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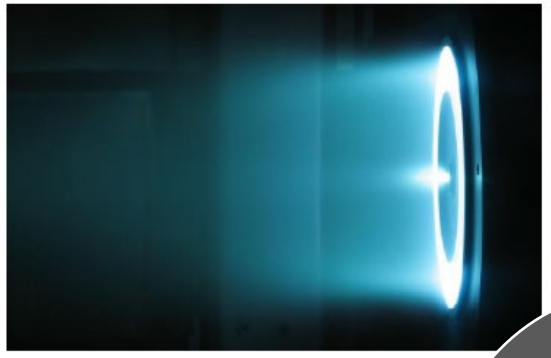
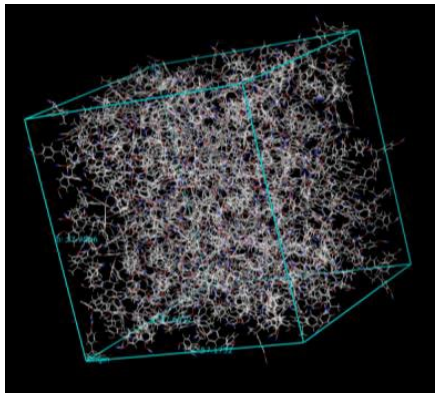
Reactivity between late first-row transition metal halides and the ligand 1,2 bis(pyridin-2-ylmethyl)disulfane: Vibrantly-colored complexes and their crystal structures

Nicolas Cena, Jacobs Inc.

Air Force Research Laboratory

AFRL RQRP 20 September 2021





Catalysts

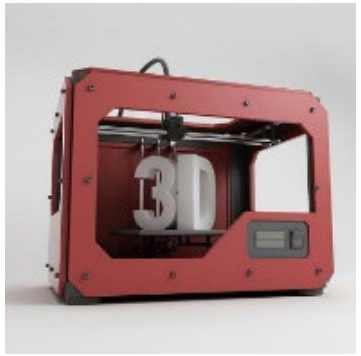
Ionic Liquids for In-Space Propulsion

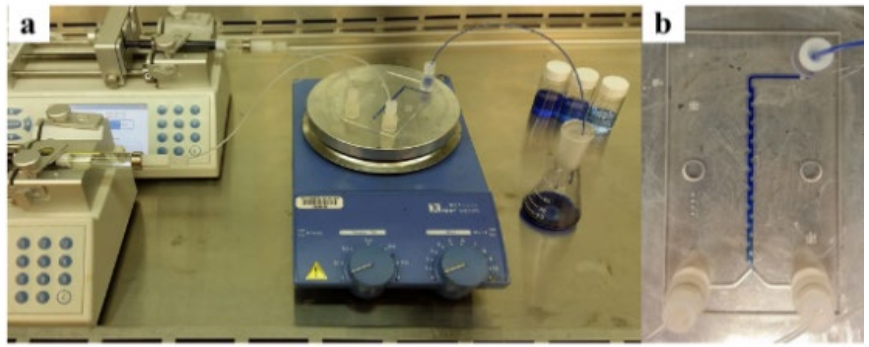
AMG Portfolio

Modeling and Simulation

Solid Rocket Materials Development

Process Development

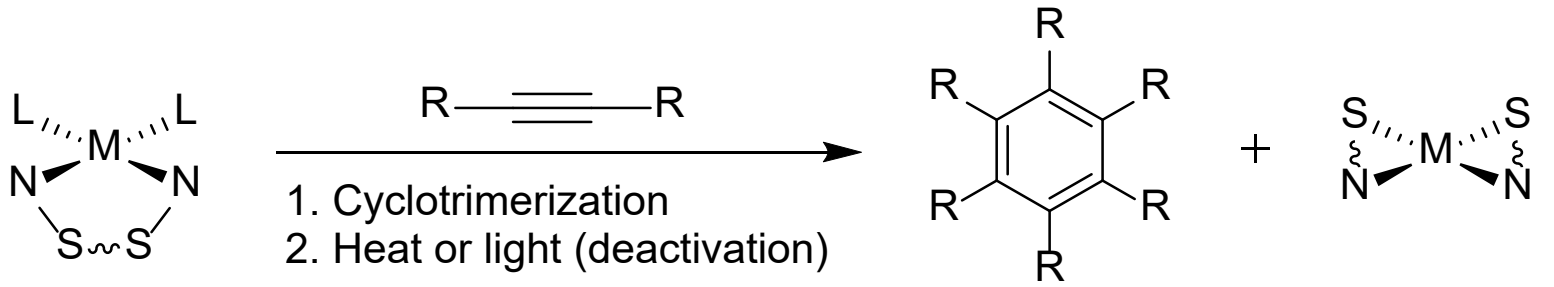




Mission: *to research and develop new materials for aerospace propulsion applications*

Motivation and Approach

- Active catalyst becomes entrained in polymer matrix and can cause degradation and unwanted side reactions over time
- Develop a catalyst for use in high temperature thermosetting resins that can be permanently deactivated after network formation
- Design, synthesize, and characterize new metal compounds with a “triggerable” ligand that is reactive towards an external stimulus (*e.g.* heat or light).
  - Test for deactivation, then catalysis



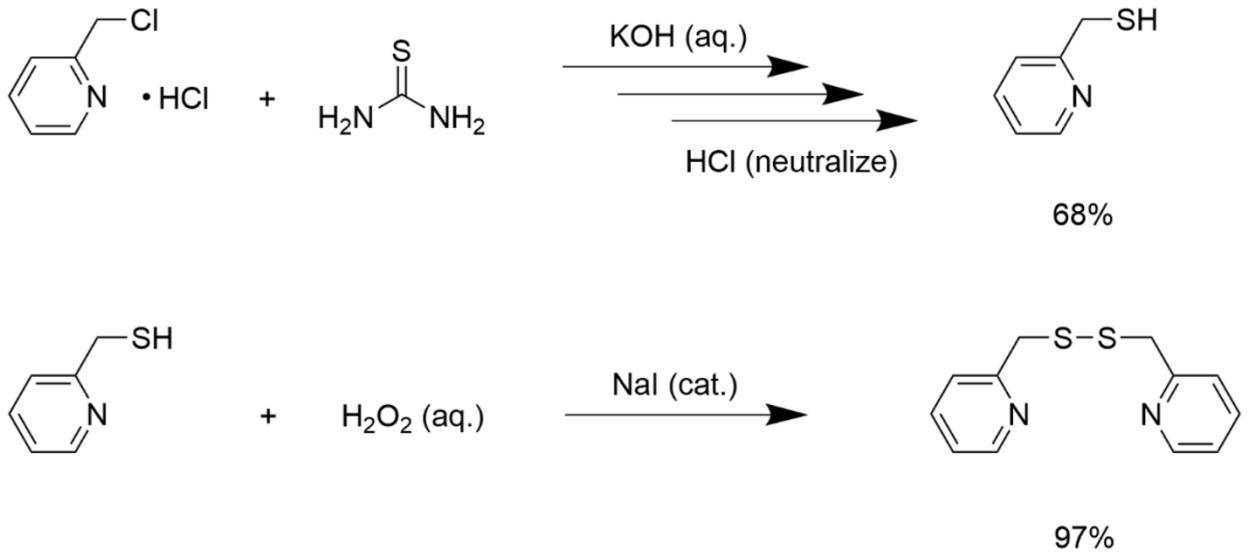
Active Catalyst

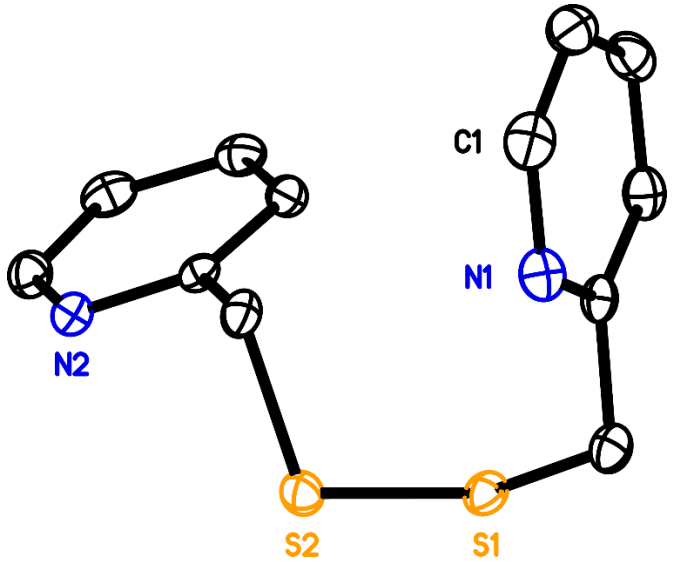
Crosslinked Polymer

Deactivated Catalyst

A Ligand Based on Disulfide

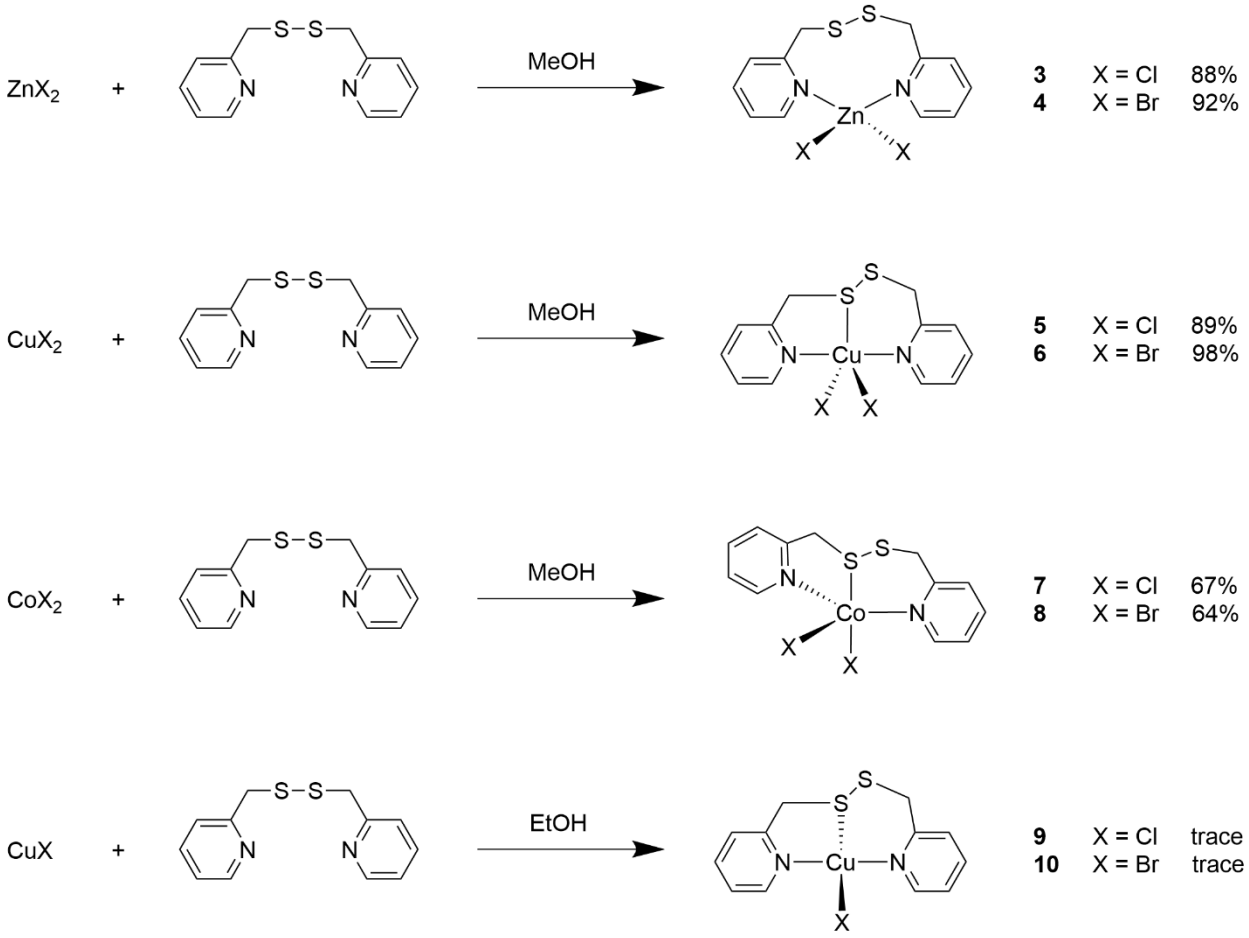
- Disulfide moiety prone to redox chemistry which allows interconversion from thiolate to disulfide
  - Sulfur poisoning of metals is well-known
  - Disulfide to thiolate interconversion has been well examined
    - Prevalent motif in enzymes and proteins

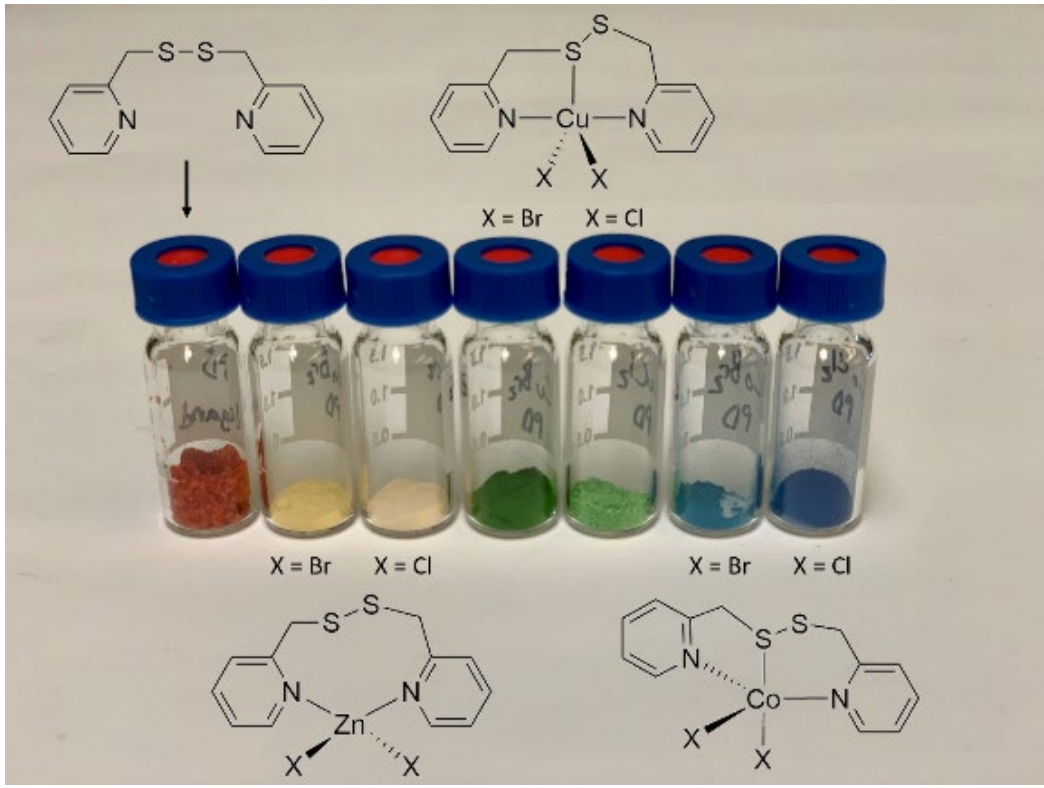




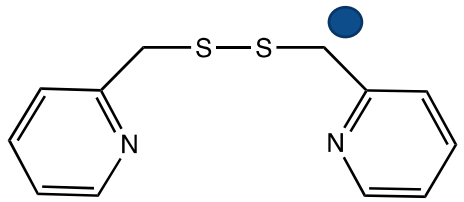
S-S length of 2.0334(6) Å

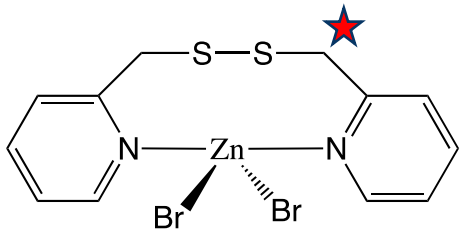
Complexation with Late First-Row Metals

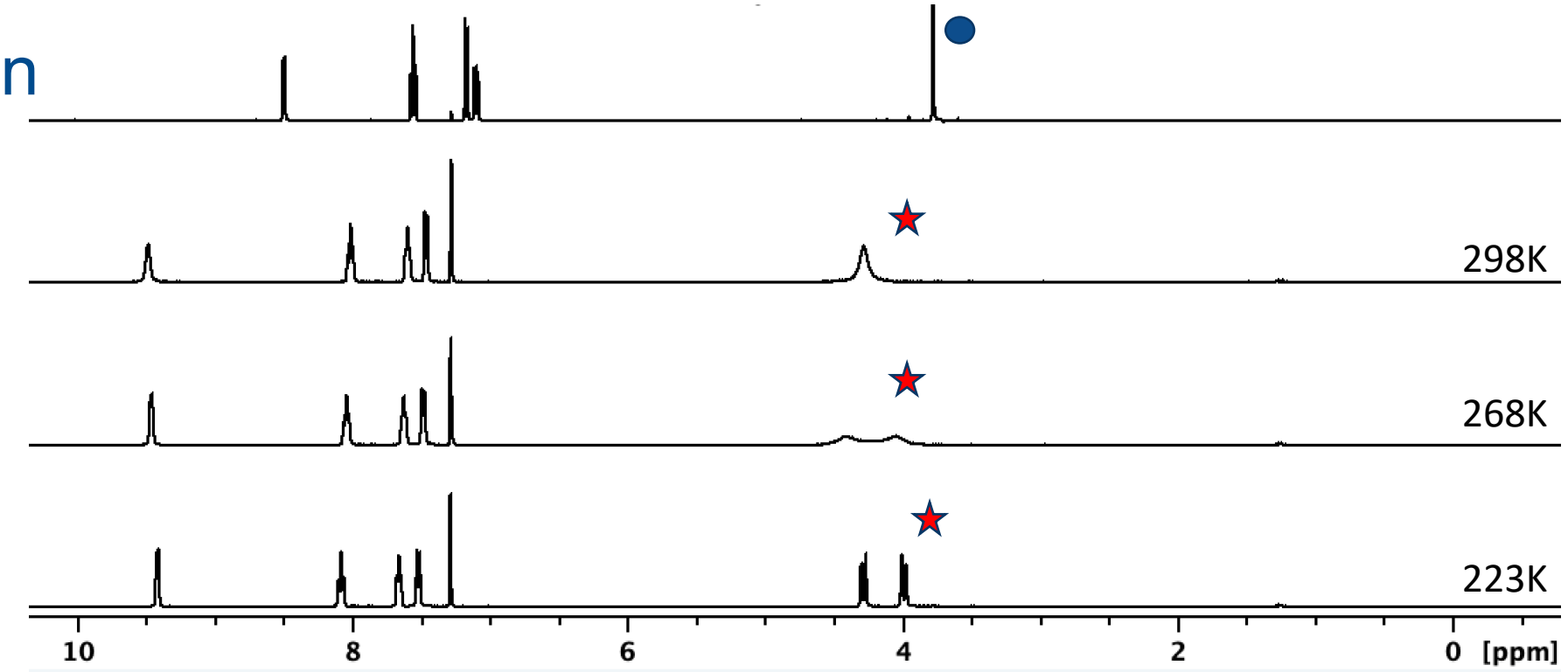




$ZnLX_2$ in Solution





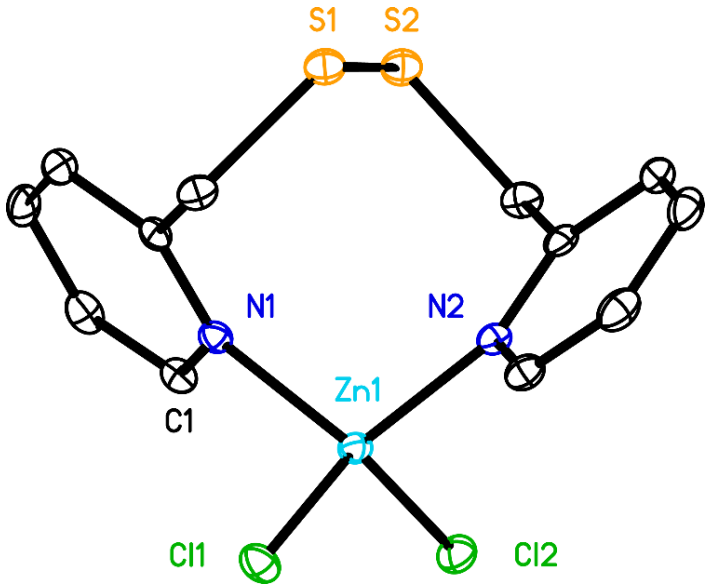


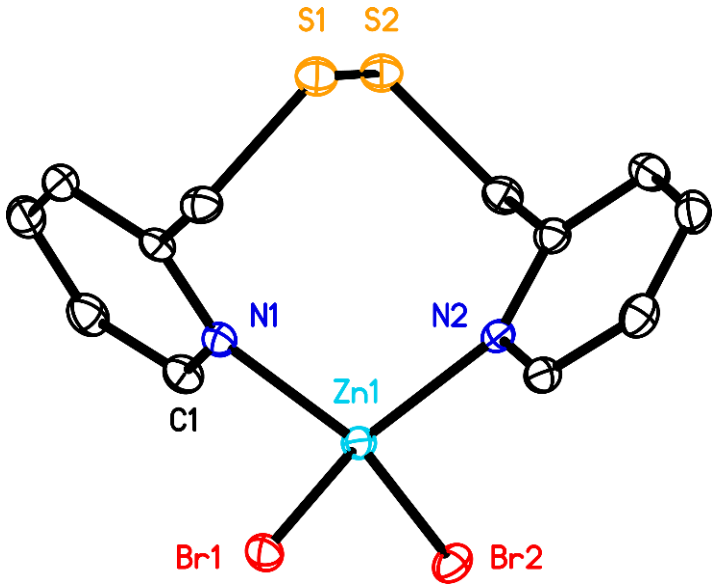
- ^{1}H NMR shows significant change in the chemical shift of methylene protons upon coordination to ZnX_2 (X = Cl, Br)
- VT ^{1}H NMR (for coalescence)
  - No halide dependency: $ZnLCl_2$ and $ZnLBr_2$ compounds nearly identical
  - No solvent dependency: $CDCl_3$ and CD_2Cl_2 show same behavior

X-ray Structures of $ZnLX_2$ in $CHCl_3$

- Structures are isomorphous
- Both systems suggest a tetrahedral coordination sphere around Zn
- S-S length
  - Chloride: 2.0182(9) Å
  - Bromide: 2.0157(7) Å
- Zn-S distances are similar
  - Chloride: 4.069(1) and 4.073(1) Å
  - Bromide: 4.0631(6) and 4.0788(6) Å

	$ZnLCl_2$ $(3•CHCl_3)$	$ZnLBr_2$ $(4•CHCl_3)$
Crystal system	triclinic	triclinic
Space group	P-1	P-1
Temperature (K)	100	100
a (Å)	8.984(3)	9.112(1)
b (Å)	9.058(3)	9.116(1)
c (Å)	12.319(4)	12.594(1)
α (deg)	106.265(5)	106.778(3)
β (deg)	91.782(6)	91.686(3)
γ (deg)	102.871(5)	104.097(3)
V (Å^3)	933.5(6)	965.80(1)
Z	2	2

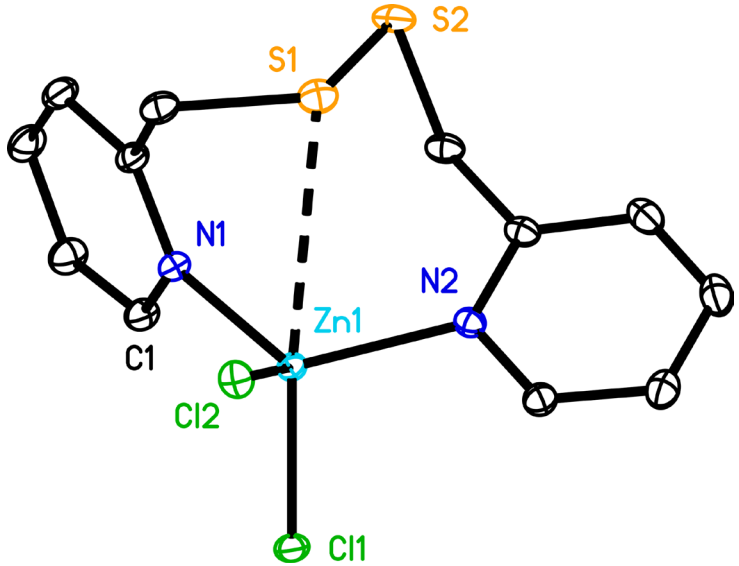


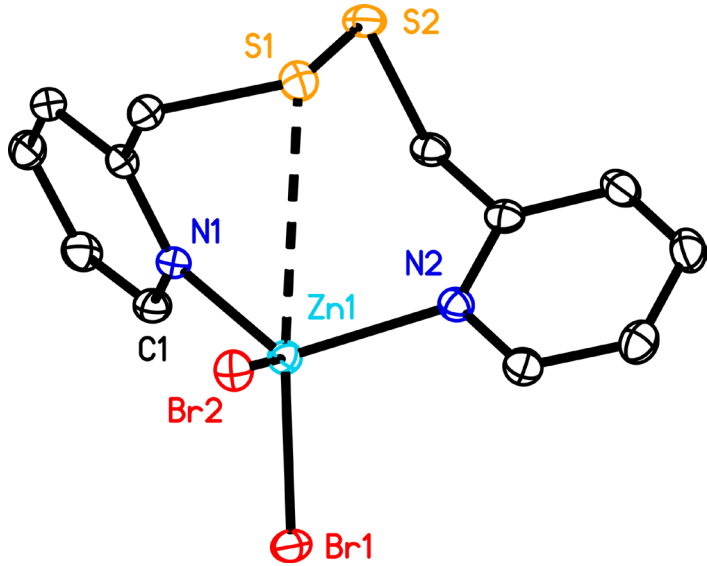


X-ray Structures of $ZnLX_2$ in CH_2Cl_2

- Structures are isomorphous
- Both systems suggest a tetrahedral coordination sphere around Zn
- S-S length
  - Chloride: 2.0348(5) Å
  - Bromide: 2.0299(8) Å
- Zn-S distances differ now
  - Chloride: 3.1978(5) and 4.1156(5) Å
  - Bromide: 3.3075(7) and 4.0910(7) Å

	$ZnLCl_2$ $(3 \bullet CH_2Cl_2)$	$ZnLBr_2$ $(4 \bullet CH_2Cl_2)$
Crystal system	triclinic	triclinic
Space group	P-1	P-1
Temperature (K)	100	100
a (Å)	8.628(1)	8.728(1)
b (Å)	9.118(1)	9.544(1)
c (Å)	13.010(1)	13.164(1)
α (deg)	78.617(4)	73.056(6)
β (deg)	84.688(4)	85.065(5)
γ (deg)	63.299(4)	63.108(5)
V (Å^3)	896.3(2)	934.0(2)
Z	2	2

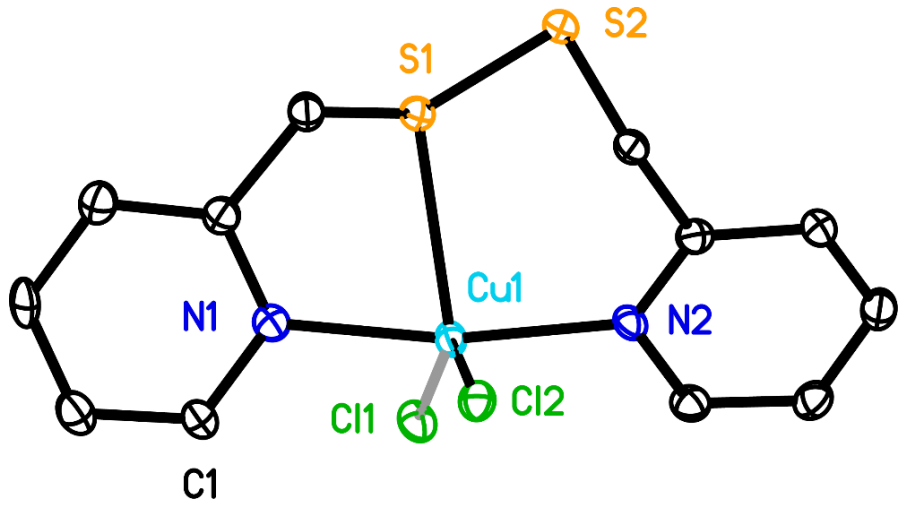




X-ray Structures of $CuLCl_2$

- Solvate free mononuclear 5 coordinate "trigonal bipyramidal" metal ligand complex
- Slightly distorted bond angles
  - N_1-M_1-N_2 ideally 180˚
    - Chloride: 169.63(1)˚
  - S_1-M_1-X_1 ideally 120˚
    - Chloride: 100.23(3)˚
- S-S length 2.045(1) Å
- Cu-S length 2.5900(9) and 3.700(1) Å

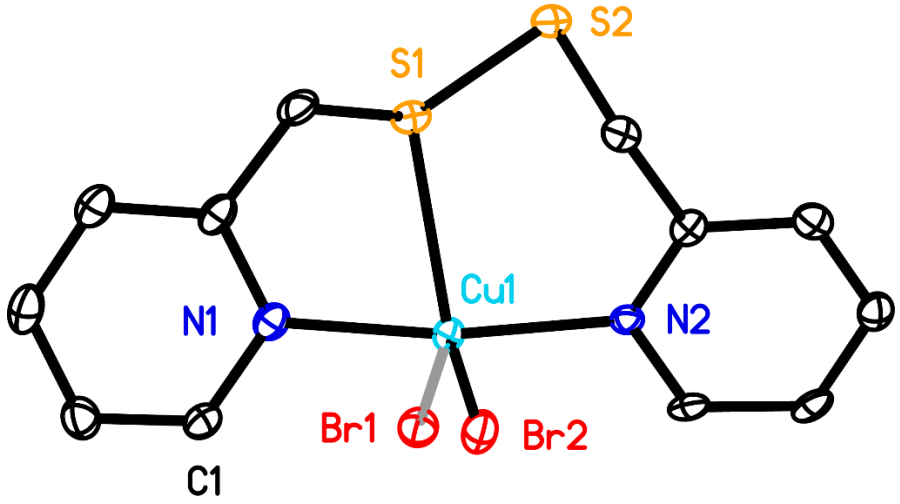
	$CuLCl_2$ (5)
Crystal system	monoclinic
Space group	$P2_1/n$
Temperature (K)	100
a (Å)	11.982(2)
b (Å)	8.300(2)
c (Å)	15.653(3)
α (deg)	90
β (deg)	106.998(3)
γ (deg)	90
V (Å^3)	1488.7(5)
Z	4



X-ray Structures of $CuLBr_2$

- Mononuclear 5 coordinate “trigonal bipyramidal” metal ligand complex
- Slightly distorted bond angles
  - N_1-M_1-N_2 ideally 180˚
    - Bromide: 170.02(1)˚
  - S_1-M_1-X_1 ideally 120˚
    - Bromide: 97.84(2)˚
- S-S lengths: 2.042(1) Å
- Cu-S lengths 2.545(1) and 3.676(1) Å

	$CuLBr_2$ (6)
Crystal system	monoclinic
Space group	$P2_1/n$
Temperature (K)	100
a (Å)	7.993(2)
b (Å)	13.473(4)
c (Å)	14.750(4)
α (deg)	90
β (deg)	102.899(5)
γ (deg)	90
V (Å^3)	1548.4(7)
Z	4

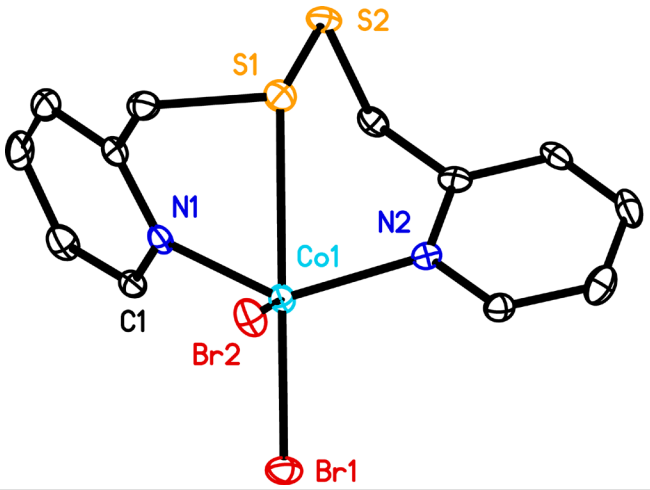


X-ray Structure of $CoLBr_2$

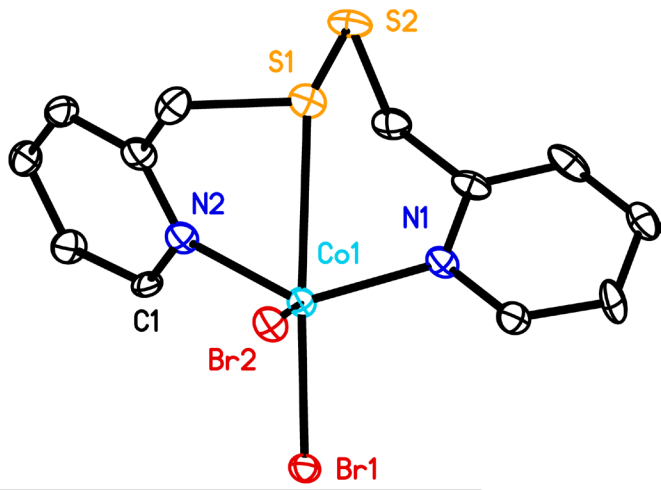
- Both $CHCl_3$ and CH_2Cl_2 solvates adopt a mononuclear trigonal bipyramidal geometry
- Axial positions now occupied by S_1-Co-Br_1
- S-S lengths: 2.03-2.05 Å
- M-S bond length
  - $CHCl_3$: 2.80 Å
  - CH_2Cl_2: 2.86 Å

	$CoLBr_2$ (8•$CHCl_3$)	$CoLBr_2$ (8•CH_2Cl_2)
Crystal system	triclinic	triclinic
Space group	P-1	P-1
Temperature (K)	100	100
a (Å)	9.032(1)	8.837(4)
b (Å)	9.398(1)	9.303(1)
c (Å)	13.033(2)	13.226(2)
α (deg)	81.093(3)	78.008(6)
β (deg)	87.909(3)	85.483(6)
γ (deg)	63.359(2)	62.181(5)
V (Å^3)	976.2(3)	940.5(2)
Z	2	2

$CHCl_3$



CH_2Cl_2



X-ray Structure of $CoLCl_2$

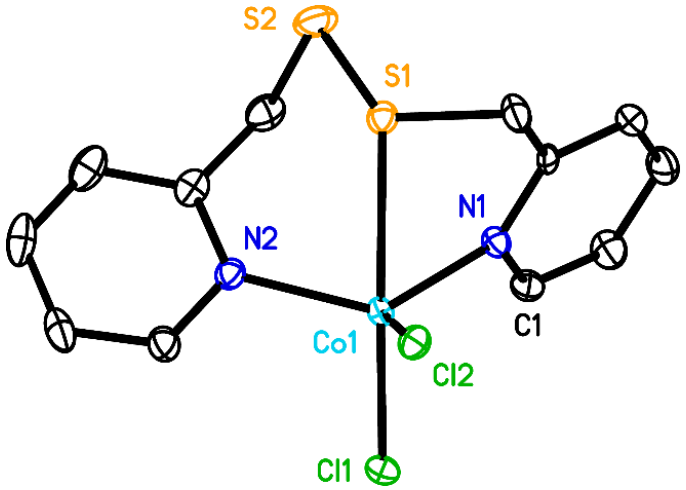
- Solvate free mononuclear trigonal bipyramidal geometry
- Axial positions occupied by S_1-Co-Br_1

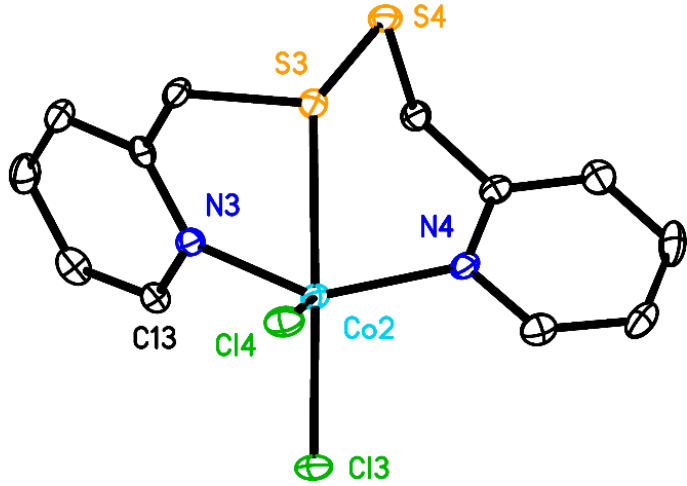
S-S lengths: 2.032(2) and 2.032(2) Å

M-S bond length: 2.755(2) - 3.903(4) Å and 2.599(2) - 3.773(3) Å

- Kryptoracemic
  - Both hands present in unit cell

	$CoLCl_2$ (7)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
Temperature (K)	100
a (Å)	7.643(7)
b (Å)	15.819(1)
c (Å)	24.520(1)
α (deg)	90
β (deg)	90
γ (deg)	90
V (Å^3)	2964.0(9)
Z	8





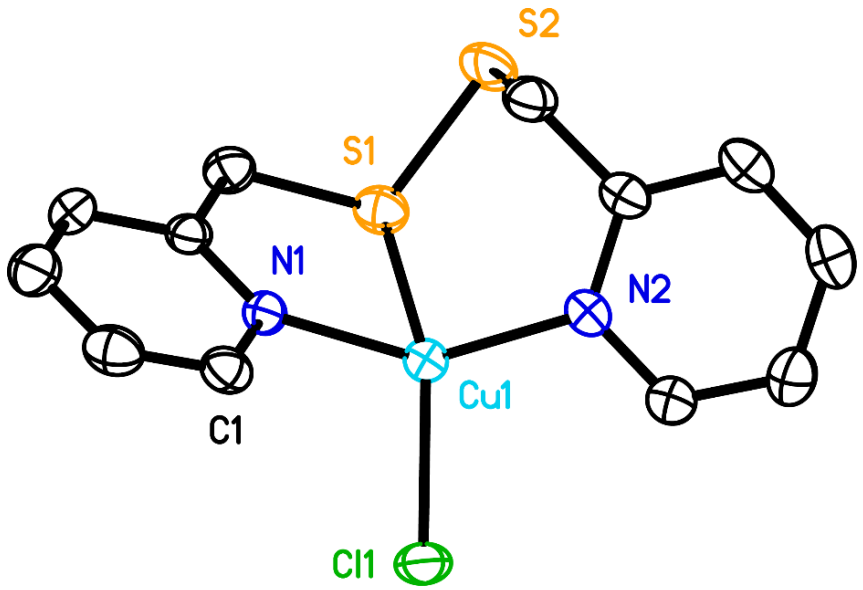
CuLCl Pyridine Disulfide

- Trace amounts of product formed
  - Enough for single crystal analysis
- Highly air sensitive
- Mononuclear tetrahedral geometries

- S-S length: 2.0483(7) Å

M-S bond length: 2.3757(6) and 3.4549(6) Å

	CuLCl (9)
Crystal system	triclinic
Space group	P-1
Temperature (K)	240
a (Å)	8.578(1)
b (Å)	8.868(1)
c (Å)	9.649(1)
α (deg)	84.028(2)
β (deg)	81.764(2)
γ (deg)	70.041(1)
V (Å^3)	681.6(2)
Z	2



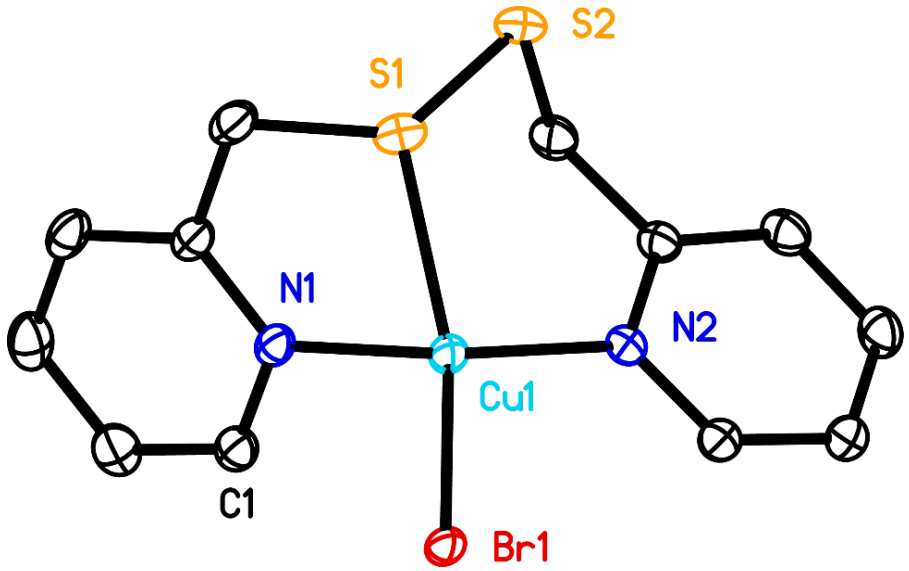
CuLBr Pyridine Disulfide

- Trace amounts of product formed
  - Enough for single crystal analysis
- Highly air sensitive
- Mononuclear tetrahedral geometries

- S-S length: 2.0543(6) Å

M-S bond length: 2.3436(5) and 3.4110(5) Å

	CuLBr (10)
Crystal system	triclinic
Space group	P-1
Temperature (K)	100
a (Å)	8.321(1)
b (Å)	8.926(1)
c (Å)	9.556(1)
α (deg)	85.023(4)
β (deg)	81.280(4)
γ (deg)	89.287(4)
V (Å^3)	698.84(1)
Z	2

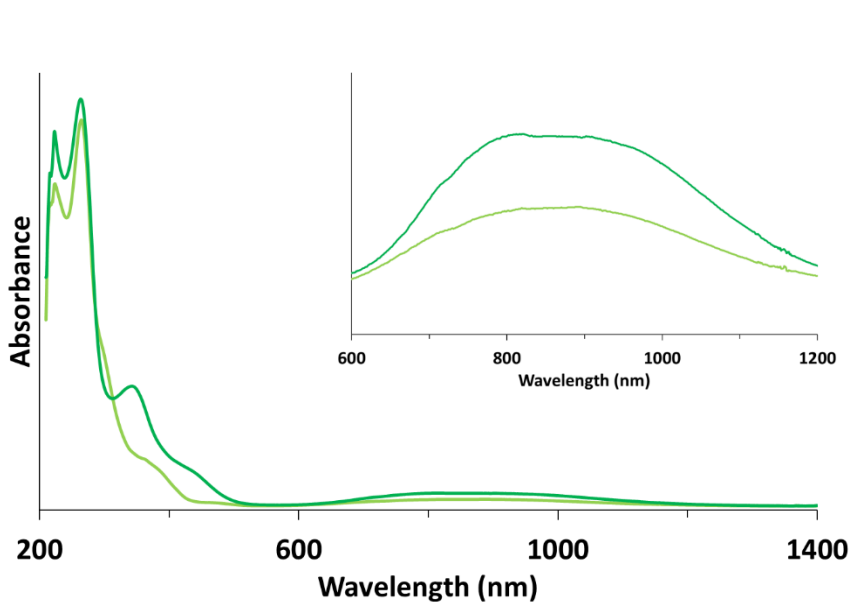


UV-vis-NIR Spectroscopy

- Ligand and Zinc complexes practically silent
- Strongest absorptions 263-272nm attributed to $\pi \rightarrow \pi^*$ from pyridiyl rings
- Cu system absorptions
  - 300-360nm Cl→Cu LMCT and Cu→π^* MLCT
  - 600-1200nm broad d→d
- Co system absorptions
  - 500-700nm
    - d→d
    - Co→π^* MLCT

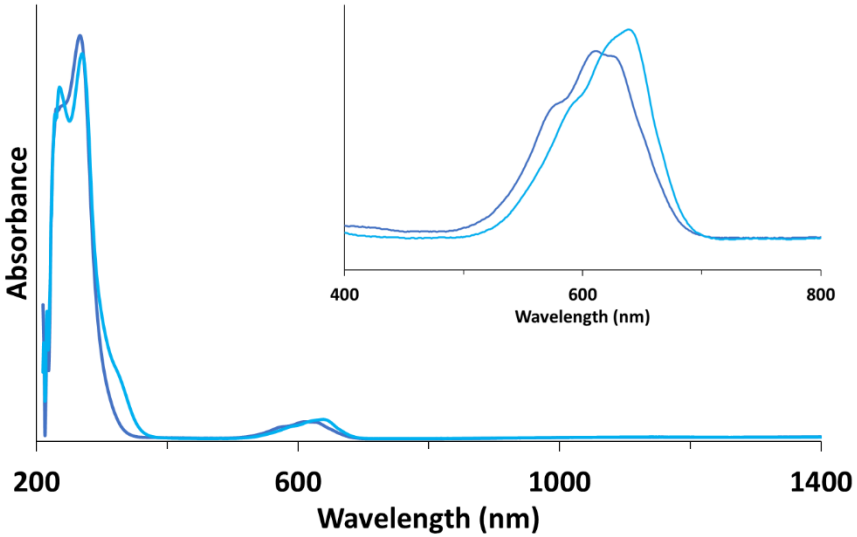
$CuLCl_2$ light green

$CuLBr_2$ dark green



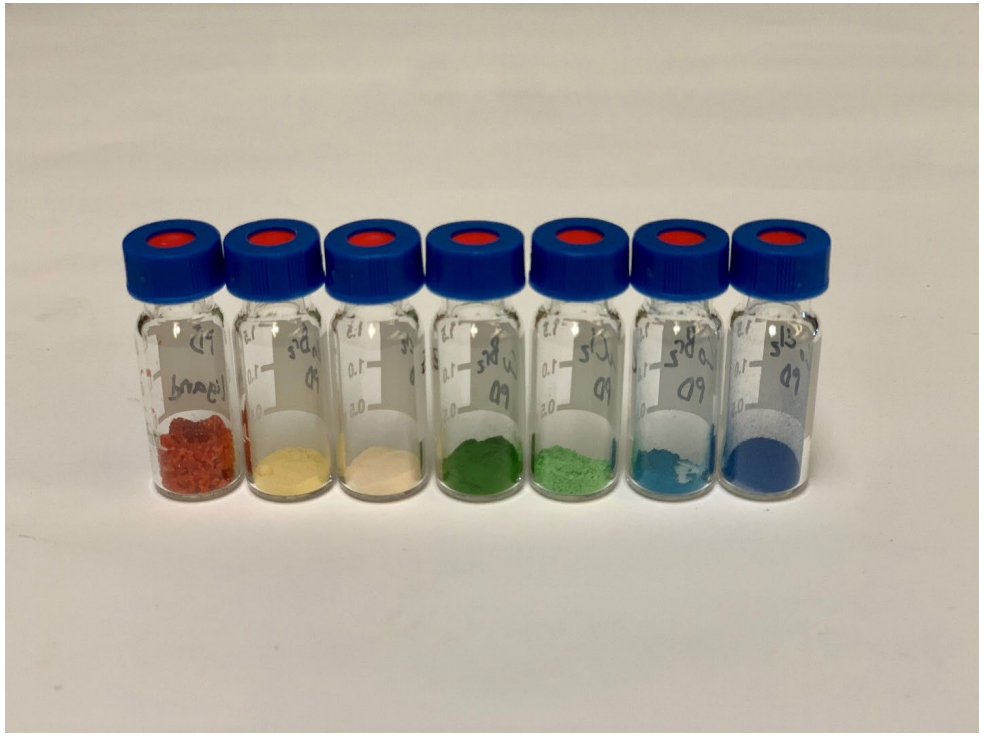
$CoLCl_2$ light blue

$CoLBr_2$ dark blue



Characterization cont.

Compound	Pyridine Disulfide	$ZnLCl_2$	$ZnLBr_2$	$CuLCl_2$	$CuLBr_2$	$CoLCl_2$	$CoLBr_2$
Melting Point/Decomp ˚C	37-39	126	123	86	79	116	121
Yield	66%	88%	92%	89%	98%	67%	64%



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- Mr. Neil Reddeker
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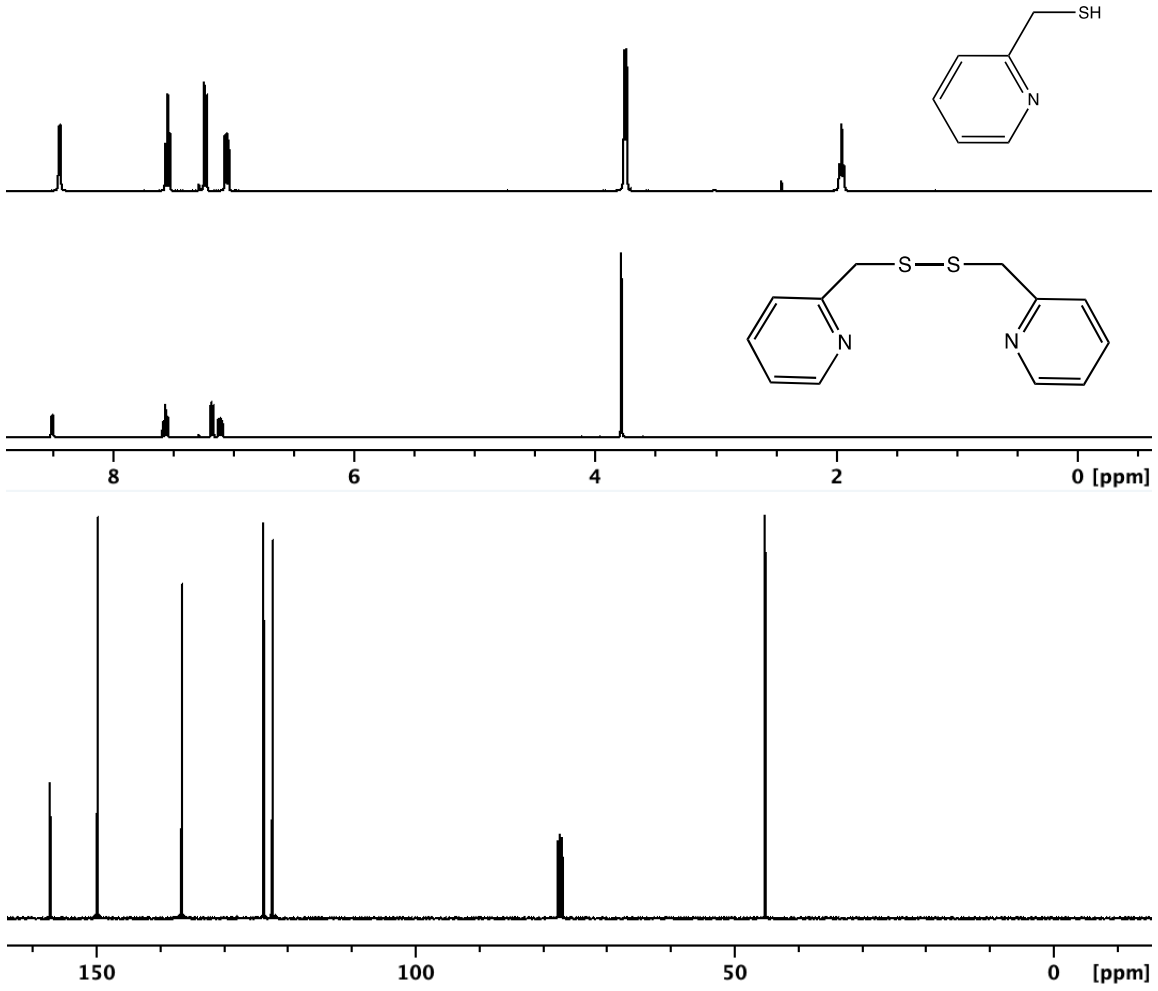
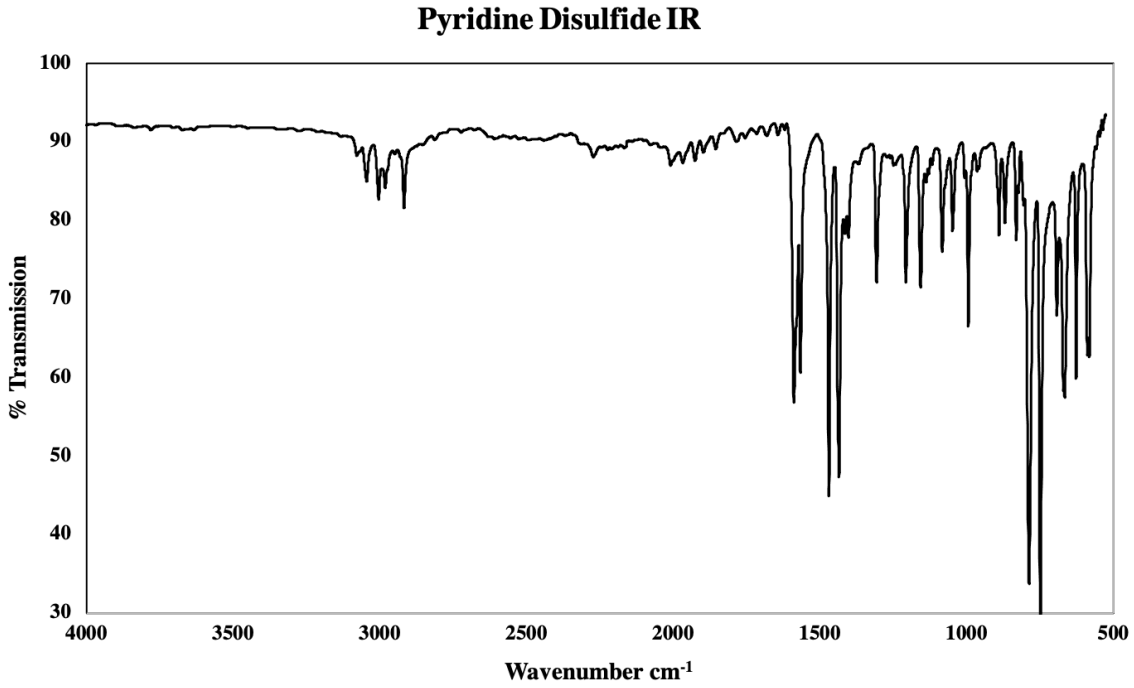
- Dr. Ken Caster
- AFOSR Project #

Questions?

Supplemental

Ligand Characterization





	%C	%H	%N	HRMS *m/z* $[M+H]^+$	M.P. ˚C
Theoretical	58.03	4.87	11.28	249.0522	
Actual	58.16	4.91	11.19	249.0515	37-39

	L (2)[a]	$ZnLCl_2$ ($3•CHCl_3$)	$ZnLCl_2$ ($3•CH_2Cl_2$)	$ZnLBr_2$ ($4•CHCl_3$)	$ZnLBr_2$ ($4•CH_2Cl_2$)	$CuLCl_2$ (5)	$CuLBr_2$ (6)	$CoLCl_2$ (7)[a]	$CoLBr_2$ ($8•CHCl_3$)	$CoLBr_2$ ($8•CH_2Cl_2$)	CuLCl (9)	CuLBr (10)
	Distances / Interactions, Å											
S1–S2	2.0334(6)	2.0182(9)	2.0348(5)	2.0157(7)	2.0299(8)	2.045(1)	2.042(1)	2.032(2)	2.050(1)	2.048(2)	2.0483(7)	2.0543(6)
S3–S4	2.0346(6)							2.032(2)				
S5–S6	2.0296(6)											
M–X1		2.2404(8)	2.2640(4)	2.3775(3)	2.3994(4)	2.3176(9)	2.4921(8)	2.269(2)	2.4313(6)	2.4280(9)	2.2844(5)	2.4125(3)
M–X2		2.2409(9)	2.2496(4)	2.3709(3)	2.3854(4)	2.2875(9)	2.4450(7)	2.273(2)	2.4336(6)	2.4219(8)		
M–X3								2.304(2)				
M–X4								2.293(2)				
M–S1		4.069(1)	3.1978(5)	4.0631(6)	3.3075(7)	2.5900(9)	2.545(1)	2.755(2)	2.7995(9)	2.858(2)	2.3757(6)	2.3436(5)
M–S2		4.073(1)	4.1156(5)	4.0788(6)	4.0910(7)	3.700(1)	3.676(1)	3.903(4)	3.8468(9)	3.906(2)	3.4549(6)	3.4110(5)
M–S3								2.599(2)				
M–S4								3.773(3)				
M–N1		2.066(2)	2.064(1)	2.074(2)	2.063(2)	2.035(3)	2.007(2)	2.068(3)	2.085(2)	2.043(5)	2.021(2)	2.035(1)
M–N2		2.079(2)	2.065(1)	2.060(2)	2.074(2)	2.023(3)	2.003(2)	2.063(3)	2.051(2)	2.072(5)	2.012(2)	2.016(1)
M–N3								2.078(3)				
M–N4								2.081(3)				
	Angles, deg											
X1–M1–X2		118.53(2)	111.74(1)	117.55(1)	110.96(1)	139.05(3)	129.22(2)	103.02(7)	104.53(2)			
N1–M1–N2		113.31(7)	116.24(5)	113.93(6)	115.16(7)	169.63(1)	170.02(1)	119.89(1)	120.08(9)	120.1(2)	122.83(6)	119.65(5)
X1–M1–N1		108.13(5)	104.27(3)	106.80(5)	105.00(5)	90.60(8)	92.23(7)	100.59(9)	100.37(7)	97.8(1)	109.44(4)	110.04(4)
X1–M1–N2		104.60(5)	100.37(3)	105.99(4)	103.10(5)	95.37(8)	95.60(7)	99.07(9)	99.81(7)	103.0(1)	110.57(5)	109.52(4)
X2–M1–N1		105.69(5)	112.24(3)	106.05(5)	115.66(5)	90.64(8)	91.73(7)	115.94(1)	114.14(7)	115.8(1)		
X2–M1–N2		106.84(5)	111.12(3)	106.83(5)	106.28(5)	90.40(8)	88.11(7)	113.75(9)	114.12(7)	111.6(1)		
S1–M1–X1						100.23(3)	97.84(2)	178.38(4)	175.55(3)	174.59(4)	121.22(2)	124.89(1)
S1–M1–X2						120.09(3)	132.54(3)	77.79(6)	79.87(2)	79.89(4)		
S1–M1–N1						78.59(8)	79.09(8)	77.79(9)	76.95(7)	78.2(1)	85.74(4)	86.11(4)
S1–M1–N2						91.98(8)	93.70(7)	81.82(9)	78.74(7)	76.2(1)	105.88(5)	105.87(4)
M1–S1–S2						105.32(4)	105.99(4)	108.29(8)	103.91(4)	104.28(7)	102.44(2)	101.52(2)
X3–M2–X4								98.30(6)				
N3–M2–N4								118.92(1)				
X3–M2–N3								99.56(1)				
X3–M2–N4								95.73(1)				
X4–M2–N3								115.77(9)				
X4–M2–N4								119.82(9)				
S3–M2–X3								178.97(3)				
S3–M2–X4								81.93(6)				
S3–M2–N3								79.45(1)				
S3–M2–N4								85.02(1)				
M2–S3–S4								108.29(8)				