-}S_4)]$. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2\ a^*2U^{11} + \ldots + 2\ h\ k\ a^*\ b^*\ U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
I(1)	16(1)	14(1)	19(1)	-3(1)	3(1)	0(1)
I(2)	37(1)	40(1)	38(1)	15(1)	3(1)	-22(1)

I(3)	32(1)	24(1)	32(1)	-7(1)	10(1)	9(1)
I(4)	26(1)	31(1)	31(1)	7(1)	5(1)	-8(1)
I(5)	35(1)	22(1)	24(1)	-6(1)	4(1)	-2(1)
I(6)	20(1)	16(1)	19(1)	-2(1)	4(1)	-5(1)
Fe(1)	24(1)	16(1)	24(1)	-2(1)	8(1)	0(1)
Fe(2)	34(1)	16(1)	22(1)	-1(1)	9(1)	-8(1)
S(1)	19(1)	17(1)	19(1)	2(1)	6(1)	2(1)
S(2)	22(1)	25(1)	16(1)	1(1)	-6(1)	0(1)
S(3)	23(2)	17(1)	17(1)	2(1)	11(1)	0(1)
S(4)	30(1)	37(1)	47(1)	-14(1)	10(1)	4(1)
C(1)	20(3)	35(4)	8(3)	-11(3)	-3(3)	7(3)
C(2)	17(3)	22(3)	8(3)	-1(2)	-5(2)	-1(2)
C(3)	22(3)	26(4)	19(3)	4(3)	-4(2)	0(3)
C(4)	34(2)	21(2)	22(3)	14(2)	2(2)	-9(2)
C(5)	34(2)	21(2)	22(3)	14(2)	2(2)	-9(2)
C(6)	38(2)	38(2)	15(2)	4(2)	16(2)	6(2)
C(7)	38(2)	38(2)	15(2)	4(2)	16(2)	6(2)
C(8)	38(2)	38(2)	15(2)	4(2)	16(2)	6(2)
C(9)	35(2)	36(3)	27(3)	25(2)	7(2)	6(2)
C(10)	35(2)	36(3)	27(3)	25(2)	7(2)	6(2)
S(1A)	45(5)	40(5)	62(7)	33(5)	-13(4)	-4(4)
S(2A)	99(6)	119(6)	70(5)	32(5)	25(5)	41(5)
S(3A)	23(2)	17(1)	17(1)	2(1)	11(1)	0(1)
S(4A)	102(6)	54(4)	57(4)	25(3)	35(4)	26(4)
C(1A)	35(2)	36(3)	27(3)	25(2)	7(2)	6(2)
C(2A)	35(2)	36(3)	27(3)	25(2)	7(2)	6(2)
C(3A)	35(2)	36(3)	27(3)	25(2)	7(2)	6(2)

C(4A)	38(2)	38(2)	15(2)	4(2)	16(2)	6(2)
C(5A)	38(2)	38(2)	15(2)	4(2)	16(2)	6(2)
C(6A)	34(2)	21(2)	22(3)	14(2)	2(2)	-9(2)
C(7A)	34(2)	21(2)	22(3)	14(2)	2(2)	-9(2)
C(8A)	34(2)	21(2)	22(3)	14(2)	2(2)	-9(2)
C(9A)	58(8)	44(8)	34(7)	7(7)	4(7)	12(7)
C(10A)	46(7)	34(7)	26(7)	2(7)	-1(6)	3(7)
Fe(11)	12(1)	10(1)	12(1)	-1(1)	2(1)	-1(1)
S(11)	17(1)	12(1)	13(1)	-1(1)	4(1)	1(1)
S(12)	14(1)	15(1)	14(1)	2(1)	3(1)	2(1)
S(13)	17(1)	12(1)	14(1)	-1(1)	4(1)	0(1)
S(14)	16(1)	16(1)	12(1)	1(1)	3(1)	2(1)
C(11)	20(2)	15(2)	18(2)	3(2)	7(2)	2(2)
C(12)	23(2)	16(2)	14(2)	2(2)	7(2)	1(2)
C(13)	19(2)	20(2)	15(2)	2(2)	6(2)	6(2)
C(14)	22(2)	20(2)	17(2)	1(2)	4(2)	9(2)
C(15)	19(2)	25(2)	18(2)	0(2)	5(2)	7(2)
C(16)	21(2)	18(2)	20(2)	4(2)	9(2)	0(2)
C(17)	22(2)	22(2)	17(2)	5(2)	7(2)	6(2)
C(18)	21(2)	17(2)	23(2)	6(2)	8(2)	1(2)
C(19)	22(2)	15(2)	19(2)	2(2)	7(2)	6(2)
C(20)	20(2)	17(2)	18(2)	1(2)	7(2)	5(2)
N(11)	18(2)	16(2)	15(2)	0(1)	4(1)	-1(1)
C(21)	23(2)	17(2)	20(2)	-2(2)	6(2)	-4(2)
C(22)	35(3)	26(3)	31(3)	-11(2)	6(2)	-15(2)
N(12)	15(2)	16(2)	16(2)	-1(1)	4(1)	2(1)
C(23)	36(3)	25(3)	33(3)	-12(2)	10(2)	-15(2)

C(24)	22(2)	20(2)	19(2)	-4(2)	3(2)	-1(2)
N(31)	63(3)	41(3)	75(4)	-23(3)	38(3)	-22(3)
C(31)	89(5)	30(3)	41(4)	-9(3)	15(3)	-10(3)
C(32)	73(4)	22(3)	49(4)	-13(2)	33(3)	-22(3)
N(41)	65(4)	38(3)	81(4)	-16(3)	31(3)	-16(3)
C(41)	101(7)	35(4)	114(8)	-11(4)	-21(5)	-22(4)
C(42)	68(4)	26(3)	62(4)	-13(3)	30(3)	-25(3)

Table S41. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for $[Fe^{II}(14\text{-}S_4)(MeCN)_2][(FeI_3)_2(14\text{-}S_4)]$.

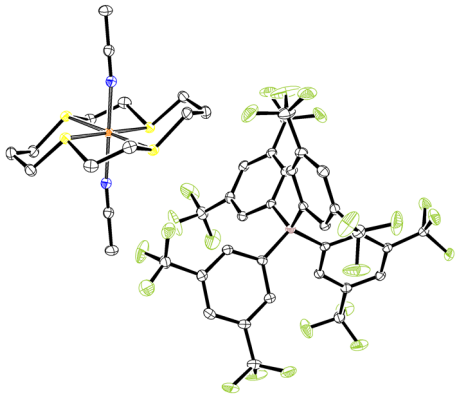
	x	y	z	U(eq)
H(1A)	5690	2551	4724	26
H(1AB)	5328	1842	5004	26
H(2A)	6156	2332	6245	21
H(2AB)	6848	2301	5715	21
H(3A)	6790	1063	5709	28
H(3AB)	6093	1094	6238	28
H(4A)	7955	498	7956	31
H(4AB)	7124	226	7492	31
H(5A)	7455	78	6164	31
H(5AB)	8163	-221	6881	31
H(6A)	9006	-147	5552	34
H(6AB)	8212	103	4948	34

H(7A)	9170	366	4162	34
H(7AB)	9674	739	5017	34
H(8A)	9170	1626	3986	34
H(8AB)	8717	1691	4808	34
H(9A)	7749	2222	3105	39
H(9AB)	7002	1814	2617	39
H(10A)	6735	2622	3671	39
H(10B)	7288	2205	4455	39
H(1AA)	6606	2721	3451	39
H(1AC)	7245	2385	4229	39
H(2AA)	7756	2436	2986	39
H(2AC)	7005	2123	2371	39
H(3AA)	7933	1267	2474	39
H(3AC)	7360	992	3100	39
H(4AA)	7929	422	4386	34
H(4AC)	8608	240	3866	34
H(5AA)	9508	499	5179	34
H(5AC)	8966	-136	5334	34
H(6AA)	7565	171	5900	31
H(6AC)	8183	-178	6686	31
H(7AA)	7954	747	7689	31
H(7AC)	7226	259	7375	31
H(8AA)	7376	1647	6682	31
H(8AC)	6818	1442	7352	31
H(9AA)	5936	2242	5948	55
H(9AC)	6726	2189	5597	55
H(10C)	5752	2540	4476	44

H(10D)	5280	1853	4607	44
H(11A)	8747	6955	3840	21
H(11B)	8775	6519	2943	21
H(12A)	7933	7402	2447	20
H(12B)	7401	6738	2479	20
H(13A)	6942	7812	3042	21
H(13B)	7636	7754	3889	21
H(14A)	6739	7807	5046	24
H(14B)	5900	7747	4426	24
H(15A)	5717	6663	5172	25
H(15B)	5843	7303	5871	25
H(16A)	6277	5971	7002	23
H(16B)	6302	5540	6101	23
H(17A)	7644	5729	7479	24
H(17B)	7101	5069	7484	24
H(18A)	7405	4738	6035	24
H(18B)	8097	4665	6883	24
H(19A)	9176	4764	5546	22
H(19B)	8342	4682	4919	22
H(20A)	9229	5208	4100	22
H(20B)	9335	5849	4796	22
H(22A)	5630	4589	3393	46
H(22B)	5747	4222	4359	46
H(22C)	6344	4083	3717	46
H(23A)	9451	8146	5567	46
H(23B)	9387	7910	6562	46
H(23C)	8778	8446	6018	46

H(31A)	5992	9905	3451	80
H(31B)	5854	9967	4459	80
H(31C)	5567	9290	3870	80
H(41A)	9153	2755	5995	134
H(41B)	8551	2414	6523	134
H(41C)	8947	3143	6851	134

$[Fe^{II}(14\text{-}S_4)(MeCN)_2](BAr^F{}_4)_2$



The structure of $[Fe^{II}(14\text{-}S_4)(MeCN)_2](BAr^F{}_4)_2$ was solved in the triclinic space group $P\bar{1}$ and the asymmetric unit contains one half molecule of $[Fe^{II}(14\text{-}S_4)(MeCN)_2](BAr^F{}_4)_2$. Two of the CF_3 groups were refined as disordered, using same distance restraints on 1,2- and 1,3-distances, similarity restraints on anisotropic displacement parameters and advanced rigid bond restraints.

Table S42. Crystal data and structure refinement for $[Fe^{II}(14\text{-}S_4)(MeCN)_2](BAr^F{}_4)_2$.

CCDC No	2107328
Empirical formula	$C_{78}\ H_{50}\ B_2\ F_{48}\ Fe\ N_2\ S_4$
Formula weight	2132.91
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic

Space group	$P\bar{1}$	
Unit cell dimensions	a = 12.2236(6) Å	α= 74.5207(16)°.
	b = 12.9921(6) Å	β= 87.2647(16)°.
	c = 14.7460(7) Å	γ = 66.8668(15)°.
Volume	2071.09(17) $Å^3$	
Z	1	
Density (calculated)	1.710 Mg/m^3	
Absorption coefficient	0.438 mm^{-1}	
F(000)	1064	
Crystal size	0.653 x 0.505 x 0.170 mm^3	
Theta range for data collection	1.955 to 27.874°.	
Index ranges	-16 ≤ h ≤ 16, -17 ≤ k ≤ 15, -19 ≤ l ≤ 19	
Reflections collected	67289	
Independent reflections	9867 [R(int) = 0.0404]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9867 / 840 / 653	
Goodness-of-fit on F^2	1.034	
Final R indices [I>2σ(I)]	R1 = 0.0342, wR2 = 0.0811	
R indices (all data)	R1 = 0.0411, wR2 = 0.0852	
Extinction coefficient	0.0100(5)	
Largest diff. peak and hole	0.534 and -0.429 $e.Å^{-3}$	

Table S43. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for $[Fe^{II}(14\text{-}S_4)(MeCN)_2](BAr^F{}_4)_2$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Fe(1)	10000	0	10000	13(1)
S(1)	8264(1)	1475(1)	9396(1)	17(1)
S(2)	10903(1)	609(1)	8727(1)	17(1)
C(1)	7946(2)	1356(1)	8247(1)	21(1)
C(2)	8840(2)	1618(2)	7560(1)	23(1)
C(3)	10110(2)	680(2)	7682(1)	21(1)
C(4)	12297(1)	-663(2)	8832(1)	22(1)
C(5)	12800(1)	-1054(1)	9850(1)	21(1)
N(1)	10284(1)	1095(1)	10530(1)	16(1)
C(6)	10369(1)	1833(1)	10763(1)	17(1)
C(7)	10459(2)	2785(1)	11060(1)	22(1)
F(11)	6192(1)	3746(1)	10225(1)	28(1)
F(12)	7848(1)	3603(1)	10756(1)	43(1)
F(13)	6208(1)	4575(1)	11290(1)	49(1)
F(14)	5589(1)	8592(1)	10361(1)	33(1)
F(15)	6832(1)	8915(1)	9355(1)	38(1)
F(16)	5001(1)	9457(1)	8904(1)	29(1)
C(11)	6673(1)	6358(1)	8090(1)	13(1)
C(12)	6794(1)	5375(1)	8834(1)	15(1)
C(13)	6612(1)	5429(1)	9761(1)	16(1)
C(14)	6329(1)	6466(1)	10001(1)	17(1)
C(15)	6192(1)	7446(1)	9276(1)	15(1)
C(16)	6341(1)	7399(1)	8344(1)	15(1)

C(17)	6709(2)	4356(1)	10508(1)	21(1)
C(18)	5900(1)	8593(1)	9479(1)	20(1)
F(21)	7626(1)	10679(1)	6120(1)	33(1)
F(22)	8734(1)	9090(1)	7105(1)	49(1)
F(23)	9244(1)	9557(1)	5697(1)	35(1)
F(24)	5671(1)	10378(1)	3331(1)	31(1)
F(25)	6712(1)	8686(1)	3162(1)	31(1)
F(26)	4946(1)	9075(1)	3631(1)	28(1)
C(21)	6871(1)	7417(1)	6262(1)	13(1)
C(22)	7562(1)	7965(1)	6500(1)	14(1)
C(23)	7639(1)	8949(1)	5892(1)	16(1)
C(24)	7086(1)	9397(1)	4989(1)	17(1)
C(25)	6444(1)	8843(1)	4722(1)	15(1)
C(26)	6317(1)	7883(1)	5352(1)	14(1)
C(27)	8306(2)	9561(1)	6198(1)	21(1)
C(28)	5936(1)	9244(1)	3724(1)	17(1)
F(31)	8955(2)	4118(1)	4488(1)	34(1)
F(32)	10812(1)	3267(1)	4914(1)	34(1)
F(33)	9665(2)	2403(1)	5456(1)	45(1)
F(31A)	9340(15)	4103(14)	4396(9)	30(5)
F(32A)	10691(10)	2591(12)	5219(11)	42(4)
F(33A)	8870(13)	2893(13)	5282(9)	33(4)
F(34)	10988(4)	3472(5)	9027(3)	52(1)
F(35)	12239(3)	2960(4)	8037(4)	49(1)
F(36)	11508(5)	4717(4)	8083(4)	58(1)
F(34A)	11291(14)	3066(13)	8944(8)	66(4)
F(35A)	12311(7)	3481(18)	7834(7)	64(3)

F(36A)	11160(12)	4739(9)	8452(14)	77(4)
C(31)	8134(1)	5214(1)	6937(1)	13(1)
C(32)	8380(1)	4743(1)	6159(1)	15(1)
C(33)	9509(1)	3959(1)	6047(1)	16(1)
C(34)	10460(1)	3628(1)	6692(1)	17(1)
C(35)	10244(1)	4098(1)	7455(1)	17(1)
C(36)	9103(1)	4862(1)	7579(1)	15(1)
C(37)	9717(2)	3438(1)	5230(1)	21(1)
C(38)	11245(1)	3822(2)	8147(1)	22(1)
F(41)	2327(1)	8431(1)	6969(1)	54(1)
F(42)	1855(1)	8206(1)	5702(1)	46(1)
F(43)	1514(1)	7232(1)	6996(1)	46(1)
F(44)	3839(1)	3584(1)	6147(1)	36(1)
F(45)	4942(1)	2835(1)	7433(1)	45(1)
F(46)	5747(1)	3022(1)	6116(1)	58(1)
C(41)	5689(1)	5983(1)	6765(1)	13(1)
C(42)	4541(1)	6863(1)	6707(1)	15(1)
C(43)	3518(1)	6678(1)	6604(1)	15(1)
C(44)	3585(1)	5609(1)	6533(1)	18(1)
C(45)	4701(1)	4734(1)	6583(1)	18(1)
C(46)	5735(1)	4914(1)	6705(1)	16(1)
C(47)	2310(1)	7628(1)	6571(1)	19(1)
C(48)	4807(2)	3555(2)	6557(1)	28(1)
B(1)	6837(1)	6239(1)	7005(1)	13(1)

Table S44. Bond lengths [Å] and angles [°] for $[Fe^{II}(14\text{-}S_4)(MeCN)_2](BAr^F{}_4)_2$.

Fe(1)-N(1)	1.9405(13)	C(7)-H(7A)	0.9800	F(25)-C(28)	1.3484(18)
Fe(1)-N(1)#1	1.9406(13)	C(7)-H(7B)	0.9800	F(26)-C(28)	1.3313(18)
Fe(1)-S(1)#1	2.2453(4)	C(7)-H(7C)	0.9800	C(21)-C(26)	1.399(2)
Fe(1)-S(1)	2.2453(4)	F(11)-C(17)	1.340(2)	C(21)-C(22)	1.406(2)
Fe(1)-S(2)	2.2503(4)	F(12)-C(17)	1.347(2)	C(21)-B(1)	1.641(2)
Fe(1)-S(2)#1	2.2504(4)	F(13)-C(17)	1.3250(19)	C(22)-C(23)	1.387(2)
S(1)-C(1)	1.8159(16)	F(14)-C(18)	1.3374(19)	C(22)-H(22)	0.9500
S(1)-C(5)#1	1.8230(16)	F(15)-C(18)	1.3499(19)	C(23)-C(24)	1.390(2)
S(2)-C(3)	1.8206(16)	F(16)-C(18)	1.341(2)	C(23)-C(27)	1.496(2)
S(2)-C(4)	1.8263(17)	C(11)-C(16)	1.399(2)	C(24)-C(25)	1.383(2)
C(1)-C(2)	1.531(2)	C(11)-C(12)	1.405(2)	C(24)-H(24)	0.9500
C(1)-H(1A)	0.9900	C(11)-B(1)	1.644(2)	C(25)-C(26)	1.401(2)
C(1)-H(1B)	0.9900	C(12)-C(13)	1.391(2)	C(25)-C(28)	1.499(2)
C(2)-C(3)	1.533(2)	C(12)-H(12)	0.9500	C(26)-H(26)	0.9500
C(2)-H(2A)	0.9900	C(13)-C(14)	1.392(2)	F(31)-C(37)	1.334(2)
C(2)-H(2B)	0.9900	C(13)-C(17)	1.495(2)	F(32)-C(37)	1.348(2)
C(3)-H(3A)	0.9900	C(14)-C(15)	1.384(2)	F(33)-C(37)	1.322(2)
C(3)-H(3B)	0.9900	C(14)-H(14)	0.9500	F(31A)-C(37)	1.282(11)
C(4)-C(5)	1.524(2)	C(15)-C(16)	1.393(2)	F(32A)-C(37)	1.267(10)
C(4)-H(4A)	0.9900	C(15)-C(18)	1.499(2)	F(33A)-C(37)	1.456(10)
C(4)-H(4B)	0.9900	C(16)-H(16)	0.9500	F(34)-C(38)	1.322(4)
C(5)-H(5A)	0.9900	F(21)-C(27)	1.3364(19)	F(35)-C(38)	1.328(3)
C(5)-H(5B)	0.9900	F(22)-C(27)	1.3478(19)	F(36)-C(38)	1.302(4)
N(1)-C(6)	1.142(2)	F(23)-C(27)	1.334(2)	F(34A)-C(38)	1.303(8)
C(6)-C(7)	1.460(2)	F(24)-C(28)	1.3414(18)	F(35A)-C(38)	1.306(7)

F(36A)-C(38)	1.348(7)	C(44)-H(44)	0.9500	C(2)-C(1)-H(1A)	109.7
C(31)-C(36)	1.400(2)	C(45)-C(46)	1.400(2)	S(1)-C(1)-H(1A)	109.7
C(31)-C(32)	1.406(2)	C(45)-C(48)	1.498(2)	C(2)-C(1)-H(1B)	109.7
C(31)-B(1)	1.641(2)	C(46)-H(46)	0.9500	S(1)-C(1)-H(1B)	109.7
C(32)-C(33)	1.390(2)			H(1A)-C(1)-H(1B)	108.2
C(32)-H(32)	0.9500	N(1)-Fe(1)-N(1)#1	180.0	C(1)-C(2)-C(3)	116.94(13)
C(33)-C(34)	1.391(2)	N(1)-Fe(1)-S(1)#1	94.43(4)	C(1)-C(2)-H(2A)	108.1
C(33)-C(37)	1.499(2)	N(1)#1-Fe(1)-S(1)#1	85.57(4)	C(3)-C(2)-H(2A)	108.1
C(34)-C(35)	1.387(2)	N(1)-Fe(1)-S(1)	85.57(4)	C(1)-C(2)-H(2B)	108.1
C(34)-H(34)	0.9500	N(1)#1-Fe(1)-S(1)	94.43(4)	C(3)-C(2)-H(2B)	108.1
C(35)-C(36)	1.396(2)	S(1)#1-Fe(1)-S(1)	180.0	H(2A)-C(2)-H(2B)	107.3
C(35)-C(38)	1.499(2)	N(1)-Fe(1)-S(2)	87.00(4)	C(2)-C(3)-S(2)	110.82(11)
C(36)-H(36)	0.9500	N(1)#1-Fe(1)-S(2)	93.00(4)	C(2)-C(3)-H(3A)	109.5
F(41)-C(47)	1.334(2)	S(1)#1-Fe(1)-S(2)	90.146(14)	S(2)-C(3)-H(3A)	109.5
F(42)-C(47)	1.3206(19)	S(1)-Fe(1)-S(2)	89.854(14)	C(2)-C(3)-H(3B)	109.5
F(43)-C(47)	1.3294(19)	N(1)-Fe(1)-S(2)#1	93.00(4)	S(2)-C(3)-H(3B)	109.5
F(44)-C(48)	1.337(2)	N(1)#1-Fe(1)-S(2)#1	87.00(4)	H(3A)-C(3)-H(3B)	108.1
F(45)-C(48)	1.350(2)	S(1)#1-Fe(1)-S(2)#1	89.854(14)	C(5)-C(4)-S(2)	107.26(11)
F(46)-C(48)	1.330(2)	S(1)-Fe(1)-S(2)#1	90.146(14)	C(5)-C(4)-H(4A)	110.3
C(41)-C(46)	1.395(2)	S(2)-Fe(1)-S(2)#1	180.0	S(2)-C(4)-H(4A)	110.3
C(41)-C(42)	1.407(2)	C(1)-S(1)-C(5)#1	104.75(8)	C(5)-C(4)-H(4B)	110.3
C(41)-B(1)	1.637(2)	C(1)-S(1)-Fe(1)	107.59(6)	S(2)-C(4)-H(4B)	110.3
C(42)-C(43)	1.386(2)	C(5)#1-S(1)-Fe(1)	101.85(5)	H(4A)-C(4)-H(4B)	108.5
C(42)-H(42)	0.9500	C(3)-S(2)-C(4)	103.96(8)	C(4)-C(5)-S(1)#1	107.68(11)
C(43)-C(44)	1.391(2)	C(3)-S(2)-Fe(1)	108.04(5)	C(4)-C(5)-H(5A)	110.2
C(43)-C(47)	1.499(2)	C(4)-S(2)-Fe(1)	101.38(5)	S(1)#1-C(5)-H(5A)	110.2
C(44)-C(45)	1.380(2)	C(2)-C(1)-S(1)	109.73(11)	C(4)-C(5)-H(5B)	110.2

S(1)#1-C(5)-H(5B)	110.2	C(11)-C(16)-H(16)	118.9	C(26)-C(25)-C(28)	119.90(13)
H(5A)-C(5)-H(5B)	108.5	F(13)-C(17)-F(11)	106.33(14)	C(21)-C(26)-C(25)	121.60(14)
C(6)-N(1)-Fe(1)	172.47(13)	F(13)-C(17)-F(12)	107.15(14)	C(21)-C(26)-H(26)	119.2
N(1)-C(6)-C(7)	179.16(16)	F(11)-C(17)-F(12)	104.57(14)	C(25)-C(26)-H(26)	119.2
C(6)-C(7)-H(7A)	109.5	F(13)-C(17)-C(13)	113.10(14)	F(23)-C(27)-F(21)	105.70(13)
C(6)-C(7)-H(7B)	109.5	F(11)-C(17)-C(13)	112.48(13)	F(23)-C(27)-F(22)	105.80(14)
H(7A)-C(7)-H(7B)	109.5	F(12)-C(17)-C(13)	112.61(13)	F(21)-C(27)-F(22)	106.04(14)
C(6)-C(7)-H(7C)	109.5	F(14)-C(18)-F(16)	106.72(13)	F(23)-C(27)-C(23)	113.40(14)
H(7A)-C(7)-H(7C)	109.5	F(14)-C(18)-F(15)	106.59(13)	F(21)-C(27)-C(23)	112.36(13)
H(7B)-C(7)-H(7C)	109.5	F(16)-C(18)-F(15)	105.76(14)	F(22)-C(27)-C(23)	112.90(13)
C(16)-C(11)-C(12)	115.45(13)	F(14)-C(18)-C(15)	113.19(14)	F(26)-C(28)-F(24)	106.60(12)
C(16)-C(11)-B(1)	124.94(13)	F(16)-C(18)-C(15)	112.26(13)	F(26)-C(28)-F(25)	105.99(13)
C(12)-C(11)-B(1)	119.48(13)	F(15)-C(18)-C(15)	111.83(13)	F(24)-C(28)-F(25)	105.42(13)
C(13)-C(12)-C(11)	122.32(14)	C(26)-C(21)-C(22)	116.04(13)	F(26)-C(28)-C(25)	113.66(13)
C(13)-C(12)-H(12)	118.8	C(26)-C(21)-B(1)	123.86(13)	F(24)-C(28)-C(25)	112.73(12)
C(11)-C(12)-H(12)	118.8	C(22)-C(21)-B(1)	119.93(12)	F(25)-C(28)-C(25)	111.83(12)
C(12)-C(13)-C(14)	121.12(14)	C(23)-C(22)-C(21)	122.23(13)	C(36)-C(31)-C(32)	115.74(13)
C(12)-C(13)-C(17)	119.23(14)	C(23)-C(22)-H(22)	118.9	C(36)-C(31)-B(1)	122.31(13)
C(14)-C(13)-C(17)	119.64(14)	C(21)-C(22)-H(22)	118.9	C(32)-C(31)-B(1)	121.47(13)
C(15)-C(14)-C(13)	117.32(13)	C(22)-C(23)-C(24)	120.78(14)	C(33)-C(32)-C(31)	122.03(14)
C(15)-C(14)-H(14)	121.3	C(22)-C(23)-C(27)	120.66(14)	C(33)-C(32)-H(32)	119.0
C(13)-C(14)-H(14)	121.3	C(24)-C(23)-C(27)	118.56(14)	C(31)-C(32)-H(32)	119.0
C(14)-C(15)-C(16)	121.53(14)	C(25)-C(24)-C(23)	118.10(14)	C(32)-C(33)-C(34)	121.20(14)
C(14)-C(15)-C(18)	120.52(14)	C(25)-C(24)-H(24)	120.9	C(32)-C(33)-C(37)	120.16(14)
C(16)-C(15)-C(18)	117.95(14)	C(23)-C(24)-H(24)	120.9	C(34)-C(33)-C(37)	118.63(14)
C(15)-C(16)-C(11)	122.18(14)	C(24)-C(25)-C(26)	121.12(13)	C(35)-C(34)-C(33)	117.79(14)
C(15)-C(16)-H(16)	118.9	C(24)-C(25)-C(28)	118.89(13)	C(35)-C(34)-H(34)	121.1

C(33)-C(34)-H(34)	121.1	F(34A)-C(38)-F(36A)	100.8(7)	C(41)-C(46)-C(45)	121.83(14)
C(34)-C(35)-C(36)	120.92(14)	F(35A)-C(38)-F(36A)	103.6(6)	C(41)-C(46)-H(46)	119.1
C(34)-C(35)-C(38)	120.25(14)	F(36)-C(38)-C(35)	112.0(2)	C(45)-C(46)-H(46)	119.1
C(36)-C(35)-C(38)	118.79(14)	F(34A)-C(38)-C(35)	115.2(5)	F(42)-C(47)-F(43)	105.83(14)
C(35)-C(36)-C(31)	122.29(14)	F(35A)-C(38)-C(35)	115.6(4)	F(42)-C(47)-F(41)	105.03(15)
C(35)-C(36)-H(36)	118.9	F(34)-C(38)-C(35)	111.9(2)	F(43)-C(47)-F(41)	107.19(15)
C(31)-C(36)-H(36)	118.9	F(35)-C(38)-C(35)	112.9(2)	F(42)-C(47)-C(43)	112.71(13)
F(32A)-C(37)-F(31A)	111.2(10)	F(36A)-C(38)-C(35)	113.2(4)	F(43)-C(47)-C(43)	112.75(13)
F(33)-C(37)-F(31)	108.64(16)	C(46)-C(41)-C(42)	115.94(13)	F(41)-C(47)-C(43)	112.74(13)
F(33)-C(37)-F(32)	105.38(14)	C(46)-C(41)-B(1)	125.17(13)	F(46)-C(48)-F(44)	107.84(15)
F(31)-C(37)-F(32)	105.54(15)	C(42)-C(41)-B(1)	118.57(13)	F(46)-C(48)-F(45)	105.52(16)
F(32A)-C(37)-F(33A)	101.0(9)	C(43)-C(42)-C(41)	122.17(14)	F(44)-C(48)-F(45)	105.72(14)
F(31A)-C(37)-F(33A)	94.3(9)	C(43)-C(42)-H(42)	118.9	F(46)-C(48)-C(45)	112.87(15)
F(32A)-C(37)-C(33)	119.3(7)	C(41)-C(42)-H(42)	118.9	F(44)-C(48)-C(45)	112.65(14)
F(31A)-C(37)-C(33)	119.4(9)	C(42)-C(43)-C(44)	120.94(14)	F(45)-C(48)-C(45)	111.72(15)
F(33)-C(37)-C(33)	112.37(13)	C(42)-C(43)-C(47)	120.58(14)	C(41)-B(1)-C(31)	114.29(12)
F(31)-C(37)-C(33)	112.73(14)	C(44)-C(43)-C(47)	118.47(14)	C(41)-B(1)-C(21)	111.92(12)
F(32)-C(37)-C(33)	111.69(14)	C(45)-C(44)-C(43)	117.92(14)	C(31)-B(1)-C(21)	104.32(11)
F(33A)-C(37)-C(33)	106.0(5)	C(45)-C(44)-H(44)	121.0	C(41)-B(1)-C(11)	104.06(11)
F(34A)-C(38)-F(35A)	106.8(6)	C(43)-C(44)-H(44)	121.0	C(31)-B(1)-C(11)	110.28(12)
F(36)-C(38)-F(34)	107.5(3)	C(44)-C(45)-C(46)	121.18(14)	C(21)-B(1)-C(11)	112.20(12)
F(36)-C(38)-F(35)	107.3(3)	C(44)-C(45)-C(48)	119.40(14)		
F(34)-C(38)-F(35)	104.9(3)	C(46)-C(45)-C(48)	119.34(14)		

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y,-z+2

Table S45. Anisotropic displacement parameters ($Å^2$ x 10^3) for $[Fe^{II}(14\text{-}S_4)(MeCN)_2](BAr^F{}_4)_2$. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Fe(1)	13(1)	13(1)	15(1)	-4(1)	0(1)	-6(1)
S(1)	15(1)	15(1)	20(1)	-5(1)	-1(1)	-6(1)
S(2)	19(1)	18(1)	17(1)	-5(1)	2(1)	-10(1)
C(1)	21(1)	20(1)	20(1)	-3(1)	-5(1)	-9(1)
C(2)	29(1)	22(1)	18(1)	-1(1)	-4(1)	-12(1)
C(3)	28(1)	24(1)	16(1)	-5(1)	1(1)	-14(1)
C(4)	18(1)	25(1)	25(1)	-11(1)	6(1)	-9(1)
C(5)	15(1)	21(1)	28(1)	-9(1)	3(1)	-8(1)
N(1)	14(1)	16(1)	17(1)	-3(1)	1(1)	-6(1)
C(6)	15(1)	17(1)	17(1)	-3(1)	0(1)	-7(1)
C(7)	24(1)	20(1)	26(1)	-10(1)	1(1)	-11(1)
F(11)	33(1)	24(1)	30(1)	1(1)	0(1)	-17(1)
F(12)	26(1)	32(1)	52(1)	15(1)	-16(1)	-7(1)
F(13)	91(1)	33(1)	20(1)	-7(1)	24(1)	-22(1)
F(14)	45(1)	30(1)	28(1)	-22(1)	8(1)	-12(1)
F(15)	27(1)	36(1)	73(1)	-37(1)	16(1)	-21(1)
F(16)	30(1)	17(1)	37(1)	-14(1)	-1(1)	-3(1)
C(11)	11(1)	15(1)	14(1)	-6(1)	0(1)	-5(1)
C(12)	14(1)	14(1)	16(1)	-6(1)	1(1)	-5(1)
C(13)	12(1)	17(1)	16(1)	-4(1)	0(1)	-5(1)
C(14)	14(1)	22(1)	16(1)	-9(1)	2(1)	-7(1)
C(15)	12(1)	17(1)	21(1)	-11(1)	2(1)	-6(1)
C(16)	12(1)	14(1)	18(1)	-6(1)	2(1)	-5(1)

C(17)	22(1)	21(1)	16(1)	-3(1)	1(1)	-6(1)
C(18)	18(1)	22(1)	26(1)	-15(1)	5(1)	-8(1)
F(21)	31(1)	24(1)	53(1)	-21(1)	2(1)	-13(1)
F(22)	85(1)	52(1)	27(1)	8(1)	-23(1)	-54(1)
F(23)	23(1)	37(1)	54(1)	-18(1)	9(1)	-19(1)
F(24)	50(1)	15(1)	24(1)	2(1)	-15(1)	-11(1)
F(25)	31(1)	35(1)	17(1)	-11(1)	2(1)	1(1)
F(26)	27(1)	37(1)	22(1)	-2(1)	-7(1)	-16(1)
C(21)	13(1)	12(1)	15(1)	-5(1)	2(1)	-3(1)
C(22)	14(1)	15(1)	14(1)	-5(1)	1(1)	-4(1)
C(23)	16(1)	16(1)	18(1)	-6(1)	2(1)	-8(1)
C(24)	20(1)	14(1)	17(1)	-3(1)	1(1)	-7(1)
C(25)	15(1)	12(1)	14(1)	-4(1)	1(1)	-3(1)
C(26)	14(1)	13(1)	16(1)	-7(1)	2(1)	-4(1)
C(27)	25(1)	19(1)	20(1)	-2(1)	-2(1)	-12(1)
C(28)	19(1)	12(1)	17(1)	-4(1)	0(1)	-4(1)
F(31)	30(1)	44(1)	21(1)	-18(1)	-2(1)	0(1)
F(32)	26(1)	47(1)	33(1)	-25(1)	16(1)	-11(1)
F(33)	93(2)	31(1)	30(1)	-19(1)	24(1)	-40(1)
F(34)	28(1)	102(3)	16(1)	-2(1)	-3(1)	-23(2)
F(35)	17(1)	65(2)	54(2)	-35(2)	-12(1)	10(1)
F(36)	63(2)	47(2)	69(2)	7(1)	-38(2)	-38(2)
F(34A)	78(7)	79(7)	44(4)	36(4)	-40(4)	-65(6)
F(35A)	15(2)	137(10)	40(3)	-37(5)	7(2)	-23(4)
F(36A)	55(5)	32(3)	138(10)	-46(5)	-67(5)	13(3)
C(31)	15(1)	12(1)	14(1)	-3(1)	2(1)	-7(1)
C(32)	17(1)	13(1)	14(1)	-3(1)	1(1)	-7(1)

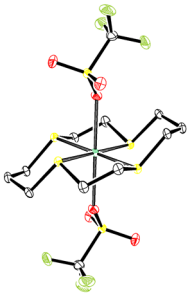
C(33)	20(1)	14(1)	16(1)	-5(1)	4(1)	-7(1)
C(34)	14(1)	14(1)	20(1)	-4(1)	4(1)	-3(1)
C(35)	15(1)	17(1)	17(1)	-2(1)	0(1)	-6(1)
C(36)	16(1)	15(1)	15(1)	-5(1)	2(1)	-6(1)
C(37)	24(1)	18(1)	20(1)	-7(1)	6(1)	-6(1)
C(38)	16(1)	26(1)	23(1)	-6(1)	-1(1)	-6(1)
F(41)	23(1)	51(1)	99(1)	-58(1)	0(1)	-1(1)
F(42)	31(1)	45(1)	30(1)	5(1)	-6(1)	10(1)
F(43)	22(1)	30(1)	70(1)	3(1)	22(1)	-5(1)
F(44)	34(1)	28(1)	55(1)	-18(1)	-10(1)	-15(1)
F(45)	51(1)	20(1)	62(1)	3(1)	-21(1)	-18(1)
F(46)	42(1)	42(1)	118(1)	-58(1)	35(1)	-25(1)
C(41)	15(1)	14(1)	11(1)	-3(1)	1(1)	-6(1)
C(42)	18(1)	12(1)	14(1)	-4(1)	2(1)	-7(1)
C(43)	16(1)	16(1)	12(1)	-3(1)	0(1)	-5(1)
C(44)	17(1)	20(1)	19(1)	-6(1)	-1(1)	-9(1)
C(45)	21(1)	16(1)	21(1)	-7(1)	0(1)	-9(1)
C(46)	16(1)	14(1)	18(1)	-6(1)	1(1)	-5(1)
C(47)	16(1)	19(1)	22(1)	-5(1)	2(1)	-7(1)
C(48)	21(1)	21(1)	46(1)	-15(1)	0(1)	-10(1)
B(1)	14(1)	12(1)	14(1)	-5(1)	1(1)	-5(1)

Table S46. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for $[Fe^{II}(14\text{-}S_4)(MeCN)_2](BAr^F{}_4)_2$.

	x	y	z	U(eq)
H(1A)	7999	561	8303	25
H(1B)	7126	1911	8006	25
H(2A)	8888	2343	7614	27
H(2B)	8519	1773	6911	27
H(3A)	10546	857	7119	26
H(3B)	10077	-84	7741	26
H(4A)	12149	-1293	8674	26
H(4B)	12868	-461	8396	26
H(5A)	12916	-412	10015	25
H(5B)	13580	-1722	9934	25
H(7A)	11300	2627	11173	32
H(7B)	10047	2854	11641	32
H(7C)	10089	3513	10563	32
H(12)	7007	4648	8698	18
H(14)	6233	6500	10637	20
H(16)	6212	8096	7864	17
H(22)	7989	7651	7099	17
H(24)	7147	10064	4567	20
H(26)	5844	7541	5157	17
H(32)	7756	4968	5695	18
H(34)	11233	3097	6611	21
H(36)	8979	5153	8119	18

H(42)	4466	7608	6740	18
H(44)	2884	5484	6453	21
H(46)	6490	4289	6748	19

$[Co^{II}(14\text{-}S_4)(OTf)_2]$



The structure of $[Co^{II}(14\text{-}S_4)(OTf)_2]$ was solved in the monoclinic space group $P2_1/c$ and the asymmetric unit contains one half molecule of $[Co^{II}(14\text{-}S_4)(OTf)_2]$ and an acetonitrile molecule.

Table S47. Crystal data and structure refinement for $[Co^{II}(14\text{-}S_4)(OTf)_2]$.

CCDC No	2107324	
Empirical formula	$C_{16}\,H_{26}\,Co\,F_6\,N_2\,O_6\,S_6$	
Formula weight	707.68	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 9.7818(8) Å	α= 90°.
	b = 17.6403(13) Å	β= 91.436(3)°.
	c = 8.0039(6) Å	γ = 90°.
Volume	1380.67(18) $Å^3$	
Z	2	
Density (calculated)	1.702 Mg/m^3	
Absorption coefficient	1.151 mm^{-1}	

F(000)	722
Crystal size	0.247 x 0.097 x 0.048 mm^3
Theta range for data collection	2.083 to 29.130°.
Index ranges	-13 ≤ h ≤ 13, -24 ≤ k ≤ 24, -10 ≤ l ≤ 10
Reflections collected	40117
Independent reflections	3717 [R(int) = 0.0926]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3717 / 0 / 170
Goodness-of-fit on F^2	1.036
Final R indices [I>2σ(I)]	R1 = 0.0334, wR2 = 0.0715
R indices (all data)	R1 = 0.0532, wR2 = 0.0788
Largest diff. peak and hole	0.448 and -0.431 e.$Å^{-3}$

Table S48. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for [Co^{II}(14-S_4)$(OTf)_2$]. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Co(1)	0	5000	5000	10(1)
S(1)	1275(1)	3958(1)	5223(1)	13(1)
S(2)	655(1)	5156(1)	2386(1)	13(1)
C(1)	1684(2)	3763(1)	3050(3)	17(1)
C(2)	2111(2)	4515(1)	2285(3)	17(1)
C(3)	1474(2)	6082(1)	2307(2)	15(1)
C(4)	435(2)	6715(1)	2499(2)	16(1)
C(5)	-139(2)	6819(1)	4249(2)	15(1)

S(11)	2506(1)	5947(1)	7541(1)	13(1)
F(11)	3490(2)	7028(1)	5666(2)	32(1)
F(12)	4516(2)	6911(1)	8066(2)	38(1)
F(13)	4879(1)	6099(1)	6112(2)	36(1)
O(11)	2015(2)	5598(1)	5994(2)	17(1)
O(12)	1581(2)	6495(1)	8227(2)	21(1)
O(13)	3143(2)	5438(1)	8729(2)	21(1)
C(11)	3916(2)	6526(1)	6815(3)	22(1)
N(21)	7170(2)	7045(1)	10528(3)	31(1)
C(21)	6378(2)	6679(1)	11158(3)	22(1)
C(22)	5348(2)	6207(1)	11949(3)	27(1)

Table S49. Bond lengths [Å] and angles [°] for [Co^{II}(14-S_4)($OTf)_2$].

Co(1)-S(2)#1	2.2206(5)	C(1)-H(1B)	0.9900	S(11)-O(12)	1.4422(16)
Co(1)-S(2)	2.2206(5)	C(2)-H(2A)	0.9900	S(11)-O(11)	1.4532(14)
Co(1)-S(1)#1	2.2262(5)	C(2)-H(2B)	0.9900	S(11)-C(11)	1.824(2)
Co(1)-S(1)	2.2262(5)	C(3)-C(4)	1.522(3)	F(11)-C(11)	1.336(3)
Co(1)-O(11)	2.3569(14)	C(3)-H(3A)	0.9900	F(12)-C(11)	1.333(2)
Co(1)-O(11)#1	2.3569(14)	C(3)-H(3B)	0.9900	F(13)-C(11)	1.341(3)
S(1)-C(5)#1	1.821(2)	C(4)-C(5)	1.533(3)	N(21)-C(21)	1.135(3)
S(1)-C(1)	1.826(2)	C(4)-H(4A)	0.9900	C(21)-C(22)	1.464(3)
S(2)-C(3)	1.820(2)	C(4)-H(4B)	0.9900	C(22)-H(22A)	0.9800
S(2)-C(2)	1.823(2)	C(5)-H(5A)	0.9900	C(22)-H(22B)	0.9800
C(1)-C(2)	1.523(3)	C(5)-H(5B)	0.9900	C(22)-H(22C)	0.9800
C(1)-H(1A)	0.9900	S(11)-O(13)	1.4375(15)		

S(2)#1-Co(1)-S(2)	180.0	C(2)-C(1)-H(1B)	110.4	C(4)-C(5)-H(5B)	109.4
S(2)#1-Co(1)-S(1)#1	90.201(18)	S(1)-C(1)-H(1B)	110.4	S(1)#1-C(5)-H(5B)	109.4
S(2)-Co(1)-S(1)#1	89.798(18)	H(1A)-C(1)-H(1B)	108.6	H(5A)-C(5)-H(5B)	108.0
S(2)#1-Co(1)-S(1)	89.798(18)	C(1)-C(2)-S(2)	107.43(14)	O(13)-S(11)-O(12)	115.62(9)
S(2)-Co(1)-S(1)	90.202(18)	C(1)-C(2)-H(2A)	110.2	O(13)-S(11)-O(11)	115.34(9)
S(1)#1-Co(1)-S(1)	180.0	S(2)-C(2)-H(2A)	110.2	O(12)-S(11)-O(11)	114.27(9)
S(2)#1-Co(1)-O(11)	89.79(4)	C(1)-C(2)-H(2B)	110.2	O(13)-S(11)-C(11)	103.99(10)
S(2)-Co(1)-O(11)	90.21(4)	S(2)-C(2)-H(2B)	110.2	O(12)-S(11)-C(11)	103.42(10)
S(1)#1-Co(1)-O(11)	96.86(4)	H(2A)-C(2)-H(2B)	108.5	O(11)-S(11)-C(11)	101.63(9)
S(1)-Co(1)-O(11)	83.14(4)	C(4)-C(3)-S(2)	111.06(14)	S(11)-O(11)-Co(1)	137.11(9)
S(2)#1-Co(1)-O(11)#1	90.21(4)	C(4)-C(3)-H(3A)	109.4	F(12)-C(11)-F(11)	107.70(18)
S(2)-Co(1)-O(11)#1	89.79(4)	S(2)-C(3)-H(3A)	109.4	F(12)-C(11)-F(13)	107.50(18)
S(1)#1-Co(1)-O(11)#1	83.13(4)	C(4)-C(3)-H(3B)	109.4	F(11)-C(11)-F(13)	107.07(18)
S(1)-Co(1)-O(11)#1	96.87(4)	S(2)-C(3)-H(3B)	109.4	F(12)-C(11)-S(11)	111.61(15)
O(11)-Co(1)-O(11)#1	180.0	H(3A)-C(3)-H(3B)	108.0	F(11)-C(11)-S(11)	111.42(15)
C(5)#1-S(1)-C(1)	103.25(9)	C(3)-C(4)-C(5)	116.14(16)	F(13)-C(11)-S(11)	111.31(16)
C(5)#1-S(1)-Co(1)	107.20(7)	C(3)-C(4)-H(4A)	108.3	N(21)-C(21)-C(22)	179.2(2)
C(1)-S(1)-Co(1)	102.38(7)	C(5)-C(4)-H(4A)	108.3	C(21)-C(22)-H(22A)	109.5
C(3)-S(2)-C(2)	102.14(10)	C(3)-C(4)-H(4B)	108.3	C(21)-C(22)-H(22B)	109.5
C(3)-S(2)-Co(1)	106.37(7)	C(5)-C(4)-H(4B)	108.3	H(22A)-C(22)-H(22B)	109.5
C(2)-S(2)-Co(1)	102.08(7)	H(4A)-C(4)-H(4B)	107.4	C(21)-C(22)-H(22C)	109.5
C(2)-C(1)-S(1)	106.78(14)	C(4)-C(5)-S(1)#1	111.22(14)	H(22A)-C(22)-H(22C)	109.5
C(2)-C(1)-H(1A)	110.4	C(4)-C(5)-H(5A)	109.4	H(22B)-C(22)-H(22C)	109.5
S(1)-C(1)-H(1A)	110.4	S(1)#1-C(5)-H(5A)	109.4		

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+1,-z+1

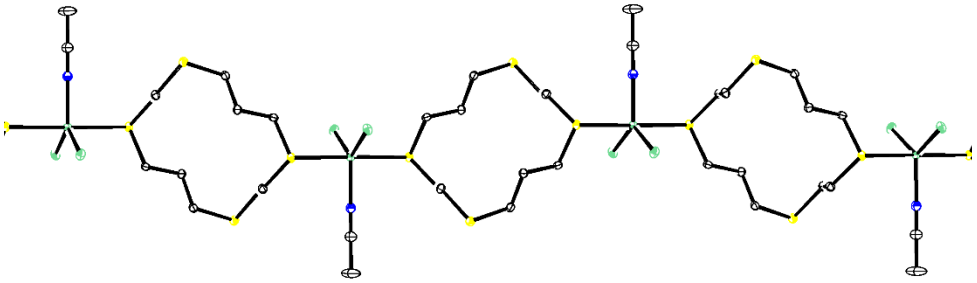
Table S50. Anisotropic displacement parameters ($Å^2$ x 10^3) for $[Co^{II}(14\text{-}S_4)(OTf)_2]$. The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [h^2 a*2U^{11} + ... + 2 h k a* b* U^{12}].

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Co(1)	12(1)	10(1)	9(1)	0(1)	2(1)	0(1)
S(1)	14(1)	12(1)	13(1)	1(1)	1(1)	1(1)
S(2)	15(1)	13(1)	9(1)	0(1)	2(1)	0(1)
C(1)	18(1)	15(1)	17(1)	-2(1)	4(1)	2(1)
C(2)	19(1)	16(1)	18(1)	1(1)	7(1)	2(1)
C(3)	19(1)	14(1)	12(1)	2(1)	4(1)	-4(1)
C(4)	20(1)	12(1)	16(1)	4(1)	1(1)	-1(1)
C(5)	19(1)	9(1)	18(1)	2(1)	1(1)	-1(1)
S(11)	16(1)	14(1)	11(1)	1(1)	-1(1)	-1(1)
F(11)	38(1)	31(1)	27(1)	14(1)	-4(1)	-13(1)
F(12)	42(1)	43(1)	29(1)	-2(1)	-10(1)	-27(1)
F(13)	19(1)	52(1)	38(1)	1(1)	9(1)	-1(1)
O(11)	20(1)	18(1)	13(1)	-2(1)	-1(1)	-6(1)
O(12)	24(1)	20(1)	17(1)	-2(1)	2(1)	5(1)
O(13)	26(1)	21(1)	16(1)	4(1)	-3(1)	3(1)
C(11)	21(1)	27(1)	17(1)	2(1)	-3(1)	-7(1)
N(21)	25(1)	38(1)	31(1)	-7(1)	2(1)	-7(1)
C(21)	19(1)	27(1)	20(1)	-7(1)	-1(1)	1(1)
C(22)	24(1)	32(1)	26(1)	1(1)	4(1)	1(1)

Table S51. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for $[Co^{II}(14\text{-}S_4)(OTf)_2]$.

	x	y	z	U(eq)
H(1A)	2438	3391	2995	20
H(1B)	875	3556	2440	20
H(2A)	2372	4439	1109	21
H(2B)	2906	4728	2914	21
H(3A)	2179	6119	3213	18
H(3B)	1935	6139	1227	18
H(4A)	-340	6620	1708	19
H(4B)	867	7198	2164	19
H(5A)	-646	7304	4295	18
H(5B)	626	6843	5081	18
H(22A)	4875	6506	12790	41
H(22B)	5794	5771	12487	41
H(22C)	4684	6029	11099	41

{[Co^{II}(14-S$_4$)(MeCN)(Cl$_2$)]}$_n$



The structure of{[Co^{II}(14-S$_4$)(MeCN)(Cl$_2$)]}$_n$ was solved in the monoclinic space group *C*2/*c* and the asymmetric unit contains one half of a ligand, cobalt ion, acetonitrile ligand and one full chloride ligand as part of the 1-dimensional coordination polymer {[Co^{II}(14-S$_4$)(MeCN)(Cl$_2$)]}$_n$.

Table S52. Crystal data and structure refinement for {[Co^{II}(14-S$_4$)(MeCN)(Cl$_2$)]}$_n$.

CCDC No	2107325	
Empirical formula	C_{12} H_{23} Cl_2 Co N S_4	
Formula weight	439.38	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	*C*2/*c*	
Unit cell dimensions	a = 21.553(4) Å	α= 90°.
	b = 8.7583(18) Å	β= 98.733(12)°.
	c = 9.884(2) Å	γ = 90°.
Volume	1844.1(6) Å^3	
Z	4	
Density (calculated)	1.583 Mg/m^3	
Absorption coefficient	1.663 mm^{-1}	
F(000)	908	
Crystal size	0.182 x 0.160 x 0.118 mm^3	
Theta range for data collection	2.514 to 30.032°.	
Index ranges	-30 ≤ h ≤ 30, -12 ≤ k ≤ 12, -13 ≤ l ≤ 13	
Reflections collected	23543	
Independent reflections	2697 [R(int) = 0.0914]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2697 / 0 / 94	
Goodness-of-fit on F^2	1.014	
Final R indices [I>2σ(I)]	R1 = 0.0327, wR2 = 0.0664	
R indices (all data)	R1 = 0.0533, wR2 = 0.0736	
Largest diff. peak and hole	0.635 and -0.501 e.Å^{-3}	

Table S53. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for{[Co^{II}(14-S_4)(MeCN)(Cl_2)]}$_n$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Co(1)	5000	3195(1)	2500	10(1)
Cl(1)	5589(1)	1967(1)	1125(1)	15(1)
S(1)	5853(1)	3213(1)	4621(1)	12(1)
S(2)	7333(1)	6074(1)	3183(1)	14(1)
C(1)	6468(1)	4607(2)	4524(2)	13(1)
C(2)	6738(1)	4614(2)	3190(2)	13(1)
C(3)	7935(1)	5475(2)	4561(2)	13(1)
C(4)	8232(1)	3940(2)	4338(2)	13(1)
C(5)	8755(1)	3599(2)	5519(2)	12(1)
N(11)	5000	5495(3)	2500	14(1)
C(11)	5000	6788(4)	2500	17(1)
C(12)	5000	8439(4)	2500	40(1)

Table S54. Bond lengths [Å] and angles [°] for $\{[Co^{II}(14\text{-}S_4)(MeCN)(Cl_2)]\}_n$.

Co(1)-N(11)	2.015(3)	N(11)-Co(1)-S(1)	89.635(15)	C(5)-C(4)-H(4B)	109.7
Co(1)-Cl(1)	2.2669(6)	Cl(1)-Co(1)-S(1)	95.48(2)	H(4A)-C(4)-H(4B)	108.2
Co(1)-Cl(1)#1	2.2669(6)	Cl(1)#1-Co(1)-S(1)	84.87(2)	C(4)-C(5)-S(1)#2	114.36(14)
Co(1)-S(1)	2.5695(7)	N(11)-Co(1)-S(1)#1	89.636(15)	C(4)-C(5)-H(5A)	108.7
Co(1)-S(1)#1	2.5695(7)	Cl(1)-Co(1)-S(1)#1	84.87(2)	S(1)#2-C(5)-H(5A)	108.7
S(1)-C(5)#2	1.813(2)	Cl(1)#1-Co(1)-S(1)#1	95.48(2)	C(4)-C(5)-H(5B)	108.7
S(1)-C(1)	1.816(2)	S(1)-Co(1)-S(1)#1	179.27(3)	S(1)#2-C(5)-H(5B)	108.7
S(2)-C(3)	1.809(2)	C(5)#2-S(1)-C(1)	103.38(10)	H(5A)-C(5)-H(5B)	107.6
S(2)-C(2)	1.812(2)	C(5)#2-S(1)-Co(1)	102.49(7)	C(11)-N(11)-Co(1)	180.0
C(1)-C(2)	1.519(3)	C(1)-S(1)-Co(1)	113.53(7)	N(11)-C(11)-C(12)	180.0
C(1)-H(1A)	0.9900	C(3)-S(2)-C(2)	102.72(10)	C(11)-C(12)-H(12A)	109.5
C(1)-H(1B)	0.9900	C(2)-C(1)-S(1)	115.28(15)	C(11)-C(12)-H(12B)	109.5
C(2)-H(2A)	0.9900	C(2)-C(1)-H(1A)	108.5	H(12A)-C(12)-H(12B)	109.5
C(2)-H(2B)	0.9900	S(1)-C(1)-H(1A)	108.5	C(11)-C(12)-H(12C)	109.5
C(3)-C(4)	1.519(3)	C(2)-C(1)-H(1B)	108.5	H(12A)-C(12)-H(12C)	109.5
C(3)-H(3A)	0.9900	S(1)-C(1)-H(1B)	108.5	H(12B)-C(12)-H(12C)	109.5
C(3)-H(3B)	0.9900	H(1A)-C(1)-H(1B)	107.5	C(11)-C(12)-H(12A)#1	109.469(7)
C(4)-C(5)	1.525(3)	C(1)-C(2)-S(2)	111.74(14)	H(12A)-C(12)-H(12A)#1	141.1
C(4)-H(4A)	0.9900	C(1)-C(2)-H(2A)	109.3	H(12B)-C(12)-H(12A)#1	56.2
C(4)-H(4B)	0.9900	S(2)-C(2)-H(2A)	109.3	H(12C)-C(12)-H(12A)#1	56.3
C(5)-H(5A)	0.9900	C(1)-C(2)-H(2B)	109.3	C(11)-C(12)-H(12B)#1	109.469(10)
C(5)-H(5B)	0.9900	S(2)-C(2)-H(2B)	109.3	H(12A)-C(12)-H(12B)#1	56.3
N(11)-C(11)	1.132(4)	H(2A)-C(2)-H(2B)	107.9	H(12B)-C(12)-H(12B)#1	141.1
C(11)-C(12)	1.446(5)	C(4)-C(3)-S(2)	114.64(14)	H(12C)-C(12)-H(12B)#1	56.2
C(12)-H(12A)	0.9800	C(4)-C(3)-H(3A)	108.6	H(12A)#1-C(12)-H(12B)#1	109.5
C(12)-H(12B)	0.9800	S(2)-C(3)-H(3A)	108.6	C(11)-C(12)-H(12C)#1	109.47(2)
C(12)-H(12C)	0.9800	C(4)-C(3)-H(3B)	108.6	H(12A)-C(12)-H(12C)#1	56.3
C(12)-H(12A)#1	0.9800	S(2)-C(3)-H(3B)	108.6	H(12B)-C(12)-H(12C)#1	56.2
C(12)-H(12B)#1	0.9800	H(3A)-C(3)-H(3B)	107.6	H(12C)-C(12)-H(12C)#1	141.1
C(12)-H(12C)#1	0.9800	C(3)-C(4)-C(5)	109.96(17)	H(12A)#1-C(12)-H(12C)#1	109.5
N(11)-Co(1)-Cl(1)	118.319(17)	C(3)-C(4)-H(4A)	109.7	H(12B)#1-C(12)-H(12C)#1	109.5
N(11)-Co(1)-Cl(1)#1	118.319(17)	C(5)-C(4)-H(4A)	109.7		
Cl(1)-Co(1)-Cl(1)#1	123.36(3)	C(3)-C(4)-H(4B)	109.7		

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y,-z+1/2 #2 -x+3/2,-y+1/2,-z+1

Table S55. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $\{[Co^{II}(14\text{-}S_4)(MeCN)(Cl_2)]\}_n$. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2 a^{*2} U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Co(1)	11(1)	9(1)	11(1)	0	3(1)	0
Cl(1)	14(1)	19(1)	12(1)	-3(1)	2(1)	4(1)
S(1)	10(1)	14(1)	10(1)	0(1)	1(1)	-1(1)
S(2)	13(1)	14(1)	13(1)	4(1)	1(1)	-1(1)
C(1)	13(1)	13(1)	12(1)	0(1)	1(1)	-1(1)
C(2)	12(1)	14(1)	11(1)	0(1)	1(1)	-1(1)
C(3)	12(1)	13(1)	12(1)	0(1)	0(1)	-2(1)
C(4)	15(1)	13(1)	10(1)	0(1)	-2(1)	0(1)
C(5)	16(1)	9(1)	12(1)	0(1)	0(1)	-2(1)
N(11)	15(1)	15(1)	12(1)	0	1(1)	0
C(11)	24(2)	15(2)	10(1)	0	2(1)	0
C(12)	80(3)	12(2)	21(2)	0	-10(2)	0

Table S56. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for {[Co^{II}(14-S_4)(MeCN)(Cl_2)]}$_n$.

	x	y	z	U(eq)
H(1A)	6299	5635	4666	15
H(1B)	6814	4412	5285	15
H(2A)	6395	4795	2419	15
H(2B)	6923	3602	3054	15
H(3A)	8269	6261	4688	15
H(3B)	7749	5426	5416	15
H(4A)	8405	3956	3466	16
H(4B)	7909	3129	4278	16
H(5A)	8576	3608	6384	15
H(5B)	9071	4426	5573	15
H(12A)	5084	8812	1610	60
H(12B)	5327	8812	3223	60
H(12C)	4590	8812	2667	60

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