Supporting Information

For

Ligand Structural Effects on Cu_2S_2 Bonding and Reactivity in Side-On Disulfido-Bridged Dicopper Complexes

Eric C. Brown, Itsik Bar-Nahum, John T. York, Nermeen W. Aboelella and William B. Tolman*

Department of Chemistry and Center for Metals in Biocatalysis, University of Minnesota, 207 Pleasant Street SE, Minneapolis, MN 55455

Experimental Procedure for the Synthesis of (HL'Me2)Cu

The ligand $HL^{Me2}(\mathbf{h})$ was prepared by a procedure analogous to that used to prepare according to HL'^{iPr2} (i) (ref. 24 in main text). A 38% yield was obtained. ¹H NMR (CDCl₃, 300 MHz): δ 10.53 (s, 1H), 8.38 (s, 1H), 7.34 (d, J = 7.8 Hz, 1H), 7.06 – 7.22 (m, 6H), 6.98 (t, J = 7.5 Hz, 1H), 6.72 (t, J = 7.5 Hz, 1H), 7.06 (t, J = 7.5= 7.5 Hz, 1H), 6.28 (d, J = 8.40 Hz, 1H), 2.25 (s, 6H), 2.19 (s, 6H) ppm. BuLi (0.366 mL of 2.5M) solution in hexane, 0.91 mmol) was added dropwise to the solution of HL'^{Me2} (300 mg, 0.91 mmol) in a pentane (10 mL) / toluene (2 mL) mixture. The reaction was stirred for 30 min, during which time a yellow - orange precipitate formed. The precipitate was collected, washed with pentane (5 mL) and dried under reduced pressure (269 mg, 88%). The product was used without any further purification or characterization. A solution of (HL'Me2)Li (269 mg, 0.80 mmol) in THF (7 mL) was added to a solution of Cu(CH₃CN)₄CF₃SO₃ (303 mg, 0.80 mmol) in THF (7 mL). The reaction was stirred for 10 min before the solvent was removed under reduced pressure. The product was extracted with toluene $(3 \times 10 \text{ mL})$ and filtered through a plug of celite. The filtrate was then concentrated under reduced pressure and washed with a minimum amount of pentane (2 mL) to give a fine yellow - orange powder (285 mg, 82%). ¹H NMR (C₆D₆, 300 MHz): δ 7.71 (s, 1H), 6.80 -7.25 (m, 8H), 6.49 (d, J = 9.00 Hz, 1H), 6.30 (t, J = 6.90 Hz, 1H), 2.06 (s, 6H), 1.90 (s, 6H). The product was used directly for the synthesis of $[(HL^{Me2})Cu]_2(S_2)$ (2h).

	$((a)Cu)_2(S_2)(2a)$	$[((\mathbf{c})C\mathbf{u})_2(S_2)](\mathbf{2c})$	$[((\mathbf{d})C\mathbf{u})_2(S_2)]$	$[((\mathbf{e})\mathrm{Cu})_2(\mathrm{S}_2)]$	
2 1			(2d)	(2e)	
formula	$C_{42}H_{50}Cu_2N_4S_2$	$C_{70}H_{106}Cu_2N_4S_2$	$C_{58}H_{66}Cu_2N_4S_2$	$C_{80}H_{98}Cu_2N_4S_2$	
Fw	802.06	1194.79	1010.35	1306.82	
space group	C2/c	C2/c	P2(1)/c	P-1	
a (A)	23.6195(18)	21.2278(15)	12.857(5)	11.7632(9)	
b (A)	10.7047(8)	21.6630(13)	8.352(3)	12.8233(9)	
c (A)	15.6798(12)	15.8530(11)	24.115(9)	13.2525(10)	
α (deg)	90	90	90	111.4280(10)	
β (deg)	95.1130(10)	98.7570(10)	94.563(7)	90.9190(10)	
γ (deg)	90	90	90	104.9470(10)	
V (Å ³)	3948.7(5)	7205.1(8)	2581.4(17)	1784.3(2)	
Z	4	4	2	1	
T(K)	173	173	173	173	
$\rho_{calcd} (Mg/m^3)$	1.349	1.101	1.300	1.216	
θ range (deg)	1.73 to 27.55	1.35 to 25.04	1.59 to 25.06	1.66 to 25.06	
μ (mm ⁻¹)	1.217	0.687	0.946	0.700	
reflens colled	22982	18439	19381	17744	
Unique	4548	6360	4556	6304	
reflens					
Params	232	376	298	422	
R1, wR2 (for	0.0321,	0.0450,	0.0386,	0.0348,	
$I > 2\sigma(I)$	0.0788	0.0957	0.0784	0.0713	
GOF	1.059	1.021	1.051	1.040	
largest peak.	0.480, -0.358	0.397, -0.326	0.805, -0.403	0.304, -0.281	
hole $(e^{-\Delta^{-3}})$,	,	,	,	
$more (0, \pi)$					
	$[((f)Cu)_2(S_2)](2f)$	$[((g)Cu)_2(S_2)](2g)$	$[((\mathbf{h})Cu)_2(S_2)]$	$[((j)Cu)_2(S_2)]$	5a
	$[((f)Cu)_2(S_2)]$ (2f)	$[((g)Cu)_2(S_2)](2g)$	$[((h)Cu)_2(S_2)]$ (2h)	[((j)Cu) ₂ (S ₂)] (2j)	5a
formula	$[((\mathbf{f})Cu)_2(S_2)] (\mathbf{2f})$ C ₅₄ H ₄₆ Cu ₂ F ₁₂ N ₄ S ₂	$[((\mathbf{g})Cu)_2(S_2)] (\mathbf{2g})$ $C_{70}H_{78}Cu_2F_{12}N_4S_2$	$[((\mathbf{h})Cu)_2(S_2)] \\ (\mathbf{2h}) \\ C_{60}H_{62}Cu_2N_4S_2$	$[((\mathbf{j})C\mathbf{u})_2(\mathbf{S}_2)] \\ (\mathbf{2j}) \\ C_{64}H_{82}C\mathbf{u}_2N_4\mathbf{S}_2$	5a C ₈₄ H ₁₀₀ Cu ₄ N ₈ S ₄
formula Fw	$\frac{[((\mathbf{f})Cu)_2(S_2)] (\mathbf{2f})}{C_{54}H_{46}Cu_2F_{12}N_4S_2}$ 1170.15	$\frac{[((\mathbf{g})Cu)_2(S_2)] (\mathbf{2g})}{C_{70}H_{78}Cu_2F_{12}N_4S_2}$ 1394.56	$[((\mathbf{h})Cu)_2(S_2)] \\ (\mathbf{2h}) \\ C_{60}H_{62}Cu_2N_4S_2 \\ 1030.34$	$[((\mathbf{j})Cu)_2(S_2)] \\ (\mathbf{2j}) \\ C_{64}H_{82}Cu_2N_4S_2 \\ 1098.54$	5a C ₈₄ H ₁₀₀ Cu ₄ N ₈ S ₄ 1604.12
formula Fw space group	$\frac{[((\mathbf{f})Cu)_2(S_2)] (\mathbf{2f})}{C_{54}H_{46}Cu_2F_{12}N_4S_2}$ 1170.15 P-1	$[((\mathbf{g})Cu)_2(S_2)] (\mathbf{2g})$ $C_{70}H_{78}Cu_2F_{12}N_4S_2$ 1394.56 P-1	$[((\mathbf{h})Cu)_2(S_2)] \\ (\mathbf{2h}) \\ C_{60}H_{62}Cu_2N_4S_2 \\ 1030.34 \\ pbca$	$[((\mathbf{j})Cu)_2(S_2)] \\ (2\mathbf{j}) \\ C_{64}H_{82}Cu_2N_4S_2 \\ 1098.54 \\ C2/c \\ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ $	5a C ₈₄ H ₁₀₀ Cu ₄ N ₈ S ₄ 1604.12 I4
formula Fw space group $a(\hat{A})$	$[((\mathbf{f})Cu)_2(S_2)] (\mathbf{2f})$ $C_{54}H_{46}Cu_2F_{12}N_4S_2$ 1170.15 P-1 8.3136(9)	$[((\mathbf{g})Cu)_2(S_2)] (\mathbf{2g})$ $C_{70}H_{78}Cu_2F_{12}N_4S_2$ 1394.56 P-1 $12.317(5)$	$[((\mathbf{h})Cu)_2(S_2)] \\ (2\mathbf{h}) \\ C_{60}H_{62}Cu_2N_4S_2 \\ 1030.34 \\ pbca \\ 16.0272(18) \\ \end{tabular}$	$[((\mathbf{j})Cu)_2(S_2)]$ (2\mathbf{j}) $C_{64}H_{82}Cu_2N_4S_2$ 1098.54 C2/c 19.927(3)	$\begin{array}{c} {\bf 5a} \\ \hline C_{84} H_{100} Cu_4 N_8 S_4 \\ 1604.12 \\ I4 \\ 25.048(4) \end{array}$
formula Fw space group $a(\hat{A})$ $b(\hat{A})$	$[((\mathbf{f})Cu)_2(S_2)] (\mathbf{2f})$ $C_{54}H_{46}Cu_2F_{12}N_4S_2$ 1170.15 P-1 8.3136(9) 12.5947(13)	$[((\mathbf{g})Cu)_2(S_2)] (\mathbf{2g})$ $C_{70}H_{78}Cu_2F_{12}N_4S_2$ 1394.56 P-1 $12.317(5)$ $13.019(5)$	$[((\mathbf{h})Cu)_2(S_2)]$ (2h) C ₆₀ H ₆₂ Cu ₂ N ₄ S ₂ 1030.34 pbca 16.0272(18) 15.9956(18)	$[((j)Cu)_2(S_2)] \\ (2j) \\ C_{64}H_{82}Cu_2N_4S_2 \\ 1098.54 \\ C2/c \\ 19.927(3) \\ 19.811(3) \\ \label{eq:constraint}$	$\begin{array}{c} \textbf{5a} \\ \hline C_{84}H_{100}Cu_4N_8S_4 \\ 1604.12 \\ I4 \\ 25.048(4) \\ 25.048(4) \end{array}$
formula Fw space group $a(\hat{A})$ $b(\hat{A})$ $c(\hat{A})$	$[((\mathbf{f})Cu)_2(S_2)] (\mathbf{2f})$ $C_{54}H_{46}Cu_2F_{12}N_4S_2$ 1170.15 P-1 8.3136(9) 12.5947(13) 14.2544(15)	$[((\mathbf{g})Cu)_2(S_2)] (\mathbf{2g})$ $C_{70}H_{78}Cu_2F_{12}N_4S_2$ 1394.56 P-1 $12.317(5)$ $13.019(5)$ $13.915(5)$	$[((\mathbf{h})Cu)_2(S_2)]$ (2h) C ₆₀ H ₆₂ Cu ₂ N ₄ S ₂ 1030.34 pbca 16.0272(18) 15.9956(18) 20.072(2)	$[((\mathbf{j})Cu)_2(S_2)]$ (2 \mathbf{j}) C ₆₄ H ₈₂ Cu ₂ N ₄ S ₂ 1098.54 C2/c 19.927(3) 19.811(3) 17.578(3)	$\begin{array}{c} \textbf{5a} \\ \hline C_{84}H_{100}Cu_4N_8S_4 \\ 1604.12 \\ I4 \\ 25.048(4) \\ 25.048(4) \\ 8.611(3) \end{array}$
formula Fw space group $a(\hat{A})$ $b(\hat{A})$ $c(\hat{A})$ α (deg)	$ \begin{bmatrix} ((\mathbf{f})C\mathbf{u})_2(S_2) \end{bmatrix} (\mathbf{2f}) \\ \hline C_{54}H_{46}C\mathbf{u}_2F_{12}N_4S_2 \\ 1170.15 \\ \hline P-1 \\ 8.3136(9) \\ 12.5947(13) \\ 14.2544(15) \\ 103.694(2) \\ \end{bmatrix} $	$[((\mathbf{g})Cu)_2(S_2)] (\mathbf{2g})$ $C_{70}H_{78}Cu_2F_{12}N_4S_2$ 1394.56 P-1 $12.317(5)$ $13.019(5)$ $13.915(5)$ $81.263(5)$	$ \begin{array}{c} [((\mathbf{h})Cu)_2(S_2)] \\ (\mathbf{2h}) \\ C_{60}H_{62}Cu_2N_4S_2 \\ 1030.34 \\ pbca \\ 16.0272(18) \\ 15.9956(18) \\ 20.072(2) \\ 90 \end{array} $	[((j)Cu) ₂ (S ₂)] (2j) C ₆₄ H ₈₂ Cu ₂ N ₄ S ₂ 1098.54 C2/c 19.927(3) 19.811(3) 17.578(3) 90	$\begin{array}{c} \textbf{5a} \\ \hline C_{84}H_{100}Cu_4N_8S_4 \\ 1604.12 \\ I4 \\ 25.048(4) \\ 25.048(4) \\ 8.611(3) \\ 90 \end{array}$
formula Fw space group $a(\hat{A})$ $b(\hat{A})$ $c(\hat{A})$ $\alpha(\text{deg})$ $\beta(\text{deg})$	$ \begin{bmatrix} ((\mathbf{f})Cu)_2(S_2) \end{bmatrix} (\mathbf{2f}) \\ \hline C_{54}H_{46}Cu_2F_{12}N_4S_2 \\ 1170.15 \\ P-1 \\ 8.3136(9) \\ 12.5947(13) \\ 14.2544(15) \\ 103.694(2) \\ 105.738(2) \end{bmatrix} $	$ \begin{bmatrix} ((\mathbf{g})Cu)_2(S_2) \end{bmatrix} (\mathbf{2g}) \\ C_{70}H_{78}Cu_2F_{12}N_4S_2 \\ 1394.56 \\ P-1 \\ 12.317(5) \\ 13.019(5) \\ 13.915(5) \\ 81.263(5) \\ 81.293(5) \end{bmatrix} $	$ \begin{array}{c} [((\mathbf{h})Cu)_2(S_2)] \\ (\mathbf{2h}) \\ \hline C_{60}H_{62}Cu_2N_4S_2 \\ 1030.34 \\ pbca \\ 16.0272(18) \\ 15.9956(18) \\ 20.072(2) \\ 90 \\ 90 \end{array} $	$[((\mathbf{j})Cu)_2(S_2)]$ (2 \mathbf{j}) C ₆₄ H ₈₂ Cu ₂ N ₄ S ₂ 1098.54 C2/c 19.927(3) 19.811(3) 17.578(3) 90 104.346(3)	$\begin{array}{c} \textbf{5a} \\ \hline C_{84}H_{100}Cu_4N_8S_4 \\ 1604.12 \\ I4 \\ 25.048(4) \\ 25.048(4) \\ 8.611(3) \\ 90 \\ 90 \\ 90 \\ \end{array}$
formula Fw space group $a(\hat{A})$ $b(\hat{A})$ $c(\hat{A})$ $\alpha(\text{deg})$ $\beta(\text{deg})$ $\gamma(\text{deg})$	$[((\mathbf{f})Cu)_2(S_2)] (\mathbf{2f})$ $C_{54}H_{46}Cu_2F_{12}N_4S_2$ 1170.15 P-1 8.3136(9) 12.5947(13) 14.2544(15) 103.694(2) 105.738(2) 105.080(2)	$[((\mathbf{g})C\mathbf{u})_2(S_2)] (\mathbf{2g})$ $C_{70}H_{78}C\mathbf{u}_2F_{12}N_4S_2$ 1394.56 P-1 $12.317(5)$ $13.019(5)$ $13.915(5)$ $81.263(5)$ $81.293(5)$ $78.555(5)$	$ \begin{array}{c} [((\mathbf{h})Cu)_2(S_2)] \\ (\mathbf{2h}) \\ \hline C_{60}H_{62}Cu_2N_4S_2 \\ 1030.34 \\ pbca \\ 16.0272(18) \\ 15.9956(18) \\ 20.072(2) \\ 90 \\ 90 \\ 90 \\ 90 \end{array} $	$ \begin{array}{c} [((\mathbf{j})\mathrm{Cu})_2(\mathrm{S}_2)] \\ (\mathbf{2j}) \\ C_{64}\mathrm{H}_{82}\mathrm{Cu}_2\mathrm{N}_4\mathrm{S}_2 \\ 1098.54 \\ \mathrm{C2/c} \\ 19.927(3) \\ 19.811(3) \\ 17.578(3) \\ 90 \\ 104.346(3) \\ 90 \end{array} $	$\begin{array}{c} \textbf{5a} \\ \hline C_{84}H_{100}Cu_4N_8S_4 \\ 1604.12 \\ I4 \\ 25.048(4) \\ 25.048(4) \\ 8.611(3) \\ 90 \\ 90 \\ 90 \\ 90 \\ 90 \\ \end{array}$
formula Fw space group $a(\hat{A})$ $b(\hat{A})$ $c(\hat{A})$ $\alpha(\text{deg})$ $\beta(\text{deg})$ $\gamma(\text{deg})$ $V(\hat{A}^3)$	$[((\mathbf{f})Cu)_2(S_2)] (\mathbf{2f})$ $C_{54}H_{46}Cu_2F_{12}N_4S_2$ 1170.15 P-1 8.3136(9) 12.5947(13) 14.2544(15) 103.694(2) 105.738(2) 105.080(2) 1309.1(2)	$[((\mathbf{g})Cu)_2(S_2)] (\mathbf{2g})$ $C_{70}H_{78}Cu_2F_{12}N_4S_2$ 1394.56 P-1 $12.317(5)$ $13.019(5)$ $13.915(5)$ $81.263(5)$ $81.293(5)$ $78.555(5)$ $2144.6(14)$	$[((\mathbf{h})Cu)_2(S_2)] \\ (\mathbf{2h}) \\ C_{60}H_{62}Cu_2N_4S_2 \\ 1030.34 \\ pbca \\ 16.0272(18) \\ 15.9956(18) \\ 20.072(2) \\ 90 \\ 90 \\ 90 \\ 90 \\ 5145.6(10) \\ [10pt]$	$[((\mathbf{j})C\mathbf{u})_2(S_2)]$ (2 j) $C_{64}H_{82}C\mathbf{u}_2N_4S_2$ 1098.54 C2/c 19.927(3) 19.811(3) 17.578(3) 90 104.346(3) 90 6722.9(18)	$\begin{array}{c} \mathbf{5a} \\ \hline \mathbf{C}_{84}\mathbf{H}_{100}\mathbf{Cu}_4\mathbf{N}_8\mathbf{S}_4 \\ 1604.12 \\ \mathbf{I4} \\ 25.048(4) \\ 25.048(4) \\ 8.611(3) \\ 90 \\ 90 \\ 90 \\ 90 \\ 5403(2) \end{array}$
formula Fw space group $a(\hat{A})$ $b(\hat{A})$ $c(\hat{A})$ $c(\hat{A})$ $\alpha(\text{deg})$ $\beta(\text{deg})$ $\gamma(\text{deg})$ $V(\hat{A}^3)$ Z	$ \begin{bmatrix} ((\mathbf{f})Cu)_2(S_2) \end{bmatrix} (\mathbf{2f}) \\ \hline C_{54}H_{46}Cu_2F_{12}N_4S_2 \\ 1170.15 \\ P-1 \\ 8.3136(9) \\ 12.5947(13) \\ 14.2544(15) \\ 103.694(2) \\ 105.738(2) \\ 105.080(2) \\ 1309.1(2) \\ 1 \end{bmatrix} $	$ \begin{bmatrix} ((\mathbf{g})Cu)_2(S_2) \end{bmatrix} (\mathbf{2g}) \\ \hline C_{70}H_{78}Cu_2F_{12}N_4S_2 \\ 1394.56 \\ P-1 \\ 12.317(5) \\ 13.019(5) \\ 13.915(5) \\ 81.263(5) \\ 81.293(5) \\ 78.555(5) \\ 2144.6(14) \\ 1 \end{bmatrix} $	$ \begin{bmatrix} ((\mathbf{h})Cu)_2(S_2) \end{bmatrix} \\ (2\mathbf{h}) \\ \hline C_{60}H_{62}Cu_2N_4S_2 \\ 1030.34 \\ pbca \\ 16.0272(18) \\ 15.9956(18) \\ 20.072(2) \\ 90 \\ 90 \\ 90 \\ 90 \\ 5145.6(10) \\ 4 \\ \end{bmatrix} $	$[((\mathbf{j})C\mathbf{u})_2(S_2)]$ (2 \mathbf{j}) C ₆₄ H ₈₂ Cu ₂ N ₄ S ₂ 1098.54 C2/c 19.927(3) 19.811(3) 17.578(3) 90 104.346(3) 90 6722.9(18) 4	$\begin{array}{c} \textbf{5a} \\ \hline C_{84}H_{100}Cu_4N_8S_4 \\ 1604.12 \\ 14 \\ 25.048(4) \\ 25.048(4) \\ 8.611(3) \\ 90 \\ 90 \\ 90 \\ 90 \\ 90 \\ 5403(2) \\ 2 \end{array}$
formula Fw space group $a(\hat{A})$ $b(\hat{A})$ $c(\hat{A})$ $\alpha(\text{deg})$ $\beta(\text{deg})$ $\gamma(\text{deg})$ $V(\hat{A}^3)$ Z T(K)	$ \begin{bmatrix} ((\mathbf{f})C\mathbf{u})_2(S_2) \end{bmatrix} (\mathbf{2f}) \\ \hline C_{54}H_{46}C\mathbf{u}_2F_{12}N_4S_2 \\ 1170.15 \\ \hline P-1 \\ 8.3136(9) \\ 12.5947(13) \\ 14.2544(15) \\ 103.694(2) \\ 105.738(2) \\ 105.080(2) \\ 1309.1(2) \\ 1 \\ 173 \end{bmatrix} $	$[((\mathbf{g})Cu)_2(S_2)] (\mathbf{2g})$ $C_{70}H_{78}Cu_2F_{12}N_4S_2$ 1394.56 P-1 $12.317(5)$ $13.019(5)$ $13.915(5)$ $81.263(5)$ $81.293(5)$ $78.555(5)$ $2144.6(14)$ 1 173	$ \begin{bmatrix} ((\mathbf{h})Cu)_2(S_2) \end{bmatrix} \\ (\mathbf{2h}) \\ C_{60}H_{62}Cu_2N_4S_2 \\ 1030.34 \\ pbca \\ 16.0272(18) \\ 15.9956(18) \\ 20.072(2) \\ 90 \\ 90 \\ 90 \\ 5145.6(10) \\ 4 \\ 173 \\ \end{bmatrix} $	$ \begin{bmatrix} ((\mathbf{j})Cu)_2(S_2) \end{bmatrix} \\ (\mathbf{2j}) \\ C_{64}H_{82}Cu_2N_4S_2 \\ 1098.54 \\ C2/c \\ 19.927(3) \\ 19.811(3) \\ 17.578(3) \\ 90 \\ 104.346(3) \\ 90 \\ 6722.9(18) \\ 4 \\ 173 \\ \end{bmatrix} $	$\begin{array}{c} \textbf{5a} \\ \hline C_{84}H_{100}Cu_4N_8S_4 \\ 1604.12 \\ 14 \\ 25.048(4) \\ 25.048(4) \\ 8.611(3) \\ 90 \\ 90 \\ 90 \\ 90 \\ 5403(2) \\ 2 \\ 173 \\ \end{array}$
formula Fw space group $a(\hat{A})$ $b(\hat{A})$ $c(\hat{A})$ $\alpha(\text{deg})$ $\beta(\text{deg})$ $\gamma(\text{deg})$ $V(\hat{A}^3)$ Z T(K) $\rho_{\text{raided}}(\text{Mg/m}^3)$	$ \begin{bmatrix} ((\mathbf{f})C\mathbf{u})_2(S_2) \end{bmatrix} (\mathbf{2f}) \\ \hline C_{54}H_{46}C\mathbf{u}_2F_{12}N_4S_2 \\ 1170.15 \\ \hline P-1 \\ 8.3136(9) \\ 12.5947(13) \\ 14.2544(15) \\ 103.694(2) \\ 105.738(2) \\ 105.080(2) \\ 1309.1(2) \\ 1 \\ 173 \\ 1.484 \end{bmatrix} $	$ \begin{bmatrix} ((\mathbf{g})Cu)_2(S_2) \end{bmatrix} (\mathbf{2g}) \\ C_{70}H_{78}Cu_2F_{12}N_4S_2 \\ 1394.56 \\ P-1 \\ 12.317(5) \\ 13.019(5) \\ 13.915(5) \\ 81.263(5) \\ 81.293(5) \\ 78.555(5) \\ 2144.6(14) \\ 1 \\ 173 \\ 1.080 \end{bmatrix} $	$ \begin{bmatrix} ((\mathbf{h})Cu)_2(S_2) \end{bmatrix} \\ (\mathbf{2h}) \\ C_{60}H_{62}Cu_2N_4S_2 \\ 1030.34 \\ pbca \\ 16.0272(18) \\ 15.9956(18) \\ 20.072(2) \\ 90 \\ 90 \\ 90 \\ 90 \\ 5145.6(10) \\ 4 \\ 173 \\ 1.330 \\ \end{bmatrix} $	[((j)Cu) ₂ (S ₂)] (2j) C ₆₄ H ₈₂ Cu ₂ N ₄ S ₂ 1098.54 C2/c 19.927(3) 19.811(3) 17.578(3) 90 104.346(3) 90 6722.9(18) 4 173 1.085	$\begin{array}{c} \textbf{5a} \\ \hline C_{84}H_{100}Cu_4N_8S_4 \\ 1604.12 \\ I4 \\ 25.048(4) \\ 25.048(4) \\ 8.611(3) \\ 90 \\ 90 \\ 90 \\ 90 \\ 5403(2) \\ 2 \\ 173 \\ 0.986 \\ \end{array}$
formula Fw space group $a(\hat{A})$ $b(\hat{A})$ $c(\hat{A})$ $\alpha(\text{deg})$ $\beta(\text{deg})$ $\gamma(\text{deg})$ $V(\hat{A}^3)$ Z T(K) $\rho_{\text{calcd}}(\text{Mg/m}^3)$ θ range (deg)	$ \begin{bmatrix} ((\mathbf{f})Cu)_2(S_2) \end{bmatrix} (\mathbf{2f}) \\ C_{54}H_{46}Cu_2F_{12}N_4S_2 \\ 1170.15 \\ P-1 \\ 8.3136(9) \\ 12.5947(13) \\ 14.2544(15) \\ 103.694(2) \\ 105.738(2) \\ 105.080(2) \\ 1309.1(2) \\ 1 \\ 173 \\ 1.484 \\ 1.57 \text{ to } 25.08 \end{bmatrix} $	$[((\mathbf{g})Cu)_2(S_2)] (\mathbf{2g})$ $C_{70}H_{78}Cu_2F_{12}N_4S_2$ 1394.56 P-1 12.317(5) 13.019(5) 13.915(5) 81.263(5) 81.293(5) 78.555(5) 2144.6(14) 1 173 1.080 1.49 to 25.04	$[((\mathbf{h})Cu)_2(S_2)]$ (2h) C ₆₀ H ₆₂ Cu ₂ N ₄ S ₂ 1030.34 pbca 16.0272(18) 15.9956(18) 20.072(2) 90 90 90 5145.6(10) 4 173 1.330 2.03 to 25.06	[((j)Cu) ₂ (S ₂)] (2j) C ₆₄ H ₈₂ Cu ₂ N ₄ S ₂ 1098.54 C2/c 19.927(3) 19.811(3) 17.578(3) 90 104.346(3) 90 6722.9(18) 4 173 1.085 1.47 to 25 14	$\begin{array}{c} \textbf{5a} \\ \hline C_{84}H_{100}Cu_4N_8S_4 \\ 1604.12 \\ I4 \\ 25.048(4) \\ 25.048(4) \\ 8.611(3) \\ 90 \\ 90 \\ 90 \\ 90 \\ 5403(2) \\ 2 \\ 173 \\ 0.986 \\ 1.63 \text{ to } 25.06 \end{array}$
formula Fw space group $a(\hat{A})$ $b(\hat{A})$ $c(\hat{A})$ $\alpha(deg)$ $\beta(deg)$ $\gamma(deg)$ $V(\hat{A}^3)$ Z T(K) $\rho_{calcd}(Mg/m^3)$ θ range (deg) $\mu(mm^{-1})$	$ \begin{bmatrix} ((\mathbf{f})Cu)_2(S_2) \end{bmatrix} (\mathbf{2f}) \\ C_{54}H_{46}Cu_2F_{12}N_4S_2 \\ 1170.15 \\ P-1 \\ 8.3136(9) \\ 12.5947(13) \\ 14.2544(15) \\ 103.694(2) \\ 105.738(2) \\ 105.080(2) \\ 1309.1(2) \\ 1 \\ 173 \\ 1.484 \\ 1.57 \text{ to } 25.08 \\ 0 975 \end{bmatrix} $	$ \begin{bmatrix} ((\mathbf{g})Cu)_2(S_2) \end{bmatrix} (\mathbf{2g}) \\ C_{70}H_{78}Cu_2F_{12}N_4S_2 \\ 1394.56 \\ P-1 \\ 12.317(5) \\ 13.019(5) \\ 13.915(5) \\ 81.263(5) \\ 81.293(5) \\ 78.555(5) \\ 2144.6(14) \\ 1 \\ 173 \\ 1.080 \\ 1.49 \text{ to } 25.04 \\ 0.605 \end{bmatrix} $	$[((\mathbf{h})Cu)_2(S_2)] (2\mathbf{h}) \\ C_{60}H_{62}Cu_2N_4S_2 \\ 1030.34 \\ pbca \\ 16.0272(18) \\ 15.9956(18) \\ 20.072(2) \\ 90 \\ 90 \\ 90 \\ 5145.6(10) \\ 4 \\ 173 \\ 1.330 \\ 2.03 \text{ to } 25.06 \\ 0.951 \\ \end{bmatrix}$	[((j)Cu) ₂ (S ₂)] (2j) C ₆₄ H ₈₂ Cu ₂ N ₄ S ₂ 1098.54 C2/c 19.927(3) 19.811(3) 17.578(3) 90 104.346(3) 90 6722.9(18) 4 173 1.085 1.47 to 25.14 0 731	$\begin{array}{c} \textbf{5a} \\ \hline C_{84}H_{100}Cu_4N_8S_4 \\ 1604.12 \\ I4 \\ 25.048(4) \\ 25.048(4) \\ 8.611(3) \\ 90 \\ 90 \\ 90 \\ 90 \\ 5403(2) \\ 2 \\ 173 \\ 0.986 \\ 1.63 \text{ to } 25.06 \\ 0.890 \\ \end{array}$
formula Fw space group $a(\hat{A})$ $b(\hat{A})$ $c(\hat{A})$ $\alpha(deg)$ $\beta(deg)$ $\gamma(deg)$ $V(\hat{A}^3)$ Z T(K) $\rho_{calcd}(Mg/m^3)$ θ range (deg) $\mu(mm^{-1})$ refleres colled	$ \begin{bmatrix} ((\mathbf{f})Cu)_2(S_2) \end{bmatrix} (\mathbf{2f}) \\ \hline C_{54}H_{46}Cu_2F_{12}N_4S_2 \\ 1170.15 \\ \hline P-1 \\ 8.3136(9) \\ 12.5947(13) \\ 14.2544(15) \\ 103.694(2) \\ 105.738(2) \\ 105.080(2) \\ 1309.1(2) \\ 1 \\ 173 \\ 1.484 \\ 1.57 \text{ to } 25.08 \\ 0.975 \\ 12758 \\ \end{bmatrix} $	$[((\mathbf{g})C\mathbf{u})_2(S_2)] (\mathbf{2g})$ $C_{70}H_{78}C\mathbf{u}_2F_{12}N_4S_2$ 1394.56 P-1 $12.317(5)$ $13.019(5)$ $13.915(5)$ $81.263(5)$ $81.293(5)$ $78.555(5)$ $2144.6(14)$ 1 173 1.080 $1.49 \text{ to } 25.04$ 0.605 21148	$[((\mathbf{h})Cu)_2(S_2)]$ (2h) C ₆₀ H ₆₂ Cu ₂ N ₄ S ₂ 1030.34 pbca 16.0272(18) 15.9956(18) 20.072(2) 90 90 90 5145.6(10) 4 173 1.330 2.03 to 25.06 0.951 45716	$[((\mathbf{j})Cu)_2(S_2)]$ $(2\mathbf{j})$ $C_{64}H_{82}Cu_2N_4S_2$ 1098.54 $C2/c$ $19.927(3)$ $19.811(3)$ $17.578(3)$ 90 $104.346(3)$ 90 $6722.9(18)$ 4 173 1.085 $1.47 \text{ to } 25.14$ 0.731 31647	$\begin{array}{c} \mathbf{5a} \\ \hline \mathbf{C}_{84}\mathbf{H}_{100}\mathbf{Cu}_4\mathbf{N}_8\mathbf{S}_4 \\ 1604.12 \\ \mathbf{I4} \\ 25.048(4) \\ 25.048(4) \\ 8.611(3) \\ 90 \\ 90 \\ 90 \\ 90 \\ 90 \\ 5403(2) \\ 2 \\ 173 \\ 0.986 \\ 1.63 \text{ to } 25.06 \\ 0.890 \\ 25405 \\ \end{array}$
formula Fw space group $a(\hat{A})$ $b(\hat{A})$ $c(\hat{A})$ $\alpha(\text{deg})$ $\beta(\text{deg})$ $\gamma(\text{deg})$ $V(\hat{A}^3)$ Z T(K) $\rho_{\text{calcd}}(\text{Mg/m}^3)$ θ range (deg) $\mu(\text{mm}^{-1})$ reflens colled Unique	$ \begin{bmatrix} ((\mathbf{f})Cu)_2(S_2) \end{bmatrix} (\mathbf{2f}) \\ \hline C_{54}H_{46}Cu_2F_{12}N_4S_2 \\ 1170.15 \\ \hline P-1 \\ 8.3136(9) \\ 12.5947(13) \\ 14.2544(15) \\ 103.694(2) \\ 105.738(2) \\ 105.738(2) \\ 105.080(2) \\ 1309.1(2) \\ 1 \\ 173 \\ 1.484 \\ 1.57 \text{ to } 25.08 \\ 0.975 \\ 12758 \\ 4618 \\ \end{bmatrix} $	$ \begin{bmatrix} ((\mathbf{g})Cu)_2(S_2) \end{bmatrix} (\mathbf{2g}) \\ C_{70}H_{78}Cu_2F_{12}N_4S_2 \\ 1394.56 \\ P-1 \\ 12.317(5) \\ 13.019(5) \\ 13.915(5) \\ 81.263(5) \\ 81.293(5) \\ 78.555(5) \\ 2144.6(14) \\ 1 \\ 173 \\ 1.080 \\ 1.49 \text{ to } 25.04 \\ 0.605 \\ 21148 \\ 7590 \\ \end{bmatrix} $	$[((\mathbf{h})Cu)_2(S_2)]$ (2h) C ₆₀ H ₆₂ Cu ₂ N ₄ S ₂ 1030.34 pbca 16.0272(18) 15.9956(18) 20.072(2) 90 90 90 5145.6(10) 4 173 1.330 2.03 to 25.06 0.951 45716 4548	$[((\mathbf{j})C\mathbf{u})_2(S_2)]$ $(\mathbf{2j})$ $C_{64}H_{82}C\mathbf{u}_2N_4S_2$ 1098.54 $C2/c$ $19.927(3)$ $19.811(3)$ $17.578(3)$ 90 $104.346(3)$ 90 $6722.9(18)$ 4 173 1.085 $1.47 \text{ to } 25.14$ 0.731 31647 6012	$\begin{array}{r} \mathbf{5a} \\ \hline \mathbf{C}_{84}\mathbf{H}_{100}\mathbf{Cu}_4\mathbf{N}_8\mathbf{S}_4 \\ 1604.12 \\ 14 \\ 25.048(4) \\ 25.048(4) \\ 8.611(3) \\ 90 \\ 90 \\ 90 \\ 90 \\ 90 \\ 5403(2) \\ 2 \\ 173 \\ 0.986 \\ 1.63 \text{ to } 25.06 \\ 0.890 \\ 25405 \\ 4813 \\ \end{array}$
formula Fw space group $a(\hat{A})$ $b(\hat{A})$ $c(\hat{A})$ $\alpha(deg)$ $\beta(deg)$ $\gamma(deg)$ $V(\hat{A}^3)$ Z T(K) $\rho_{calcd}(Mg/m^3)$ θ range (deg) $\mu(mm^{-1})$ reflens colled Unique reflens	$ \begin{bmatrix} ((\mathbf{f})Cu)_2(S_2) \end{bmatrix} (\mathbf{2f}) \\ \hline C_{54}H_{46}Cu_2F_{12}N_4S_2 \\ 1170.15 \\ \hline P-1 \\ 8.3136(9) \\ 12.5947(13) \\ 14.2544(15) \\ 103.694(2) \\ 105.738(2) \\ 105.080(2) \\ 1309.1(2) \\ 1 \\ 173 \\ 1.484 \\ 1.57 \text{ to } 25.08 \\ 0.975 \\ 12758 \\ 4618 \\ \end{bmatrix} $	$ \begin{bmatrix} ((\mathbf{g})Cu)_2(S_2) \end{bmatrix} (\mathbf{2g}) \\ C_{70}H_{78}Cu_2F_{12}N_4S_2 \\ 1394.56 \\ P-1 \\ 12.317(5) \\ 13.019(5) \\ 13.915(5) \\ 81.263(5) \\ 81.293(5) \\ 78.555(5) \\ 2144.6(14) \\ 1 \\ 173 \\ 1.080 \\ 1.49 \text{ to } 25.04 \\ 0.605 \\ 21148 \\ 7590 \\ \end{bmatrix} $	$ \begin{bmatrix} ((\mathbf{h})Cu)_2(S_2) \end{bmatrix} \\ (2\mathbf{h}) \\ C_{60}H_{62}Cu_2N_4S_2 \\ 1030.34 \\ pbca \\ 16.0272(18) \\ 15.9956(18) \\ 20.072(2) \\ 90 \\ 90 \\ 90 \\ 90 \\ 5145.6(10) \\ 4 \\ 173 \\ 1.330 \\ 2.03 \text{ to } 25.06 \\ 0.951 \\ 45716 \\ 4548 \\ \end{bmatrix} $	$ \begin{bmatrix} ((\mathbf{j})C\mathbf{u})_2(S_2) \end{bmatrix} \\ (\mathbf{2j}) \\ C_{64}H_{82}C\mathbf{u}_2N_4S_2 \\ 1098.54 \\ C2/c \\ 19.927(3) \\ 19.811(3) \\ 17.578(3) \\ 90 \\ 104.346(3) \\ 90 \\ 6722.9(18) \\ 4 \\ 173 \\ 1.085 \\ 1.47 \text{ to } 25.14 \\ 0.731 \\ 31647 \\ 6012 \\ \end{bmatrix} $	$\begin{array}{r} {\color{black} 5a} \\ \hline C_{84}H_{100}Cu_4N_8S_4 \\ 1604.12 \\ 14 \\ 25.048(4) \\ 25.048(4) \\ 8.611(3) \\ 90 \\ 90 \\ 90 \\ 90 \\ 90 \\ 5403(2) \\ 2 \\ 173 \\ 0.986 \\ 1.63 \text{ to } 25.06 \\ 0.890 \\ 25405 \\ 4813 \\ \end{array}$
formula Fw space group $a(\hat{A})$ $b(\hat{A})$ $c(\hat{A})$ $\alpha(\text{deg})$ $\beta(\text{deg})$ $\gamma(\text{deg})$ $V(\hat{A}^3)$ Z T(K) $\rho_{\text{calcd}}(\text{Mg/m}^3)$ θ range (deg) $\mu(\text{mm}^{-1})$ reflens colled Unique reflens Params	$[((\mathbf{f})Cu)_2(S_2)] (\mathbf{2f})$ $C_{54}H_{46}Cu_2F_{12}N_4S_2$ 1170.15 P-1 8.3136(9) 12.5947(13) 14.2544(15) 103.694(2) 105.738(2) 105.080(2) 1309.1(2) 1 173 1.484 1.57 to 25.08 0.975 12758 4618 348	$[((\mathbf{g})Cu)_2(S_2)] (\mathbf{2g})$ $C_{70}H_{78}Cu_2F_{12}N_4S_2$ 1394.56 P-1 $12.317(5)$ $13.019(5)$ $13.915(5)$ $81.263(5)$ $81.293(5)$ $78.555(5)$ $2144.6(14)$ 1 173 1.080 $1.49 \text{ to } 25.04$ 0.605 21148 7590 416	$[((\mathbf{h})Cu)_2(S_2)]$ (2h) C ₆₀ H ₆₂ Cu ₂ N ₄ S ₂ 1030.34 pbca 16.0272(18) 15.9956(18) 20.072(2) 90 90 90 90 5145.6(10) 4 173 1.330 2.03 to 25.06 0.951 45716 4548 312	$[((\mathbf{j})C\mathbf{u})_2(S_2)]$ $(\mathbf{2j})$ $C_{64}H_{82}C\mathbf{u}_2N_4S_2$ 1098.54 $C2/c$ $19.927(3)$ $19.811(3)$ $17.578(3)$ 90 $104.346(3)$ 90 $6722.9(18)$ 4 173 1.085 $1.47 \text{ to } 25.14$ 0.731 31647 6012 335	$\begin{array}{c} \mathbf{5a} \\ \hline \mathbf{C}_{84}\mathbf{H}_{100}\mathbf{Cu}_4\mathbf{N}_8\mathbf{S}_4 \\ 1604.12 \\ 14 \\ 25.048(4) \\ 25.048(4) \\ 8.611(3) \\ 90 \\ 90 \\ 90 \\ 90 \\ 90 \\ 90 \\ 5403(2) \\ 2 \\ 173 \\ 0.986 \\ 1.63 \text{ to } 25.06 \\ 0.890 \\ 25405 \\ 4813 \\ 232 \end{array}$
formula Fw space group $a(\hat{A})$ $b(\hat{A})$ $c(\hat{A})$ $\alpha(\text{deg})$ $\beta(\text{deg})$ $\gamma(\text{deg})$ $V(\hat{A}^3)$ Z T(K) $\rho_{\text{calcd}}(\text{Mg/m}^3)$ θ range (deg) $\mu(\text{mm}^{-1})$ reflens colled Unique reflens Params Params Pal wP2 (for	$ \begin{bmatrix} ((\mathbf{f})Cu)_2(S_2) \end{bmatrix} (\mathbf{2f}) \\ \hline C_{54}H_{46}Cu_2F_{12}N_4S_2 \\ 1170.15 \\ \hline P-1 \\ 8.3136(9) \\ 12.5947(13) \\ 14.2544(15) \\ 103.694(2) \\ 105.738(2) \\ 105.080(2) \\ 1309.1(2) \\ 1 \\ 173 \\ 1.484 \\ 1.57 \text{ to } 25.08 \\ 0.975 \\ 12758 \\ 4618 \\ 348 \\ 0.0419 \\ \end{bmatrix} $	$[((\mathbf{g})Cu)_2(S_2)] (\mathbf{2g})$ $C_{70}H_{78}Cu_2F_{12}N_4S_2$ 1394.56 P-1 $12.317(5)$ $13.019(5)$ $13.915(5)$ $81.263(5)$ $81.293(5)$ $78.555(5)$ $2144.6(14)$ 1 173 1.080 $1.49 \text{ to } 25.04$ 0.605 21148 7590 416 0.0380	$[((\mathbf{h})Cu)_2(S_2)]$ (2h) C ₆₀ H ₆₂ Cu ₂ N ₄ S ₂ 1030.34 pbca 16.0272(18) 15.9956(18) 20.072(2) 90 90 90 5145.6(10) 4 173 1.330 2.03 to 25.06 0.951 45716 4548 312 0.0410	$[((\mathbf{j})C\mathbf{u})_2(S_2)]$ $(\mathbf{2j})$ $C_{64}H_{82}C\mathbf{u}_2N_4S_2$ 1098.54 $C2/c$ $19.927(3)$ $19.811(3)$ $17.578(3)$ 90 $104.346(3)$ 90 $6722.9(18)$ 4 173 1.085 $1.47 \text{ to } 25.14$ 0.731 31647 6012 335 0.0446	$\begin{array}{c} \mathbf{5a} \\ \hline \mathbf{C}_{84}\mathbf{H}_{100}\mathbf{Cu}_4\mathbf{N}_8\mathbf{S}_4 \\ 1604.12 \\ 14 \\ 25.048(4) \\ 25.048(4) \\ 8.611(3) \\ 90 \\ 90 \\ 90 \\ 90 \\ 90 \\ 90 \\ 90 \\ 5403(2) \\ 2 \\ 173 \\ 0.986 \\ 1.63 \text{ to } 25.06 \\ 0.890 \\ 25405 \\ 4813 \\ 232 \\ 0.0570 \\ 0.1272 \\ \end{array}$
formula Fw space group $a(\hat{A})$ $b(\hat{A})$ $c(\hat{A})$ $\alpha(deg)$ $\beta(deg)$ $\gamma(deg)$ $V(\hat{A}^3)$ Z T(K) $\rho_{calcd}(Mg/m^3)$ θ range (deg) $\mu(mm^{-1})$ reflens colled Unique reflens Params R1, wR2 (for	$ \begin{bmatrix} ((\mathbf{f})Cu)_2(S_2) \end{bmatrix} (\mathbf{2f}) \\ \hline C_{54}H_{46}Cu_2F_{12}N_4S_2 \\ 1170.15 \\ \hline P-1 \\ 8.3136(9) \\ 12.5947(13) \\ 14.2544(15) \\ 103.694(2) \\ 105.738(2) \\ 105.080(2) \\ 1309.1(2) \\ 1 \\ 173 \\ 1.484 \\ 1.57 \text{ to } 25.08 \\ 0.975 \\ 12758 \\ 4618 \\ 348 \\ 0.0419, \\ 0.0915 \\ \end{bmatrix} $	$ \begin{bmatrix} ((\mathbf{g})Cu)_2(S_2) \end{bmatrix} (\mathbf{2g}) \\ \hline C_{70}H_{78}Cu_2F_{12}N_4S_2 \\ 1394.56 \\ P-1 \\ 12.317(5) \\ 13.019(5) \\ 13.915(5) \\ 81.263(5) \\ 81.293(5) \\ 78.555(5) \\ 2144.6(14) \\ 1 \\ 173 \\ 1.080 \\ 1.49 \text{ to } 25.04 \\ 0.605 \\ 21148 \\ 7590 \\ \hline 416 \\ 0.0380, \\ 0.1007 \\ \end{bmatrix} $	$[((\mathbf{h})Cu)_2(S_2)]$ (2h) C ₆₀ H ₆₂ Cu ₂ N ₄ S ₂ 1030.34 pbca 16.0272(18) 15.9956(18) 20.072(2) 90 90 90 5145.6(10) 4 173 1.330 2.03 to 25.06 0.951 45716 4548 312 0.0410, 0.0945	$[((\mathbf{j})C\mathbf{u})_2(S_2)]$ $(\mathbf{2j})$ $C_{64}H_{82}C\mathbf{u}_2N_4S_2$ 1098.54 $C2/c$ $19.927(3)$ $19.811(3)$ $17.578(3)$ 90 $104.346(3)$ 90 $6722.9(18)$ 4 173 1.085 $1.47 \text{ to } 25.14$ 0.731 31647 6012 335 $0.0446,$ 0.1104	$\begin{array}{r} {\color{black} 5a} \\ \hline C_{84}H_{100}Cu_4N_8S_4 \\ 1604.12 \\ 14 \\ 25.048(4) \\ 25.048(4) \\ 8.611(3) \\ 90 \\ 90 \\ 90 \\ 90 \\ 90 \\ 90 \\ 5403(2) \\ 2 \\ 173 \\ 0.986 \\ 1.63 \text{ to } 25.06 \\ 0.890 \\ 25405 \\ 4813 \\ 232 \\ 0.0570, 0.1272 \end{array}$
formula Fw space group $a(\hat{A})$ $b(\hat{A})$ $c(\hat{A})$ $\alpha(\text{deg})$ $\beta(\text{deg})$ $\gamma(\text{deg})$ $V(\hat{A}^3)$ Z T(K) $\rho_{\text{calcd}}(\text{Mg/m}^3)$ θ range (deg) $\mu(\text{mm}^{-1})$ reflens colled Unique reflens Params R1, wR2 (for $I > 2\sigma(I)$) COE	$ \begin{bmatrix} ((\mathbf{f})Cu)_2(S_2) \end{bmatrix} (\mathbf{2f}) \\ \hline C_{54}H_{46}Cu_2F_{12}N_4S_2 \\ 1170.15 \\ P-1 \\ 8.3136(9) \\ 12.5947(13) \\ 14.2544(15) \\ 103.694(2) \\ 105.738(2) \\ 105.080(2) \\ 1309.1(2) \\ 1 \\ 173 \\ 1.484 \\ 1.57 \text{ to } 25.08 \\ 0.975 \\ 12758 \\ 4618 \\ 348 \\ 0.0419 \\ 0.0915 \\ 1.057 \\ \end{bmatrix} $	$ \begin{bmatrix} ((\mathbf{g})Cu)_2(S_2) \end{bmatrix} (\mathbf{2g}) \\ \hline C_{70}H_{78}Cu_2F_{12}N_4S_2 \\ 1394.56 \\ P-1 \\ 12.317(5) \\ 13.019(5) \\ 13.915(5) \\ 81.263(5) \\ 81.293(5) \\ 78.555(5) \\ 2144.6(14) \\ 1 \\ 173 \\ 1.080 \\ 1.49 \text{ to } 25.04 \\ 0.605 \\ 21148 \\ 7590 \\ \hline 416 \\ 0.0380, \\ 0.1007 \\ 1.050 \\ \end{bmatrix} $	$[((\mathbf{h})Cu)_2(S_2)]$ (2h) C ₆₀ H ₆₂ Cu ₂ N ₄ S ₂ 1030.34 pbca 16.0272(18) 15.9956(18) 20.072(2) 90 90 90 5145.6(10) 4 173 1.330 2.03 to 25.06 0.951 45716 4548 312 0.0410, 0.0945 1.080	$ \begin{bmatrix} ((\mathbf{j})C\mathbf{u})_2(S_2) \end{bmatrix} \\ (\mathbf{2j}) \\ C_{64}H_{82}C\mathbf{u}_2N_4S_2 \\ 1098.54 \\ C2/c \\ 19.927(3) \\ 19.811(3) \\ 17.578(3) \\ 90 \\ 104.346(3) \\ 90 \\ 6722.9(18) \\ 4 \\ 173 \\ 1.085 \\ 1.47 \text{ to } 25.14 \\ 0.731 \\ 31647 \\ 6012 \\ 335 \\ 0.0446, \\ 0.1104 \\ 1.011 \\ \end{bmatrix} $	$\begin{array}{r} \textbf{5a} \\ \hline \textbf{C}_{84}\textbf{H}_{100}\textbf{Cu}_4\textbf{N}_8\textbf{S}_4 \\ 1604.12 \\ 14 \\ 25.048(4) \\ 25.048(4) \\ 8.611(3) \\ 90 \\ 90 \\ 90 \\ 90 \\ 90 \\ 90 \\ 5403(2) \\ 2 \\ 173 \\ 0.986 \\ 1.63 \text{ to } 25.06 \\ 0.890 \\ 25405 \\ 4813 \\ 232 \\ 0.0570, 0.1272 \\ 1.074 \end{array}$
formula Fw space group $a(\hat{A})$ $b(\hat{A})$ $c(\hat{A})$ $\alpha(deg)$ $\beta(deg)$ $\gamma(deg)$ $V(\hat{A}^3)$ Z T(K) $\rho_{calcd}(Mg/m^3)$ θ range (deg) $\mu(mm^{-1})$ reflcns colled Unique reflcns Params R1, wR2 (for $I > 2\sigma(I)$) GOF	$ \begin{bmatrix} ((\mathbf{f})Cu)_2(S_2) \end{bmatrix} (\mathbf{2f}) \\ C_{54}H_{46}Cu_2F_{12}N_4S_2 \\ 1170.15 \\ P-1 \\ 8.3136(9) \\ 12.5947(13) \\ 14.2544(15) \\ 103.694(2) \\ 105.738(2) \\ 105.738(2) \\ 105.080(2) \\ 1309.1(2) \\ 1 \\ 173 \\ 1.484 \\ 1.57 \text{ to } 25.08 \\ 0.975 \\ 12758 \\ 4618 \\ 348 \\ 0.0419 \\ 0.0915 \\ 1.057 \\ 0.515 \\ 0.276 \end{bmatrix} $	$[((\mathbf{g})Cu)_2(S_2)] (\mathbf{2g})$ $C_{70}H_{78}Cu_2F_{12}N_4S_2$ 1394.56 P-1 12.317(5) 13.019(5) 13.915(5) 81.263(5) 81.293(5) 78.555(5) 2144.6(14) 1 173 1.080 1.49 to 25.04 0.605 21148 7590 416 0.0380, 0.1007 1.059 0.964 0.425	$[((\mathbf{h})Cu)_2(S_2)]$ (2h) C ₆₀ H ₆₂ Cu ₂ N ₄ S ₂ 1030.34 pbca 16.0272(18) 15.9956(18) 20.072(2) 90 90 90 5145.6(10) 4 173 1.330 2.03 to 25.06 0.951 45716 4548 312 0.0410, 0.0945 1.080 0.861 0.486	$[((\mathbf{j})C\mathbf{u})_2(S_2)]$ $(\mathbf{2j})$ $C_{64}H_{82}C\mathbf{u}_2N_4S_2$ 1098.54 $C2/c$ $19.927(3)$ $19.811(3)$ $17.578(3)$ 90 $104.346(3)$ 90 $6722.9(18)$ 4 173 1.085 $1.47 \text{ to } 25.14$ 0.731 31647 6012 335 $0.0446,$ 0.1104 1.011 $0.662 + 0.282$	$\begin{array}{r} \textbf{5a} \\ \hline \textbf{C}_{84}\textbf{H}_{100}\textbf{Cu}_4\textbf{N}_8\textbf{S}_4 \\ 1604.12 \\ 14 \\ 25.048(4) \\ 25.048(4) \\ 8.611(3) \\ 90 \\ 90 \\ 90 \\ 90 \\ 90 \\ 90 \\ 5403(2) \\ 2 \\ 173 \\ 0.986 \\ 1.63 \text{ to } 25.06 \\ 0.890 \\ 25405 \\ 4813 \\ 232 \\ 0.0570, 0.1272 \\ 1.074 \\ 0.887 \\ 0.594 \end{array}$
formula Fw space group $a(\hat{A})$ $b(\hat{A})$ $c(\hat{A})$ $\alpha(deg)$ $\beta(deg)$ $\gamma(deg)$ $V(\hat{A}^3)$ Z T(K) $\rho_{calcd}(Mg/m^3)$ θ range (deg) $\mu(mm^{-1})$ reflcns collcd Unique reflcns Params R1, wR2 (for $I > 2\sigma(I)$) GOF largest peak, hole (a, \hat{A}^{-3})	$ \begin{bmatrix} ((\mathbf{f})Cu)_2(S_2) \end{bmatrix} (\mathbf{2f}) \\ \hline C_{54}H_{46}Cu_2F_{12}N_4S_2 \\ 1170.15 \\ \hline P-1 \\ 8.3136(9) \\ 12.5947(13) \\ 14.2544(15) \\ 103.694(2) \\ 105.738(2) \\ 105.738(2) \\ 105.080(2) \\ 1309.1(2) \\ 1 \\ 173 \\ 1.484 \\ 1.57 \text{ to } 25.08 \\ 0.975 \\ 12758 \\ 4618 \\ \hline 348 \\ 0.0419 \\ 0.0915 \\ 1.057 \\ 0.515 \\ , -0.376 \\ \end{bmatrix} $	$ \begin{bmatrix} ((\mathbf{g})Cu)_2(S_2) \end{bmatrix} (\mathbf{2g}) \\ C_{70}H_{78}Cu_2F_{12}N_4S_2 \\ 1394.56 \\ P-1 \\ 12.317(5) \\ 13.019(5) \\ 13.915(5) \\ 81.263(5) \\ 81.293(5) \\ 78.555(5) \\ 2144.6(14) \\ 1 \\ 173 \\ 1.080 \\ 1.49 \text{ to } 25.04 \\ 0.605 \\ 21148 \\ 7590 \\ \hline 416 \\ 0.0380, \\ 0.1007 \\ 1.059 \\ 0.964, -0.435 \\ \end{bmatrix} $	$ \begin{bmatrix} ((\mathbf{h})Cu)_2(S_2) \end{bmatrix} \\ (\mathbf{2h}) \\ C_{60}H_{62}Cu_2N_4S_2 \\ 1030.34 \\ pbca \\ 16.0272(18) \\ 15.9956(18) \\ 20.072(2) \\ 90 \\ 90 \\ 90 \\ 90 \\ 5145.6(10) \\ 4 \\ 173 \\ 1.330 \\ 2.03 \text{ to } 25.06 \\ 0.951 \\ 45716 \\ 4548 \\ 312 \\ 0.0410, \\ 0.0945 \\ 1.080 \\ 0.861, -0.486 \\ \end{bmatrix} $	$ \begin{bmatrix} ((\mathbf{j})C\mathbf{u})_2(S_2) \\ (\mathbf{2j}) \end{bmatrix} \\ C_{64}H_{82}C\mathbf{u}_2N_4S_2 \\ 1098.54 \\ C2/c \\ 19.927(3) \\ 19.811(3) \\ 17.578(3) \\ 90 \\ 104.346(3) \\ 90 \\ 6722.9(18) \\ 4 \\ 173 \\ 1.085 \\ 1.47 \\ to 25.14 \\ 0.731 \\ 31647 \\ 6012 \\ 335 \\ 0.0446, \\ 0.1104 \\ 1.011 \\ 0.662, -0.282 \\ \end{bmatrix} $	$\begin{array}{c} \mathbf{5a} \\ \hline \\ C_{84}H_{100}Cu_4N_8S_4 \\ 1604.12 \\ 14 \\ 25.048(4) \\ 25.048(4) \\ 8.611(3) \\ 90 \\ 90 \\ 90 \\ 90 \\ 90 \\ 5403(2) \\ 2 \\ 173 \\ 0.986 \\ 1.63 \text{ to } 25.06 \\ 0.890 \\ 25405 \\ 4813 \\ 232 \\ 0.0570, 0.1272 \\ 1.074 \\ 0.887, -0.594 \\ \end{array}$

 Table S1. Summary of X-ray Crystallographic Data.



Figure S1. X-ray crystal structure of [H(Me₂L^{Me2})Cu]₂(S₂) (**2a**), with all nonhydrogen atoms shown as 50 % thermal ellipsoids. Selected bond distances (Å) and angles (deg): Cu1-N1, 1.8964(17); Cu1-N2, 1.8994(17); Cu1-S1, 2.1842(6); Cu1-S1A, 2.1868(6); Cu1-••Cu1A, 3.7687(5); S1-S1A, 2.2140(10); N1-Cu-N2, 99.43(7); N1-Cu-S1, 160.55(5); N2-Cu-S1, 99.98(5); N1-Cu1-S1A, 99.72(5); N2-Cu-S1A, 160.85(5); S1-Cu-S1A, 60.87(2); Cu1-S1-Cu1A, 119.13(2); Cu1A-S1-S1A, 59.51(2).



Figure S2. X-ray crystal structure of [H(tBu₂L^{iPr2})Cu]₂(S₂) (**2c**), with all nonhydrogen atoms shown as 50 % thermal ellipsoids. Selected bond distances (Å) and angles (deg): Cu1-N1, 1.942(2); Cu1-N2, 1.936(2); Cu1-S1, 2.2572(6); Cu1-S2, 2.2674(6); Cu1-••Cu1A, 3.9950(7); S1-S2, 2.1242(13); N1-Cu-N2, 99.50(10); N1-Cu-S1, 102.47(7); N2-Cu-S1, 103.63(7); N1-Cu1-S2, 155.81(7); N2-Cu-S2, 103.63(7); S1-Cu-S2, 56.00(3); Cu1-S1-Cu1A, 124.49(5); Cu1-S2-Cu1A, 123.51(5); Cu1-S1-S2, 62.24(2).



Figure S3. X-ray crystal structure of $[Ph(H_2L^{iPr2})Cu]_2(S_2)$ (2e), with all nonhydrogen atoms shown as 50 % thermal ellipsoids. Selected bond distances (Å) and angles (deg): Cu1-N1, 1.9054(16); Cu1-N2, 1.9127(16); Cu1-S1, 2.1984(6); Cu1-S1A, 2.2051(6); Cu1-••Cu1A, 3.8143(5); S1-S1A, 2.2007(10); N1-Cu-N2, 96.95(7); N1-Cu-S1, 160.35(5); N2-Cu-S1, 102.53(5); N1-Cu1-S1A, 100.48(5); N2-Cu-S1A, 162.45(5); S1-Cu-S1A, 59.97(2); Cu1-S1-Cu1A, 120.03(2); Cu1A-S1-S1A, 59.87(2).



Figure S4. X-ray crystal structure of $[3,5-(CF_3)_2C_6H_3(H_2L^{Me2})Cu]_2(S_2)$ (**2f**), with all nonhydrogen atoms shown as 50 % thermal ellipsoids. Selected bond distances (Å) and angles (deg): Cu1-N1, 1.912(2); Cu1-N2, 1.906(2); Cu1-S1, 2.1978(8); Cu1-S1A, 2.1976(8); Cu1-···Cu1A, 3.8045(7); S1-S1A, 2.2013(15); N1-Cu-N2, 98.07(10); N1-Cu-S1, 100.19(7); N2-Cu-S1, 161.67(7); N1-Cu1-S1A, 160.29(7); N2-Cu-S1A, 101.61(7); S1-Cu-S1A, 60.11(4); Cu1-S1-Cu1A, 119.89(4); Cu1-S1-S1A, 59.94(3).



Figure S5. X-ray crystal structure of $[3,5-(CF_3)_2C_6H_3(H_2L^{iPr2})Cu]_2(S_2)$ (**2g**), with all nonhydrogen atoms shown as 50 % thermal ellipsoids. Selected bond distances (Å) and angles (deg): Cu1-N1, 1.9213(18); Cu1-N2, 1.9047(17); Cu1-S1, 2.2060(9); Cu1-S1A, 2.1941(9); Cu1-••Cu1A, 3.8072(10); S1-S1A, 2.2060(12); N1-Cu-N2, 97.07(7); N1-Cu-S1, 163.41(5); N2-Cu-S1, 99.45(5); N1-Cu1-S1A, 103.32(5); N2-Cu-S1A, 159.60(5); S1-Cu-S1A, 60.18(2); Cu1-S1-Cu1A, 119.82(2); Cu1A-S1-S1A, 60.18(3).



Figure S6. X-ray crystal structure of $[(HL'^{Me2})Cu]_2(S_2)$ (**2h**), with all nonhydrogen atoms shown as 50 % thermal ellipsoids. Selected bond distances (Å) and angles (deg): Cu1-N1, 1.925(2); Cu1-N2, 1.893(2); Cu1-S1, 2.1936(8); Cu1-S1A, 2.1916(8); Cu1-••Cu1A, 3.7858(7); S1-S1A, 2.2130(15); N1-Cu-N2, 98.12(10); N1-Cu-S1, 160.10(8); N2-Cu-S1, 101.55(8); N1-Cu1-S1A, 99.60(8); N2-Cu-S1A, 162.05(8); S1-Cu-S1A, 60.62(3); Cu1-S1-Cu1A, 119.38(3); Cu1A-S1-S1A, 59.74(3).



Figure S7. X-ray crystal structure of $[(MeL'^{iPr2})Cu]_2(S_2)$ (**2j**), with all nonhydrogen atoms shown as 50 % thermal ellipsoids. Selected bond distances (Å) and angles (deg): Cu1-N1, 1.889(2); Cu1-N2, 1.929(2); Cu1-S1, 2.2278(6); Cu1-S2, 2.2224(6); Cu1-··Cu1A, 3.8857(8); S1-S2, 2.1691(13); N1-Cu-N2, 96.10(10); N1-Cu-S1, 161.05(7); N2-Cu-S1, 102.73(7); N1-Cu1-S2, 102.83(7); N2-Cu-S2, 161.07(7); S1-Cu-S2, 58.34(3); Cu1-S1-Cu1A, 121.41(5); Cu1-S2-Cu1A, 121.91(5); Cu1-S1-S2, 60.71(2).



Figure S8. Electronic absorption spectra for the indicated disulfido dicopper complexes, shown as extinction vs. (a) wavelength and (b) energy. All data collected in THF at ambient temperature.



Figure S9. Resonance Raman spectra ($\lambda_{ex} = 457.9 \text{ nm}$) of frozen benzene solutions (77K) of $[H(Me_2L^{Me2})Cu]_2(S_2)$ (2a) (solid line for ³²S, dashed line for ³⁴S).



Figure S10. Resonance Raman spectra ($\lambda_{ex} = 457.9 \text{ nm}$) of frozen benzene solutions (77K) of [H(Me₂L^{Et2})Cu]₂(S₂) (**2b**) (solid line for ³²S, dashed line for ³⁴S).



Figure S11. Resonance Raman spectra ($\lambda_{ex} = 457.9 \text{ nm}$) of frozen benzene solutions (77K) of [H(tBu₂L^{iPr2})Cu]₂(S₂) (**2c**) (solid line for ³²S, dashed line for ³⁴S).



Figure S12. Resonance Raman spectra ($\lambda_{ex} = 457.9 \text{ nm}$) of frozen benzene solutions (77K) of [Ph(H₂L^{Et2})Cu]₂(S₂) (**2d**) (solid line for ³²S, dashed line for ³⁴S).



Figure S13. Resonance Raman spectra ($\lambda_{ex} = 457.9 \text{ nm}$) of frozen benzene solutions (77K) of [Ph(H₂L^{iPr2})Cu]₂(S₂) (**2e**) (solid line for ³²S, dashed line for ³⁴S).



Figure S14. Resonance Raman spectra ($\lambda_{ex} = 457.9 \text{ nm}$) of frozen benzene solutions (77K) of [3,5-(CF₃)₂C₆H₃(H₂L^{Me2})Cu]₂(S₂) (**2f**) (solid line for ³²S, dashed line for ³⁴S).



Figure S15. Resonance Raman spectra ($\lambda_{ex} = 457.9 \text{ nm}$) of frozen benzene solutions (77K) of [3,5-(CF₃)₂C₆H₃(H₂L^{iPr2})Cu]₂(S₂) (**2g**) (solid line for ³²S, dashed line for ³⁴S).



Figure S16. Resonance Raman spectra ($\lambda_{ex} = 457.9 \text{ nm}$) of frozen benzene solutions (77K) of $[(\text{HL}'^{\text{Me2}})\text{Cu}]_2(\text{S}_2)$ (**2h**) (solid line for ³²S, dashed line for ³⁴S).



Figure S17. Resonance Raman spectra ($\lambda_{ex} = 457.9 \text{ nm}$) of frozen benzene solutions (77K) of [(HL'^{iPr2})Cu]₂(S₂) (**2i**) (solid line for ³²S, dashed line for ³⁴S).



Figure S18. Resonance Raman spectra ($\lambda_{ex} = 457.9 \text{ nm}$) of frozen benzene solutions (77K) of [(MeL'^{iPr2})Cu]₂(S₂) (**2j**) (solid line for ³²S, dashed line for ³⁴S).

compound	S-S distance (Å)	³² S
$[H(Me_2L^{Me2})Cu]_2(S_2)$	2.214	442 ^a
$[H(Me_2L^{Et2})Cu]_2(S_2)$	2.2007	443 ^a
$[H(tBu_2L^{iPr2})Cu]_2(S_2)$	2.1265	454 ^a
$[Ph(H_2L^{Et2})Cu]_2(S_2)$	2.2138	424 ^a
$[Ph(H_2L^{iPr2})Cu]_2(S_2)$	2.2007	435 ^a
$[3,5-(CF_3)_2C_6H_3(H_2L^{Me2})Cu]_2(S_2)$	2.2013	441 ^a
$[3,5-(CF_3)_2C_6H_3(H_2L^{iPr2})Cu]_2(S_2)$	2.2060	428 ^a
$[(HL'^{Me2})Cu]_2(S_2)$	2.2130	432 ^a
$[(HL'^{iPr2})Cu]_2(S_2)$	2.165	440^{a}
$[(MeL'^{iPr2})Cu]_2(S_2)$	2.1691	443 ^a
$[{Cu[HB(3,5-Pr^{i}_{2}pz)_{3}]}_{2}(S_{2})],$	2.073 ^b	500 ^c
$[((TMPA)Cu)_2(S_2)]^{2+},$	2.044	499 ^d
$[Cu_2(tmeda)_2(\mu-1,2-S_2)_2]^{2+}$	1.9500	613 ^e
$\left[\operatorname{Ir}(\operatorname{dppe})_2(S_2)\right]^+$	2.07	528 ^f
$[MoO(S_2)(mtox)_2]^2$	2.01	530 ^f
$MoO(S_2)(dtc)_2$	2.02	558 ^f
$Cp_2Nb(S_2)Me$	2.01	540 ^f
$[Mo_2O_2S_2(S_2)_2]^{2}$	2.08	510 ^f
$[Mo_4(NO)_4(S_2)_5S_3]^{4-1}$	2.04	536 ^f
$[Mo_4(NO)_4(S_2)_5S_3]^{4-1}$	2.05	550 ^f
$[(NH_3)_5Ru(S_2)Ru(NH_3)_5]^{4+}$	2.01	514 ^f
$Cp_2Fe_2(S_2)(Set)_2$	2.02	$507^{\rm f}$
$[Mo_4(NO)_4(S_2)_6O]^{2^-}$	2.08	480^{f}
$Cp_4Fe_4(S_2)_2S_2$	2.04	503 ^f
$[(Cp_4Fe_4(S_2)_2S_2)_2Ag]^+$	2.05	478^{f}
$[Mo_2(S_2)_6]^{2-1}$	2.04	550 ^f
${Mo_2(S_2)_2Cl_4Cl_{4/2}}_n$	1.98	561 ^f
$Nb_2(S_2)_2Cl_4$	2.03	588 ^f
$[Mo_3S(S_2)_6]^{2-1}$	2.02	545 ^f
$Mo_3S(S_2)_3Cl_4$	2.03	562 ^f
$Fe_2(S_2)(CO)_6$	2.01	555 ^f
$Mo_2(S_2)(S_2C_2Ph_2)_4$	2.04	518 ^f
$[Mo_2(S_2)(SO_2)(CN)_8]^{4-}$	2.00	520 ^f
S2	1.892 ^g	718 ^h

Table S2. S-S Bond Lengths (Å) and Vibrational Frequencies (cm⁻¹).

^a This work. ^b Reference 1. ^c Reference 2. ^d Reference 3. ^e Reference 4. ^f Reference 5. ^g Reference 6. ^h Reference 7.

References:

1. Fujisawa, K.; Moro-oka, Y.; Kitajima, N. J. Chem. Soc., Chem. Commun. 1994, 623-624.

2. Chen, P.; Fujisawa, K.; Helton, M. E.; Karlin, K. D.; Solomon, E. I. J. Am. Chem. Soc. 2003, 125, 6394-6408.

3. Helton, M. E.; Chen, P.; Paul, P. P.; Tyeklár, Z.; Sommer, R. D.; Zakharov, L. N.; Rheingold, A. L.; Solomon, E. I.; Karlin, K. D. J. Am. Chem. Soc. 2003, 125, 1160-1161.

4. York, J. T.; Brown, E. C.; Tolman, W. B. Angew. Chem. Int. Ed. 2005, 44, 7745-7748.

5. Selected examples were taken from the following and the original literature cited therein. Müller, A.; Jaegermann, W.; Enemark, J. H. *Coord. Chem. Rev.* **1982**, *46*, 245-280.

6. Meyer, B. Chem. Rev. 1976, 76, 370.

7. Yee, K. K.; Barrow, R. F.; Rogstad, A. J. Chem. Soc. Faraday Trans. 1972, 68, 1808.