

A Single Carbon Atom Controls Geometry and Reactivity of Co^{II}(N₂S₂) Complexes

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Supporting Information

Methods and Materials. All reactions and manipulations were performed either under inert atmosphere N₂ glove box or using standard Schlenk-line and syringe/rubber septa techniques under N₂ atmosphere. Dry solvents were purified and degassed via a Bruker solvent system. Reagents were purchased from commercial sources and used as received. The ligands¹ and the tungsten synthon [(pip)₂W(CO)₄]₂² were synthesized following the literature reported procedures.

Physical measurements. Solution infrared spectrum were recorded on a Bruker Tensor 37 Fourier transform IR (FTIR) spectrometer in CaF₂ solution cell with a 0.2 mm path length. ¹H NMR spectra was recorded using the Bruker Avance NEO 400 MHz system with an automated tuning 5mm broadband iProbe (Acend magnet). Atmospheric pressure chemical ionization mass spectrometry (APCI-MS) was performed by the Laboratory for Biological Mass Spectrometry at Texas A&M University. UV vis spectrum were recorded on a SHIMADZU UV-2450 UV-Vis spectrophotometer.

Single crystal X-ray diffraction measurements were carried out at a low temperature employing a (three circle or kappa) Bruker-AXS (Quest or Venture) with I μ S source and a Photon III area detector diffractometer for (Mo K α radiation, λ = 0.71073 Å or Cu K α radiation, λ = 1.54178 Å) (NSF-CHE-9807975, NSF-CHE-0079822 and NSF-CHE-0215838). For complex **1**, Rigaku synergy dual source (Cu K α radiation, λ = 1.54178 Å) with hybrid pixel array detector was used for data collection. Crystals (for color, habit, size see corresponding CIF files) were mounted on a nylon or Kapton® loops and cooled in a cold nitrogen stream (OXFORD Cryosystems (700 or 800), to 110(2) K. Bruker AXS APEX 3/4³ software was used for data collection and reduction. Absorption corrections were applied using SADABS.⁴ Space group assignments were determined by examination of systematic absences, E-statistics, and successive refinement of the structures. Structures were solved using SHELXT⁵ and refined by least-squares refinement on F² followed by difference Fourier synthesis (OLEX2, SHELXL).^{6,7} All hydrogen atoms were included in the final structure factor calculation at idealized positions and were allowed to ride on the neighbouring atoms with relative isotropic displacement coefficients. Thermal parameters were refined anisotropically for all non-hydrogen atoms to convergence. The MERCURY 2022.1.0⁸ interface was used for structure visualization, analysis of bond distances and angles, and drawing ORTEP plots.

Cyclic Voltammetry. Cyclic voltammograms were recorded on a CHI600E electrochemical analyzer (HCH instruments, Inc.). All experiments were performed under Ar atmosphere in CH₃CN solutions containing a 0.1 M [ⁿBu₄N][PF₆] electrolyte and 2.0 mM analyte at room temperature. A 0.071 cm² glassy carbon disk was used as the working electrode, platinum wire as the counter electrode, and Ag⁰/AgCl as the reference electrode. All potentials were referenced to the Fc⁺/Fc couple at 0.00 V.

Synthesis of Complex 1

2.1 g (0.0058 mmol) of H₂-bme-dabz ligand is taken up in 15 mL of toluene and a suspension of 1.49 g (0.0058 mmol) anhydrous cobalt(II) acetylacetonate, Co(acac)₂ in toluene is added to it. The reaction is allowed to stir under inert atmosphere overnight and the color changes from dark purple to dark green with formation of solids. The crude solid is collected on a glass-fritted funnel under anaerobic conditions. The solid is washed thoroughly with toluene and hexane to remove the unreacted ligand. Yield: 2.0 g (41%). The green solid is found to be insoluble in most organic solvents. Crystals suitable for x-ray diffraction analysis can be obtained from layering a hot dimethyl formamide solution of the complex with hexane. UV-vis spectrum in DMF [λ_{max} (nm)]: 267, 286, 338, 369, 533, 631. *Anal.* Calcd. for C₄₀H₅₂Co₂N₄S₄·(0.5·hexane): C, 58.82; H, 6.77; N, 6.38. Found: C, 58.74; H, 6.45; N, 6.41.

Synthesis of Complex 2

1.1 g (0.0028 mmol) of H₂dadt^{Bz} ligand is taken up in 15 mL of toluene and a suspension of 0.69 g (0.0026 mmol) anhydrous cobalt(II) acetylacetonate, Co(acac)₂ in toluene is added to it. The ligand is taken in slight excess as it is readily soluble in ether or toluene and can be removed by washing with ether or toluene. The reaction is allowed to stir under inert atmosphere overnight and the color changes from dark purple to dark blue with formation of solids. The crude solid is collected on a glass-fritted funnel under anaerobic conditions. The solid is washed thoroughly with toluene and ether to remove the unreacted ligand. Yield: 0.8 g (66 %). Crystals suitable for x-ray diffraction analysis can be obtained by layering a concentrated solution of DCM with hexane. UV-vis spectrum in DMF [λ_{max} (nm)]: 267, 303, 368, 405, 545, 625, 664. *Anal.* Calcd. for C₂₁H₂₈N₂CoS₂: C, 58.45; H, 6.54; N, 6.49. Found: C, 58.44; H, 6.67; N, 6.51.

Synthesis of Complex 3

In a 40 mL vial, 92.8 mg (0.2 mmol) of (pip)₂W(CO)₄ and 83.4 mg (0.1 mmol) of complex 1 ([Co(bme-dabz)]₂) were dissolved in 5.0 mL of DMF. The mixture was stirred at 80°C for 2 h. The color of the solution became dark brown. The vial was allowed to cool down to room temperature, and the addition of 20 mL of diethyl ether led to a precipitate formation over the course of a few hours. The resulting mixture was anaerobically filtered, and the solid was dried in vacuo to produce 60 mg (76%, based on amount of complex 1) of a brown solid. The solid was dissolved in concentrated DMF solution, filtered and ether was allowed to diffuse into the DMF solution for 3-4 days at room temperature to obtain needle shaped X-ray-quality crystals. UV-vis spectrum in DMF [λ_{max} (nm)]: 269, 296, 384, 449, 519, 595. IR (DMF): $\nu(\text{CO})$ (cm⁻¹) 1991 (m), 1872 (s), 1835 (s) and 1816 (s) (in DMF); 1995 (m), 1877(s), 1840(s) and 1819(s) (in MeCN); 1988(m), 1864(s), 1833(s) and 1791(s) (in ATR). *Anal.* Calcd. for C₂₇H₃₃CoN₃O₅S₂W·(0.5 Et₂O): C, 42.3; H, 4.65; N, 5.1. Found: C, 42.20; H, 4.85; N, 5.63.

Synthesis of Complex 4

In a 40 mL vial, 92.8 mg (0.2 mmol) of $(\text{pip})_2\text{W}(\text{CO})_4$ and 86.22 mg (0.2 mmol) of complex **2** ($[\text{Co}(\text{dadt}^{\text{Bz}})]$) were dissolved in 5.0 mL of DMF. The mixture was stirred at 80°C for 2 h. The colour of the solution became dark green. The vial was allowed to cool down to room temperature, and the addition of 20 mL of diethyl ether led to a precipitate that was formed over the course of a few hours. The resulting mixture was anaerobically filtered, and the solid was dried in vacuo to produce 73 mg (24%, based on amount of Complex **2**) of a green solid. The solid was dissolved in concentrated DMF solution, filtered and ether was allowed to diffuse into the DMF solution over 3-4 days at room temperature to obtain block shaped X-ray-quality crystals. UV-vis spectrum in DMF [λ_{max} (nm)]: 268, 296, 419, 550, 602. IR: $\nu(\text{CO})$ (cm^{-1}) 1885 and 1785 (in DMF); 1870, 1777 and 1742 (in ATR). *Anal.* Calcd. for $\text{C}_{54}\text{H}_{70}\text{Co}_2\text{N}_6\text{O}_8\text{S}_4\text{W}_2$: C, 41.98; H, 4.57; N, 5.44. Found: C, 42.29; H, 4.72; N, 5.35.

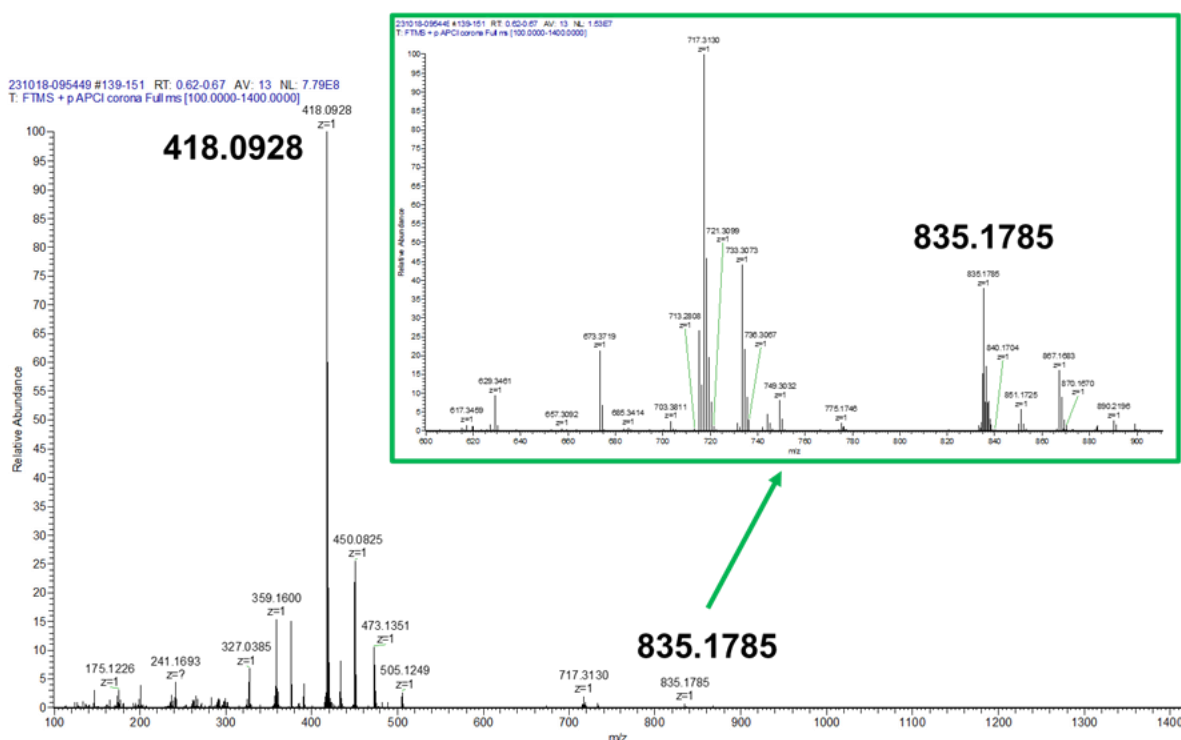


Figure S1. APCI-MS for complex **1** in DMF/MeCN mixture. The strong peak at $m/z = 418.0928$ is for the monomeric form of complex **1**.

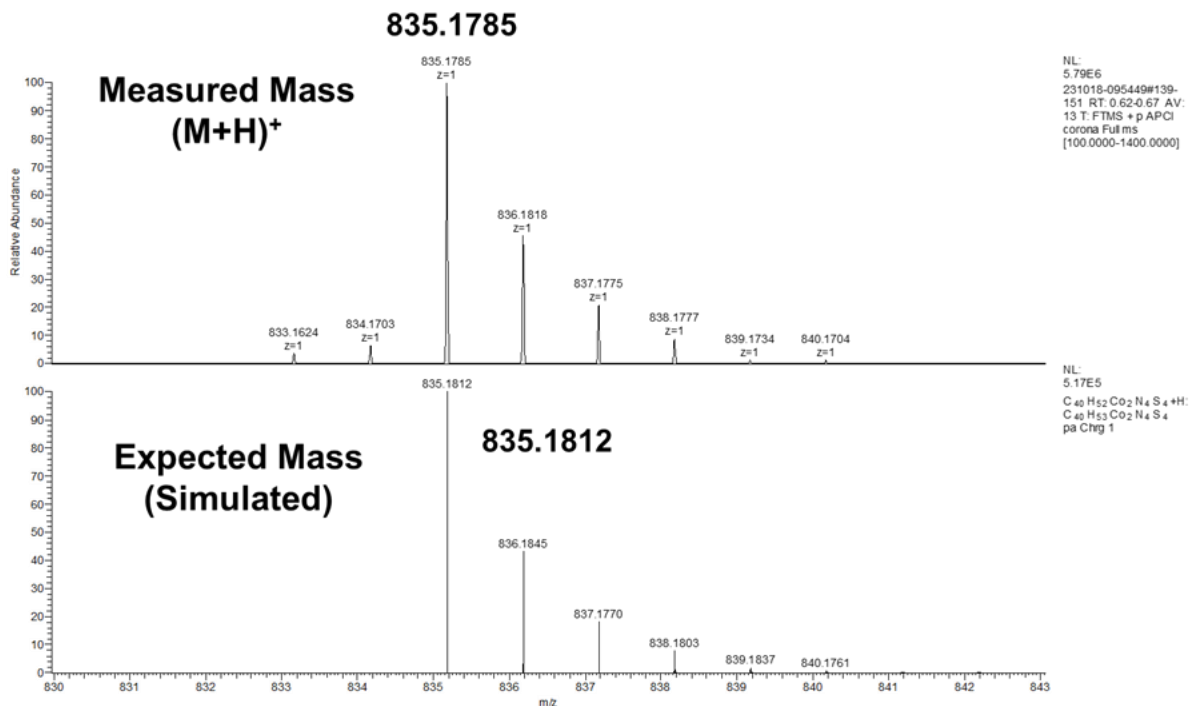


Figure S2. Isotopic bundles for complex 1 (measured mass) showing exact match with the expected mass in DMF/MeCN mixture.

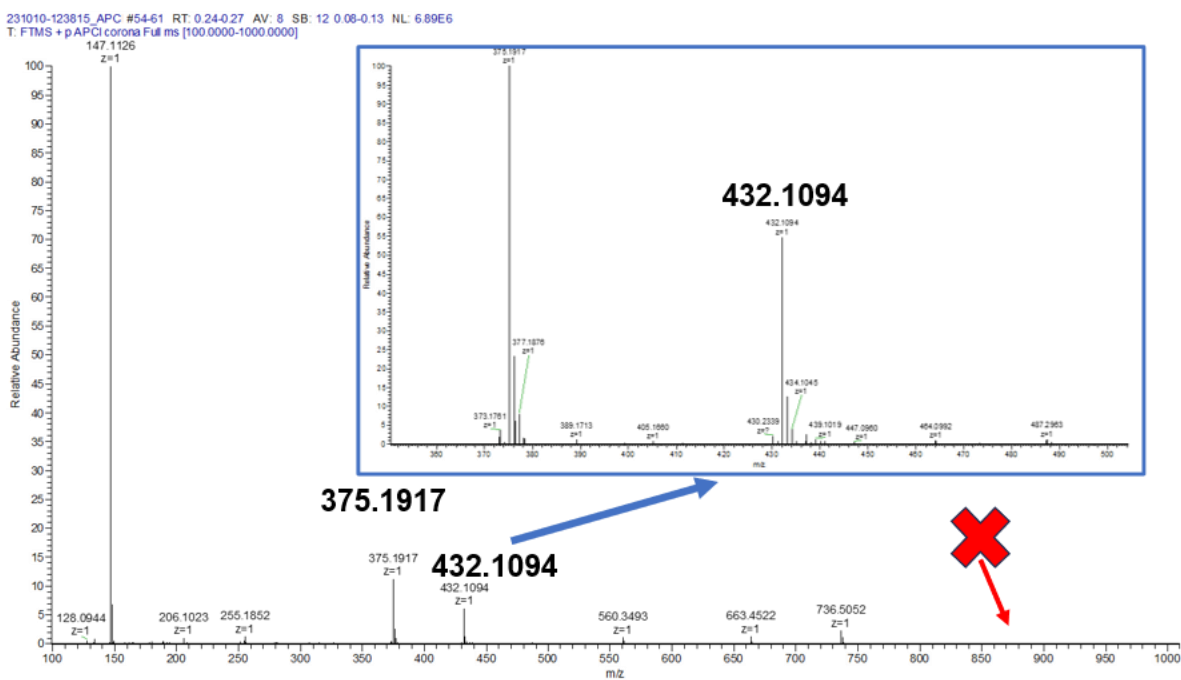


Figure S3. APCI-MS for complex 2 in DCM. No dimeric complex was indicated in the mass spectrum for complex 2 ($m/z = 862.2052$).

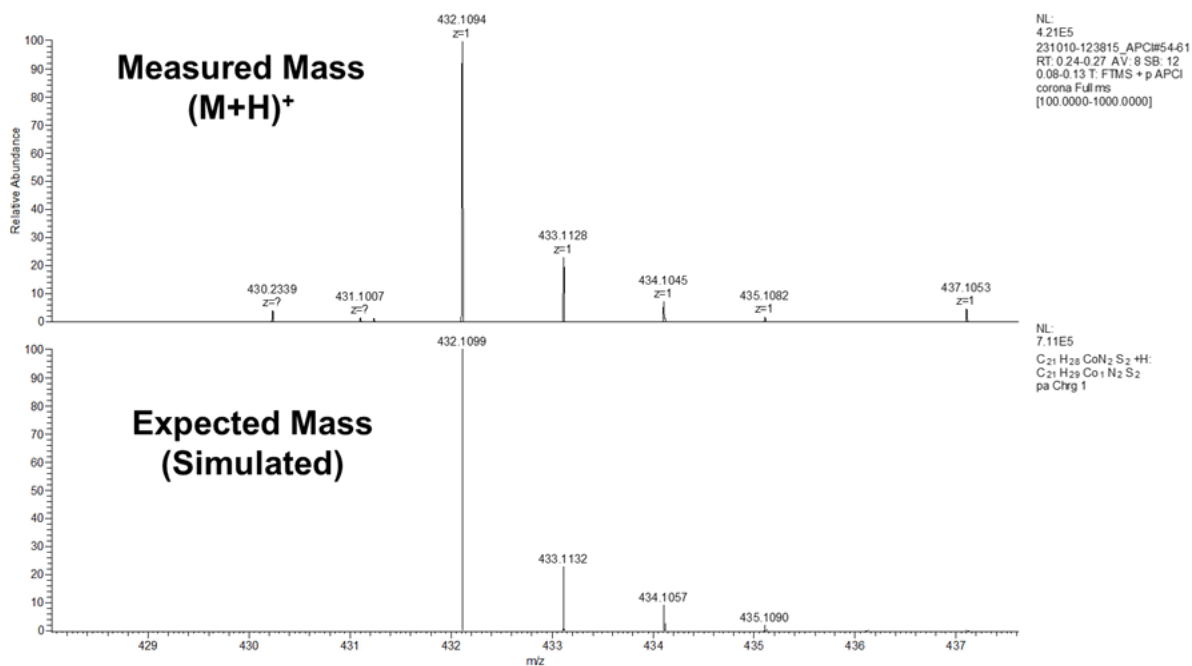


Figure S4. Isotopic bundles for complex **2** (measured mass) showing exact match with the expected mass in DCM.

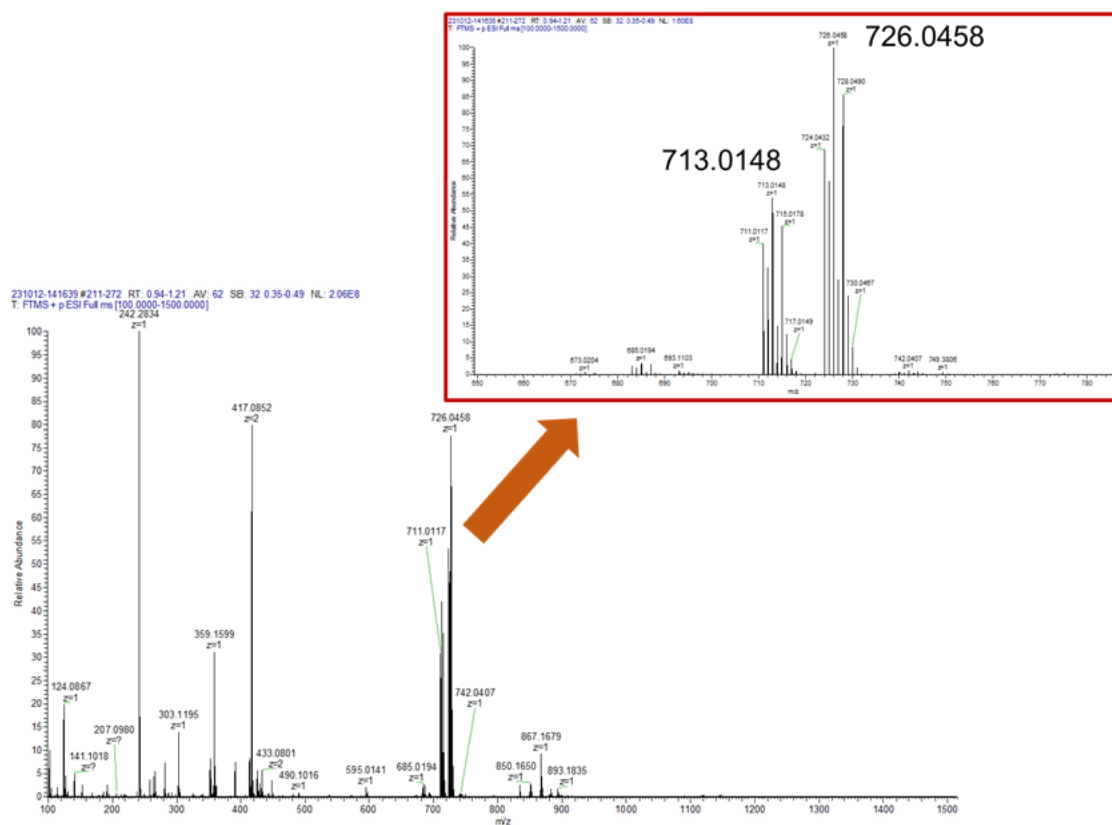


Figure S5. ESI-MS for complex **3** in DMF/MeCN mixture. The peak at $m/z = 713.0148$ corresponds to the $[M-(DMF)]^+$ species.

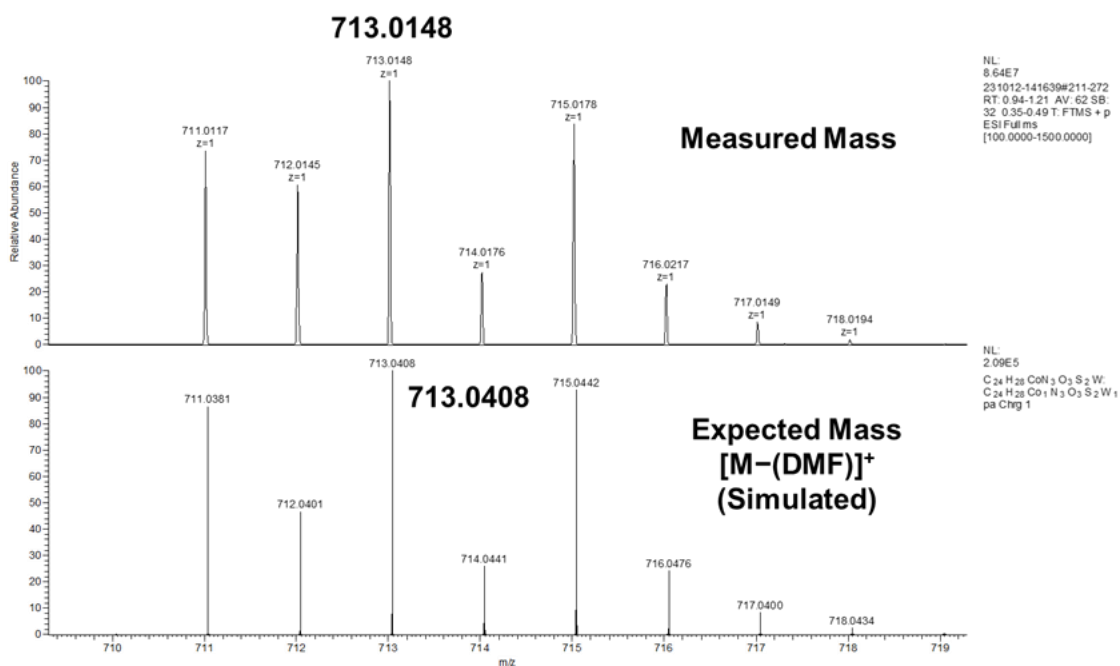


Figure S6. Isotopic bundles for complex **3** (measured mass) showing exact match with the $[M-(DMF)]^+$ species in solution.

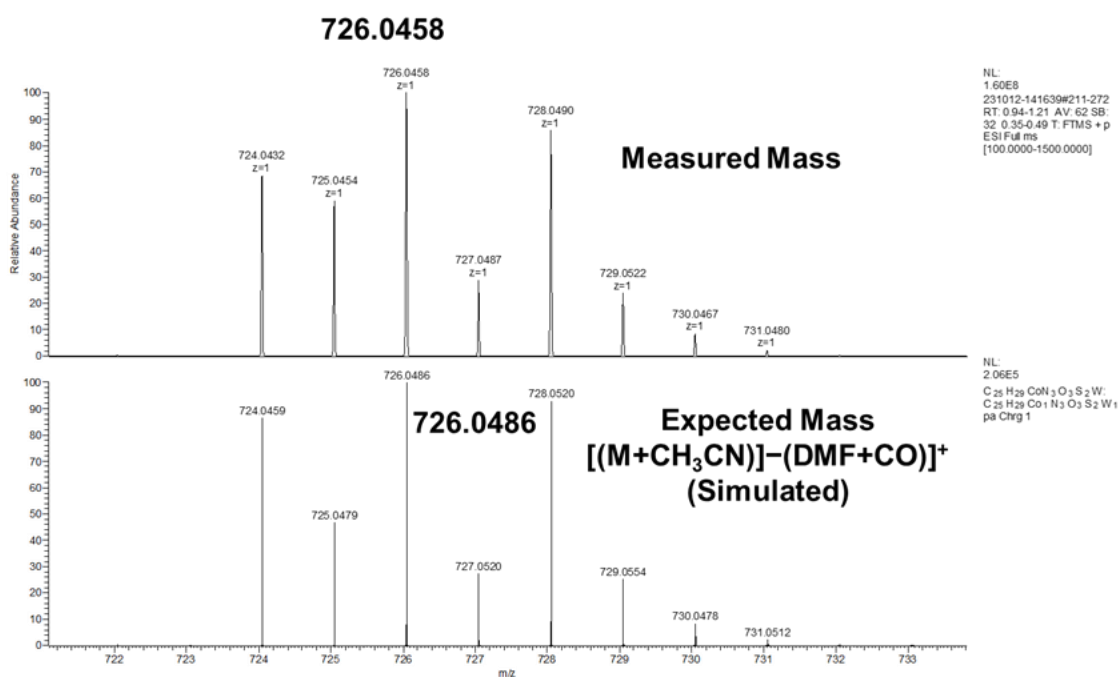


Figure S7. Isotopic bundles for complex **3** (measured mass) showing exact match with the $[(M+CH_3CN)-(DMF+CO)]^+$ species in solution.

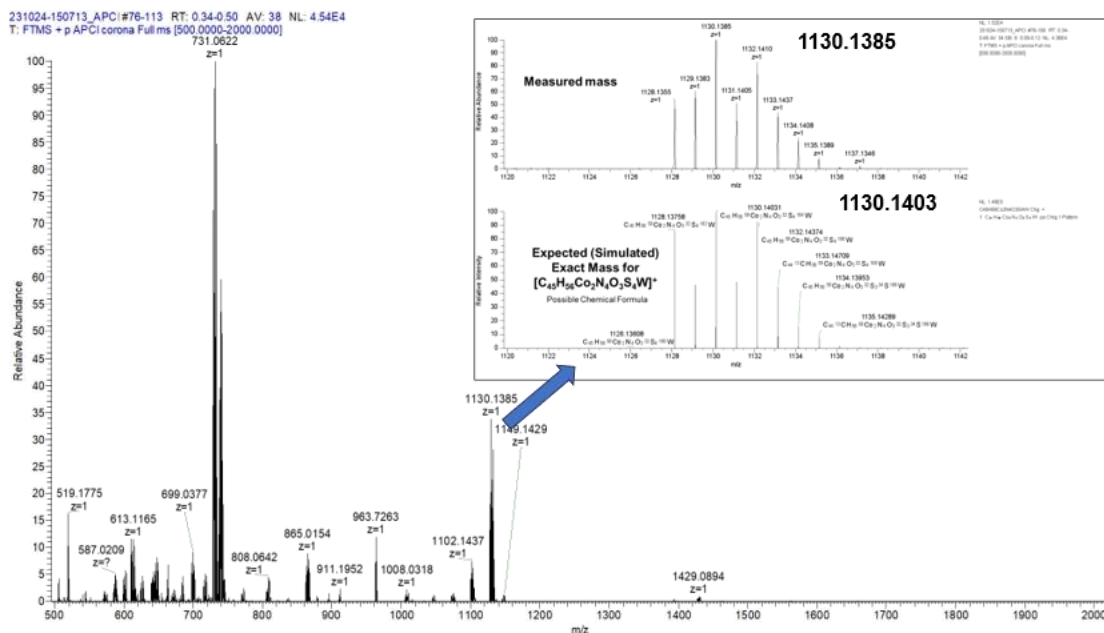


Figure S8. APCI-MS for complex **4** in DMF/MeCN mixture. The peak at $m/z = 1130.1403$ corresponds to the $[M-\{(W(CO)_3)+2\cdot(DMF)\}]^+$ species.

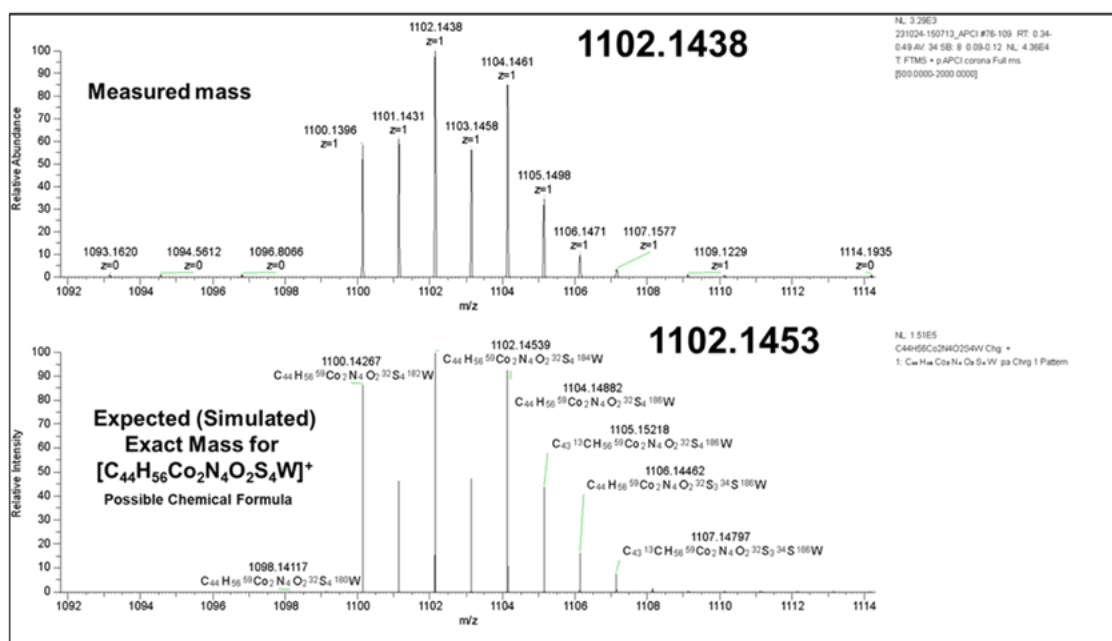


Figure S9. Isotopic bundle for the peak at $m/z = 1102.1438$ corresponds to the $[M-\{(W(CO)_3)+2\cdot(DMF)+CO\}]^+$ species.

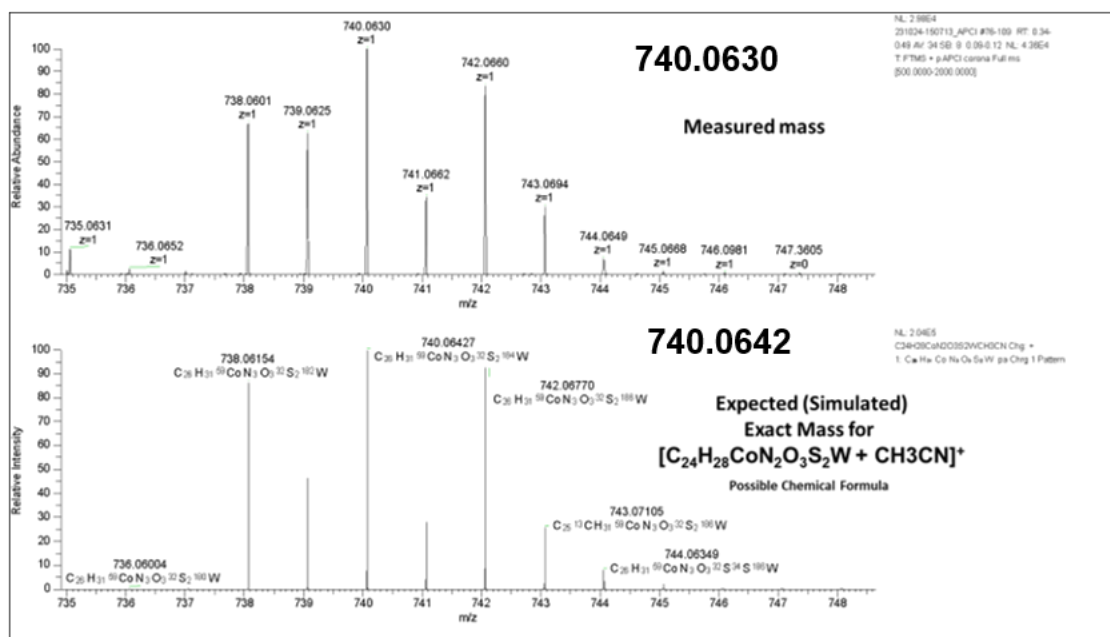


Figure S10. Isotopic bundle for the peak at $m/z = 740.0630$ corresponds to the $[(M+MeCN)-\{(Co(N_2S_2)W(CO)_3)+2\cdot(DMF)\}]^+$ species.

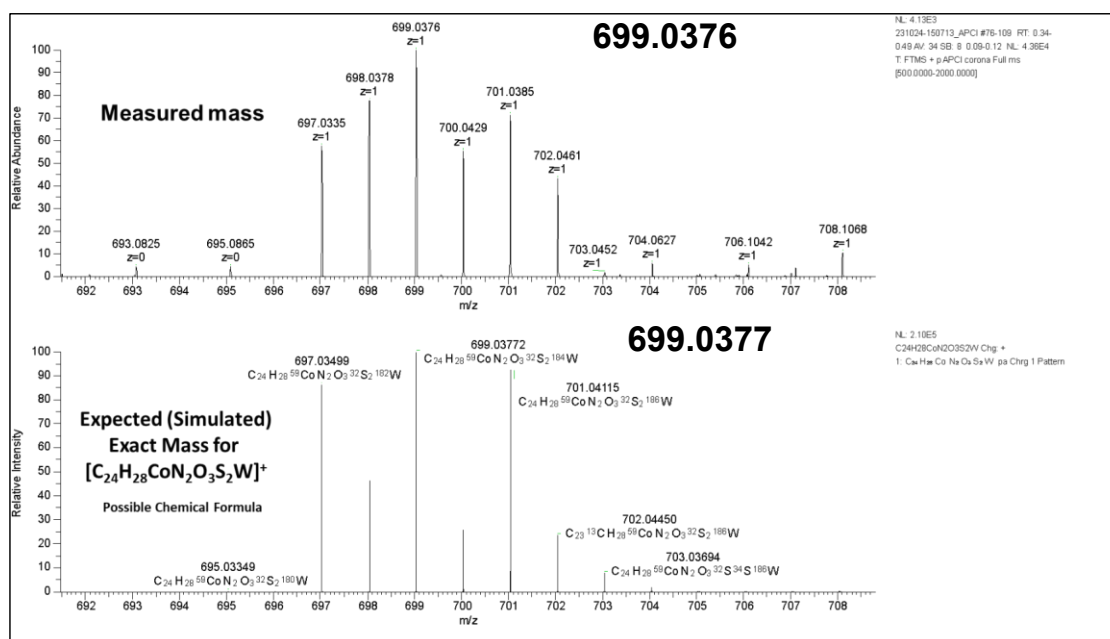


Figure S11. Isotopic bundle for the peak at $m/z = 699.0376$ corresponds to the $[(M)-\{(Co(N_2S_2)W(CO)_3)+2\cdot(DMF)\}]^+$ species.

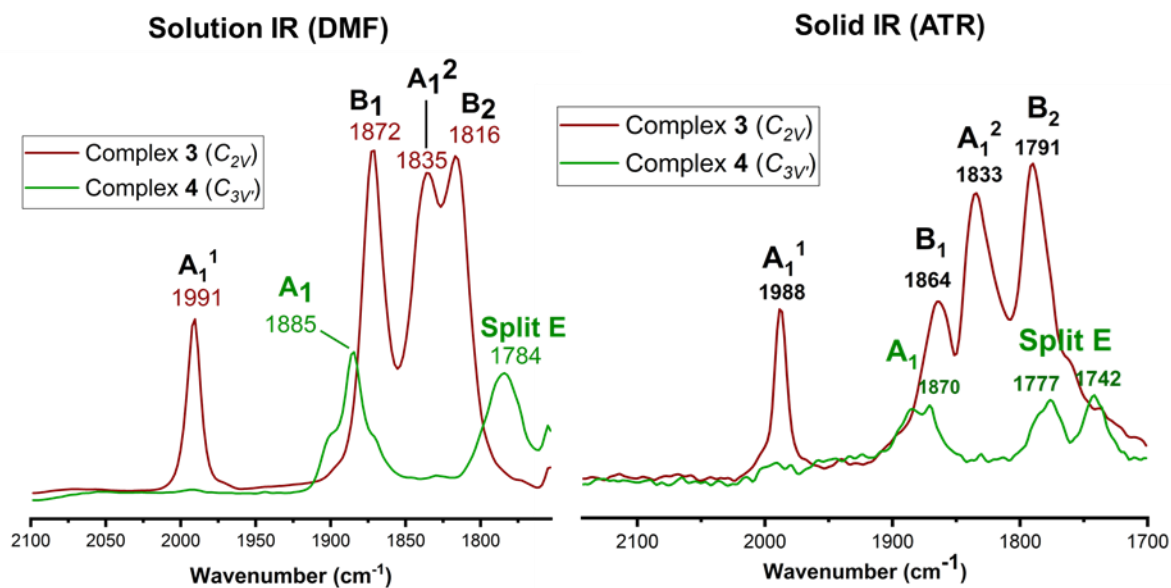


Figure S12. $\nu(\text{CO})$ solution (DMF) and solid (ATR) IR spectra of complexes **3** and **4**; assignments according to their symmetries from XRD analysis.

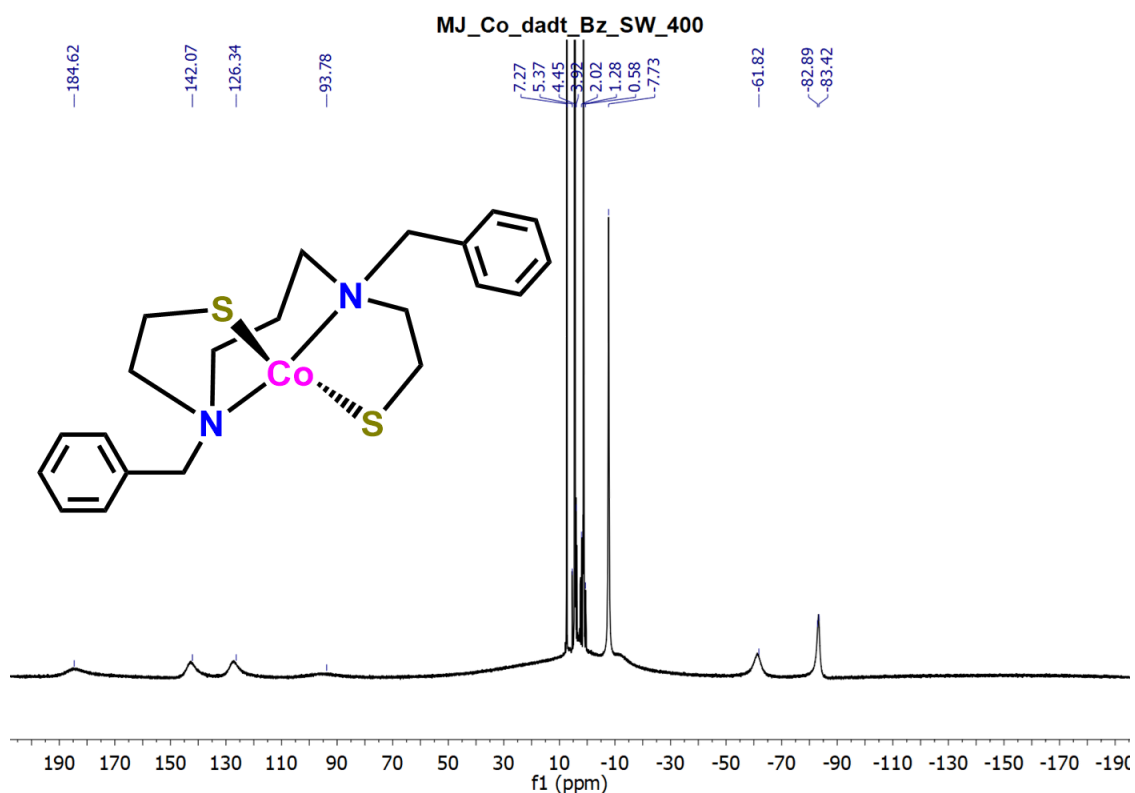


Figure S13: ^1H NMR of Complex **2** ($\text{Co_dadt}^{\text{Bz}}$) at 295 K using a 400 MHz NMR.

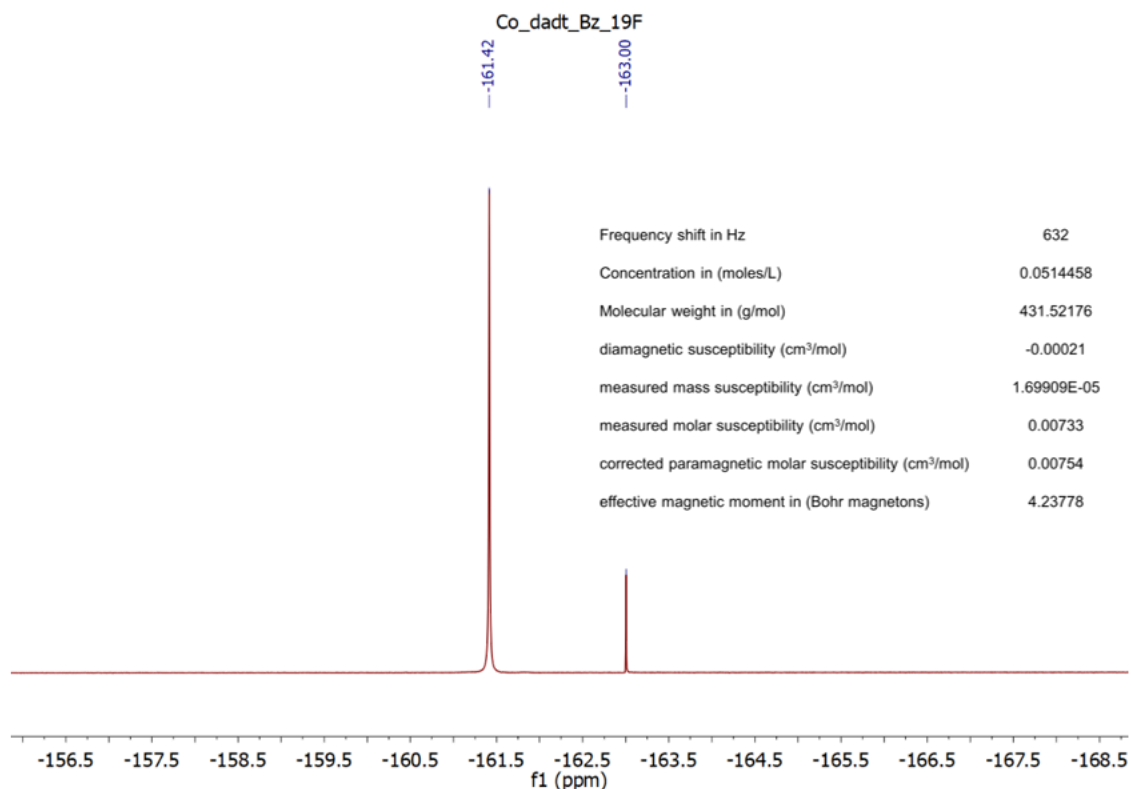


Figure S14: ¹⁹F NMR of Complex **2** (Co(dadt^{Bz})) at 295 K in CDCl₃ using a 400 MHz NMR under argon for Evans Method determination of magnetic susceptibility.

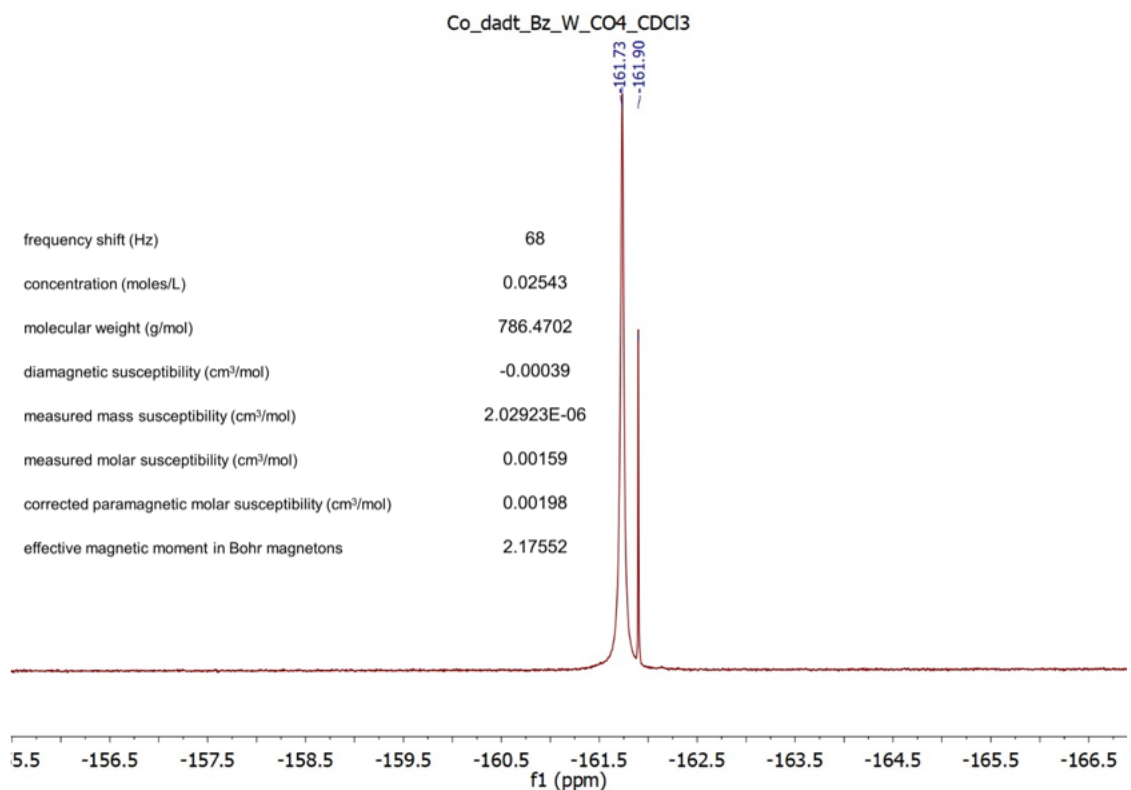


Figure S15: ¹⁹F NMR of Complex **3** {Co(bme-dabz)•W(CO)₄} at 295 K in CDCl₃ using a 400 MHz NMR under argon for Evans Method determination of magnetic susceptibility.

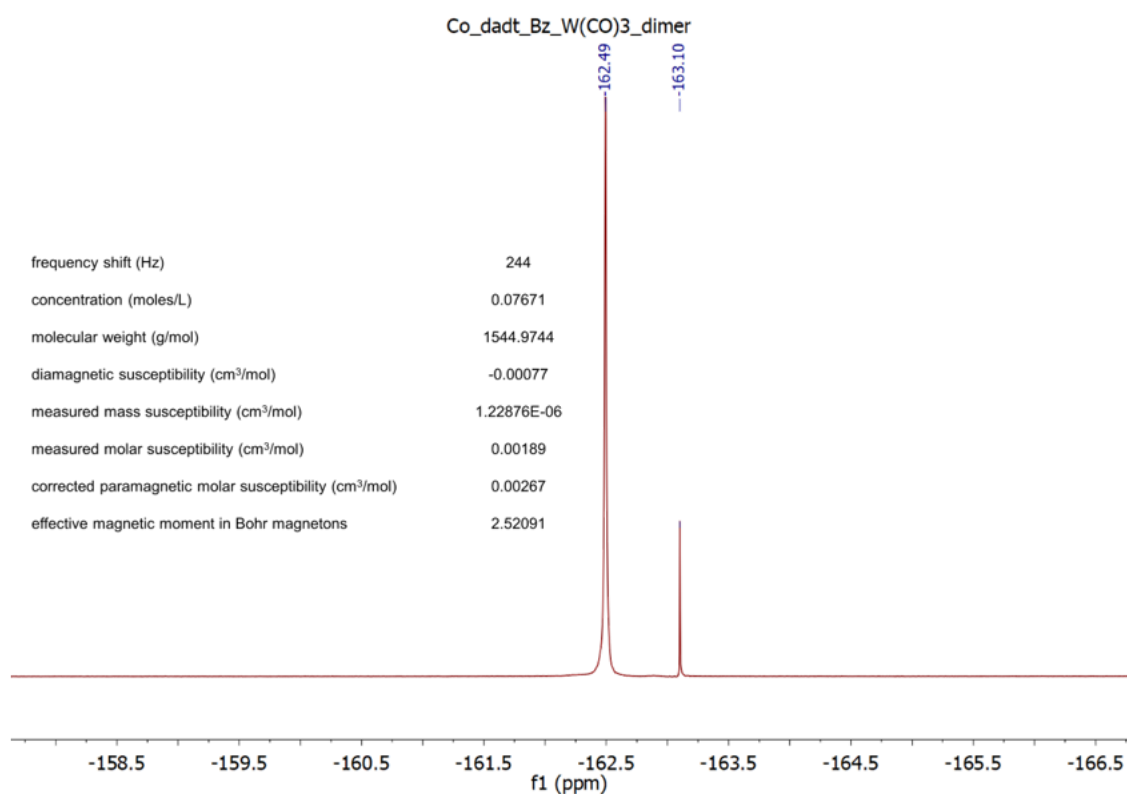


Figure S16: ¹⁹F NMR of Complex 4, [Co(dadt^{Bz})•W(CO)₃]₂ at 295 K in DMSO-d₆ using a 400 MHz NMR under argon for Evans Method determination of magnetic susceptibility.

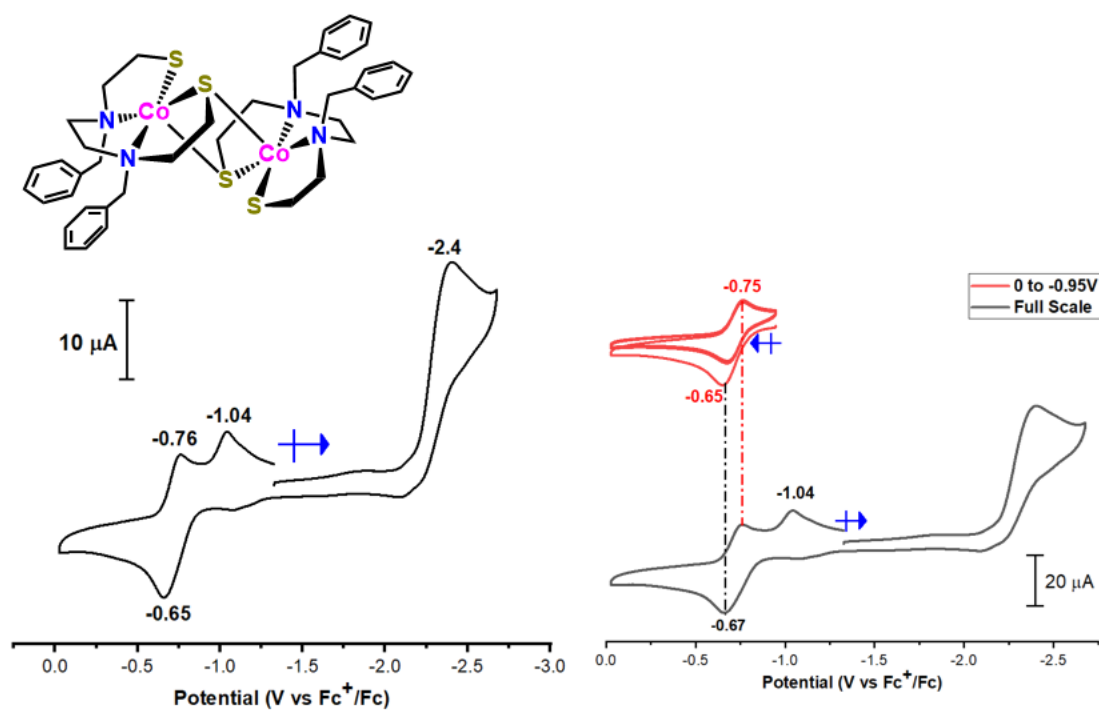


Figure S17. Cyclic voltammograms of 1 mM DMF solutions of Complex 1, recorded at a scan rate of 100 mV/s. Arrows indicate initial sweep direction.

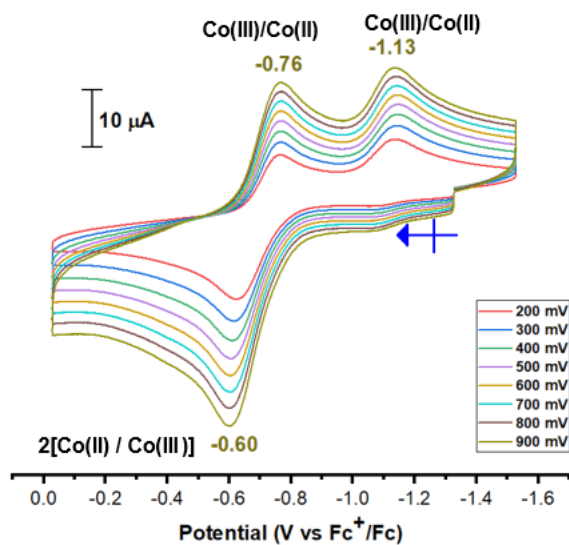


Figure S18: Scan rate dependence (200 – 900 mV/s) of Complex 1 in a 1 mM DMF solution. Arrows indicate initial sweep direction.

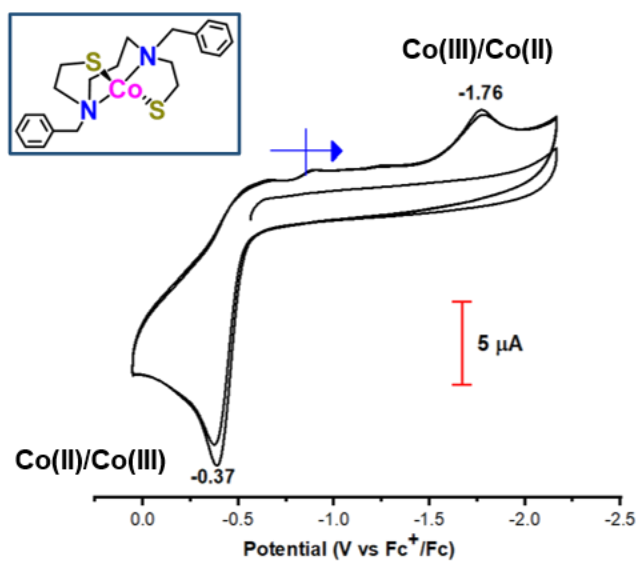


Figure S19. Cyclic voltammograms of 1 mM DMF solutions of Complex 2, recorded at a scan rate of 100 mV/s. Arrows indicate initial sweep direction.

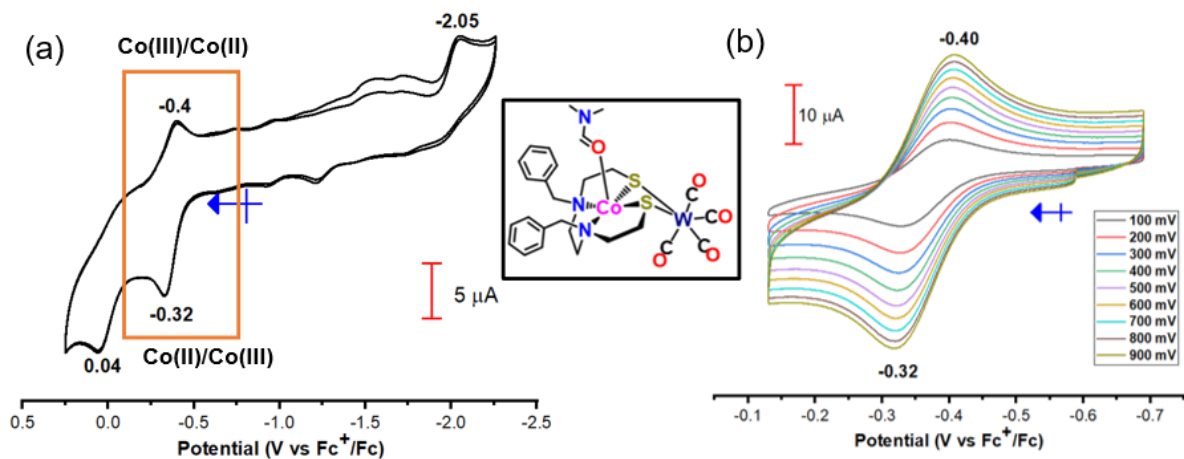


Figure S20. (a) Cyclic voltammograms of 1 mM DMF solutions of Complex 3, recorded at a scan rate of 100 mV/s. (b) The reversible oxidation event taken at different scan speed in DMF. Arrows indicate initial sweep direction.

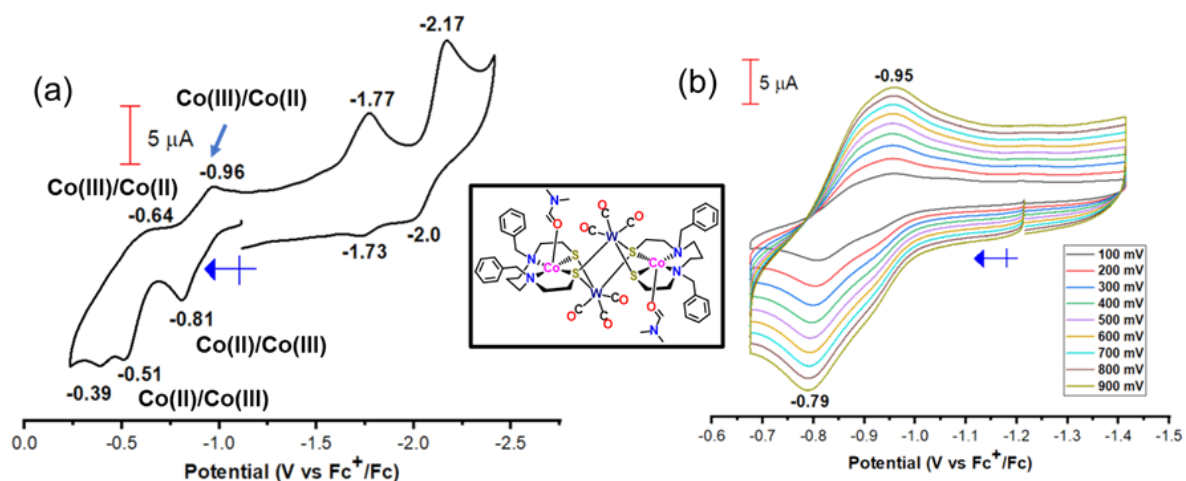


Figure S21. (a) Cyclic voltammograms of 1 mM DMF solutions of Complex 4, recorded at a scan rate of 100 mV/s. (b) The quasi-reversible oxidation event around -0.8 V taken at different scan speed in DMF. Arrows indicate initial sweep direction.

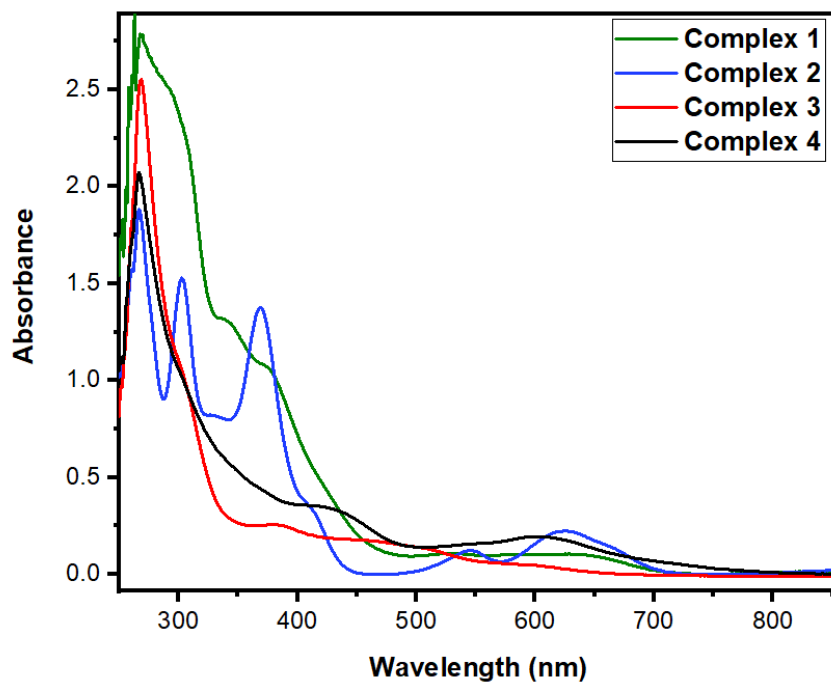


Figure S22: UV Vis spectra of all the complexes in DMF.

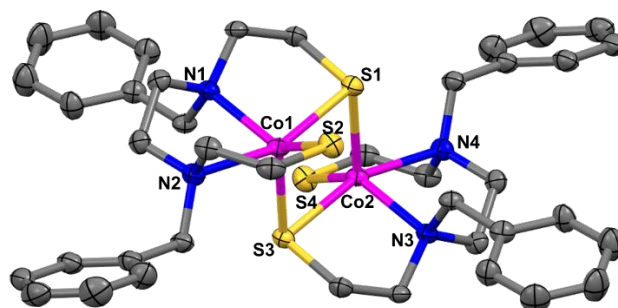


Table S1. Crystal data and structure refinement for Complex **1** (Co_bme_dabz).

CCDC Number	2302282
Empirical formula	C ₄₀ H ₅₂ Co ₂ N ₄ S ₄
Formula weight	834.95
Temperature/K	100.01(12)
Crystal system	monoclinic
Space group	<i>I</i> 2/ <i>a</i>
<i>a</i> /Å	17.8761(3)
<i>b</i> /Å	13.6323(3)
<i>c</i> /Å	15.8821(3)
α /°	90
β /°	102.083(2)
γ /°	90
Volume/Å ³	3784.60(13)
<i>Z</i>	4
ρ_{calc} /cm ³	1.465
μ /mm ⁻¹	9.195
F(000)	1752.0
Crystal size/mm ³	0.081 × 0.03 × 0.025
Radiation	Cu K α (λ = 1.54184)
2 Θ range for data collection/°	8.226 to 140.15
Index ranges	-20 ≤ <i>h</i> ≤ 21, -16 ≤ <i>k</i> ≤ 16, -19 ≤ <i>l</i> ≤ 19
Reflections collected	31776
Independent reflections	3587 [<i>R</i> _{int} = 0.0821, <i>R</i> _{sigma} = 0.0326]
Data/restraints/parameters	3587/0/226
Goodness-of-fit on F ²	1.076
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0435, <i>wR</i> ₂ = 0.0950
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0518, <i>wR</i> ₂ = 0.0988
Largest diff. peak/hole / e Å ⁻³	0.42/-0.41

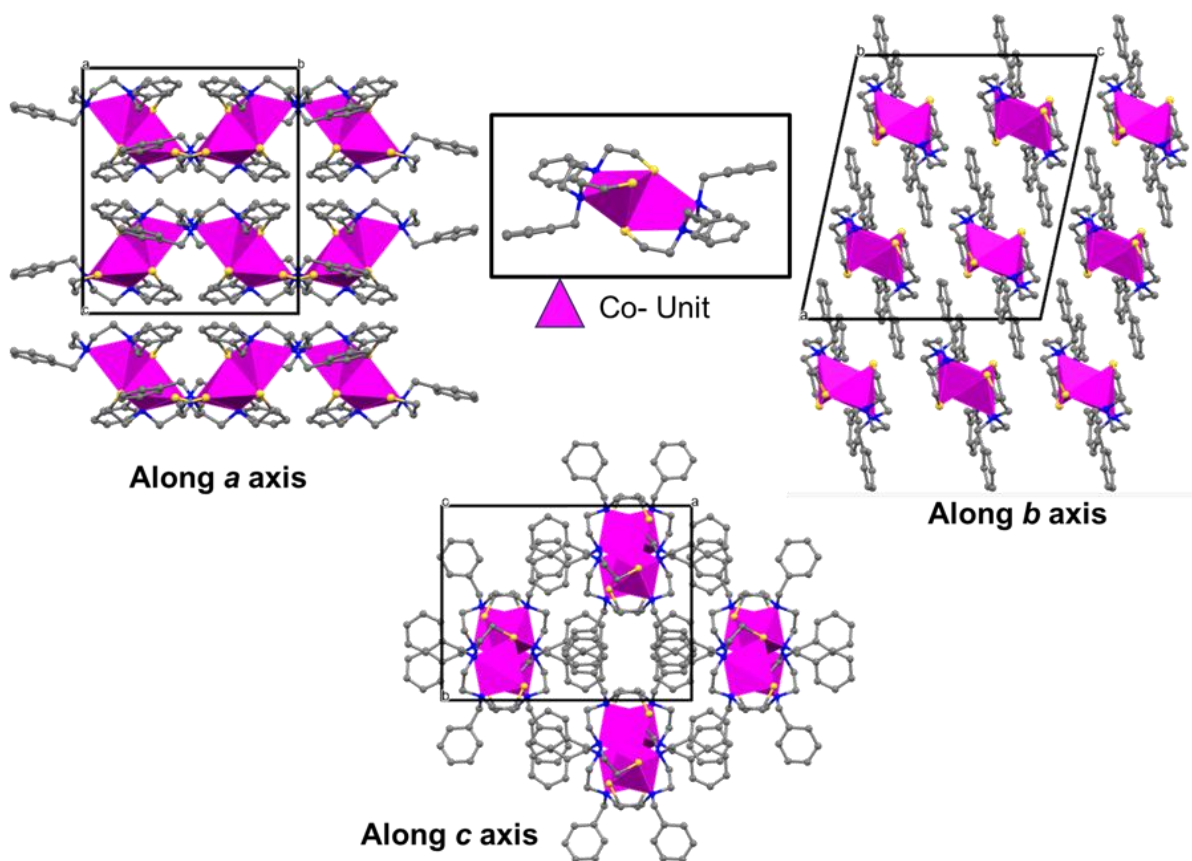


Figure S23. Crystal packing diagram of Complex 1 viewed along *a*, *b*, and *c* axis.

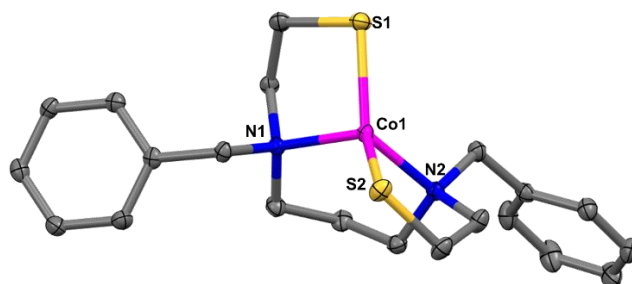


Table S2. Crystal data and structure refinement for Complex **2** (Co_dadt^{Bz}).

CCDC Number	2258956
Empirical formula	C ₂₁ H ₂₈ CoN ₂ S ₂
Formula weight	431.50
Temperature/K	110.00
Crystal system	orthorhombic
Space group	<i>Pbca</i>
a/Å	15.9232(10)
b/Å	15.0712(11)
c/Å	16.8379(11)
α/°	90
β/°	90
γ/°	90
Volume/Å ³	4040.8(5)
Z	8
ρ _{calc} /cm ³	1.419
μ/mm ⁻¹	1.064
F(000)	1816.0
Crystal size/mm ³	0.5 × 0.5 × 0.3
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	5.116 to 50.406
Index ranges	-18 ≤ h ≤ 19, -18 ≤ k ≤ 18, -20 ≤ l ≤ 20
Reflections collected	80281
Independent reflections	3627 [R _{int} = 0.0780, R _{sigma} = 0.0238]
Data/restraints/parameters	3627/0/235
Goodness-of-fit on F ²	1.161
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0291, wR ₂ = 0.0619
Final R indexes [all data]	R ₁ = 0.0486, wR ₂ = 0.0741
Largest diff. peak/hole / e Å ⁻³	0.39/-0.34

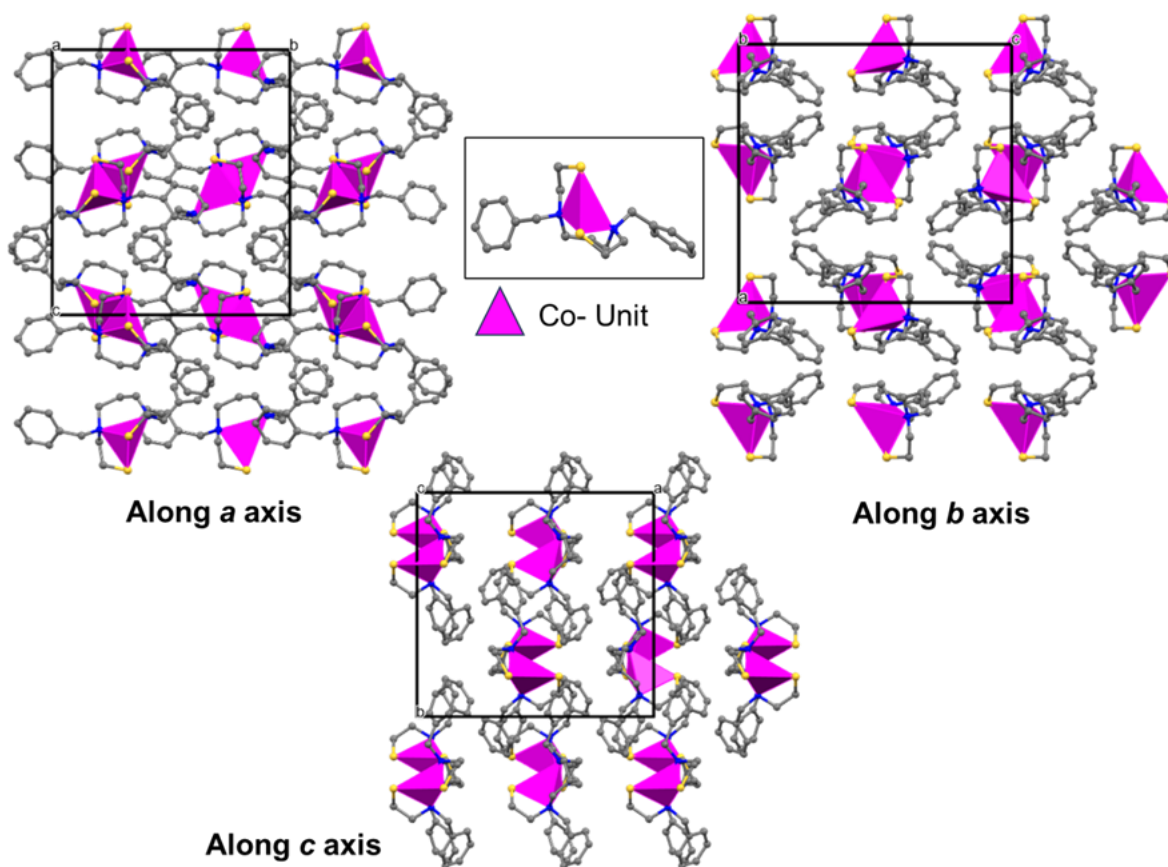


Figure S24. Crystal packing diagram of Complex 2 viewed along *a*, *b*, and *c* axis.

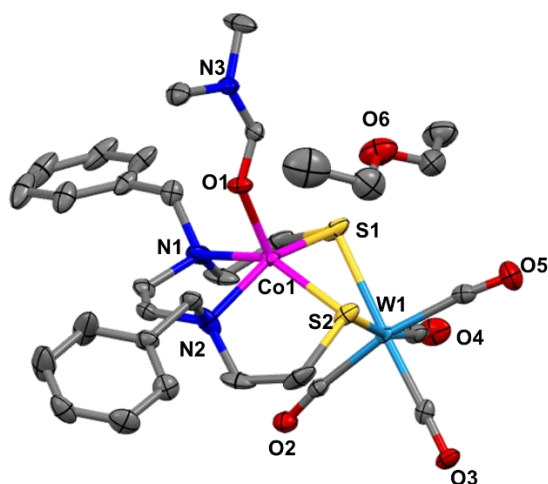


Table S3. Crystal data and structure refinement for Complex **3** (Co-bme-dabz•W(CO)₄).

CCDC Number	2302283
Empirical formula	C ₃₁ H ₄₃ CoN ₃ O ₆ S ₂ W
Formula weight	860.58
Temperature/K	110.00
Crystal system	monoclinic
Space group	<i>P2₁/c</i>
<i>a</i> /Å	13.2062(12)
<i>b</i> /Å	14.5330(13)
<i>c</i> /Å	18.5933(17)
α /°	90
β /°	105.716(2)
γ /°	90
Volume/Å ³	3435.1(5)
<i>Z</i>	4
ρ_{calc} /cm ³	1.664
μ /mm ⁻¹	3.995
<i>F</i> (000)	1724.0
Crystal size/mm ³	0.5 × 0.3 × 0.2
Radiation	MoK α (λ = 0.71073)
2 Θ range for data collection/°	4.552 to 50.11
Index ranges	-15 ≤ <i>h</i> ≤ 15, -17 ≤ <i>k</i> ≤ 17, -22 ≤ <i>l</i> ≤ 22
Reflections collected	61741
Independent reflections	6066 [<i>R</i> _{int} = 0.0562, <i>R</i> _{sigma} = 0.0263]
Data/restraints/parameters	6066/1/417
Goodness-of-fit on <i>F</i> ²	1.019
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0276, <i>wR</i> ₂ = 0.0692
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0300, <i>wR</i> ₂ = 0.0711
Largest diff. peak/hole / e Å ⁻³	1.82/-0.99

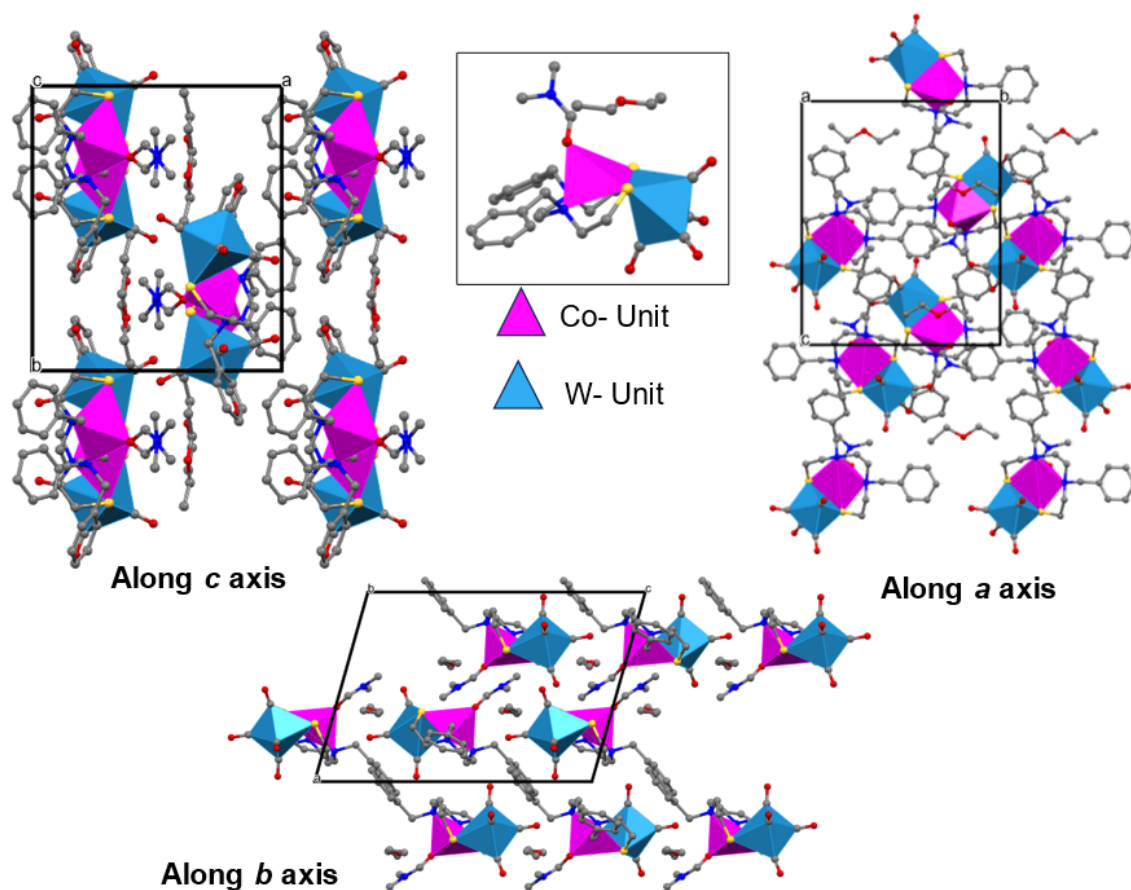


Figure S25. Crystal packing diagram of Complex 3 viewed along *a*, *b*, and *c* axis.

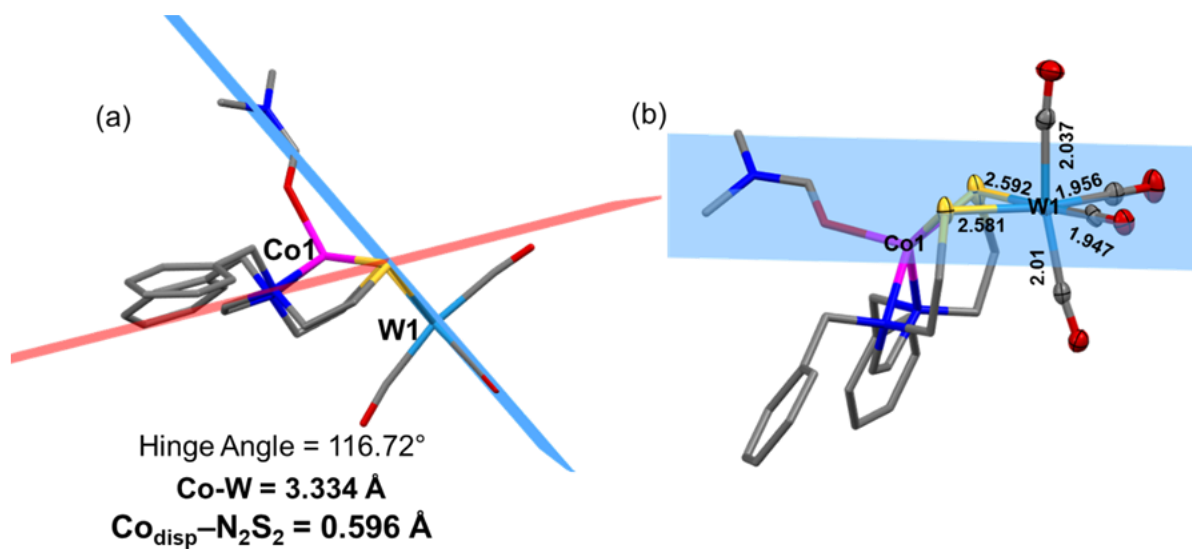


Figure S26. (a) Hinge Angle, displacement of Co from N_2S_2 plane and the M-M distance for Complex 3. (b) Distance of the CO and the S from the W center.

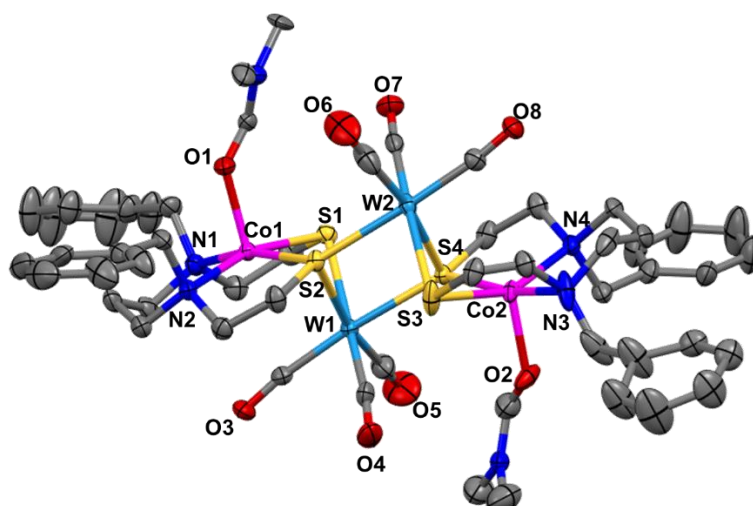


Table S4. Crystal data and structure refinement for Complex 4.

CCDC Number	2302284
Empirical formula	$C_{54}H_{70}Co_2N_6O_8S_4W_2$
Formula weight	1544.96
Temperature/K	110.0
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	24.5425(16)
b/Å	11.5431(8)
c/Å	24.7944(17)
$\alpha/^\circ$	90
$\beta/^\circ$	115.177(3)
$\gamma/^\circ$	90
Volume/Å ³	6356.9(8)
Z	4
$\rho_{\text{calc}}/\text{cm}^3$	1.614
μ/mm^{-1}	12.185
F(000)	3064.0
Crystal size/mm ³	0.3 × 0.3 × 0.2
Radiation	CuK α ($\lambda = 1.54178$)
2 Θ range for data collection/ $^\circ$	4.242 to 133.962
Index ranges	-29 ≤ h ≤ 29, -13 ≤ k ≤ 13, -29 ≤ l ≤ 29
Reflections collected	219133
Independent reflections	11307 [$R_{\text{int}} = 0.0919$, $R_{\text{sigma}} = 0.0270$]
Data/restraints/parameters	11307/1/704
Goodness-of-fit on F ²	1.020
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0308$, $wR_2 = 0.0692$
Final R indexes [all data]	$R_1 = 0.0424$, $wR_2 = 0.0747$
Largest diff. peak/hole / e Å ⁻³	1.39/-0.94

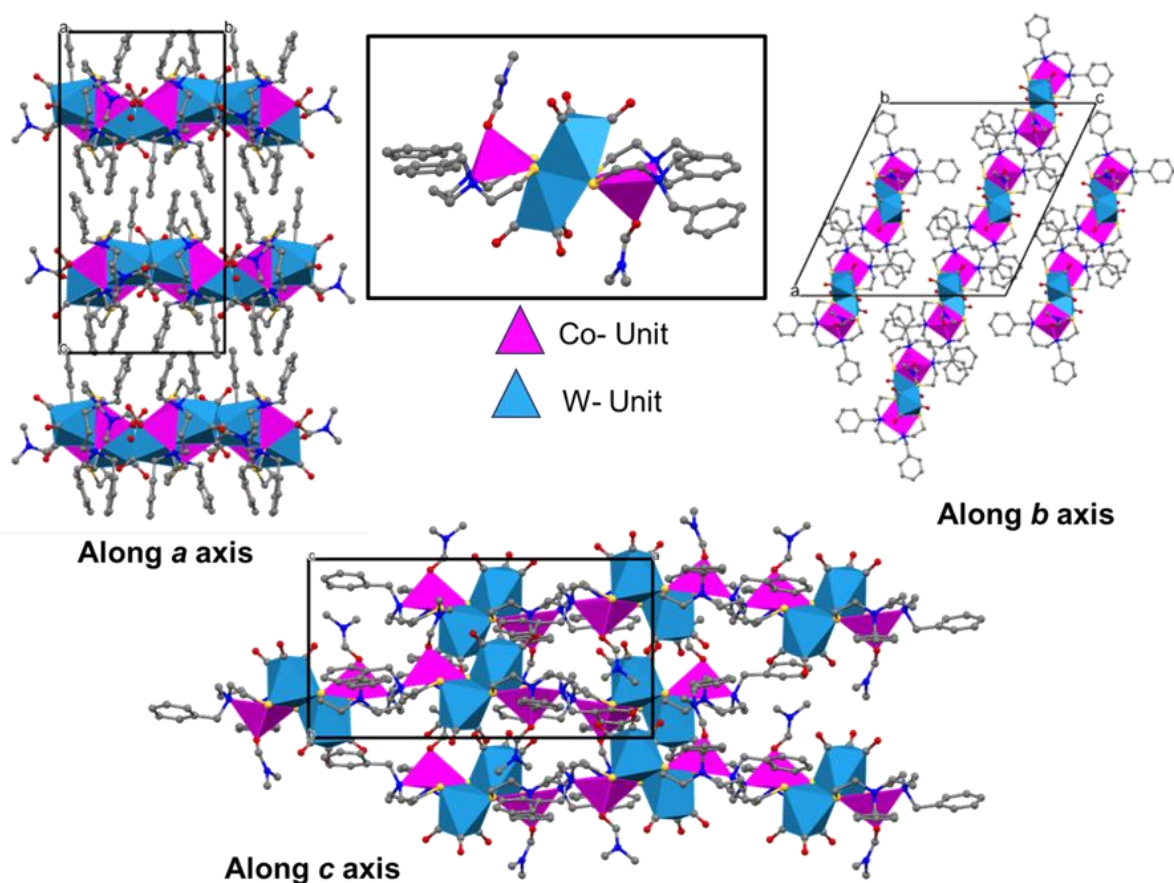


Figure S27. Crystal packing diagram of Complex 4 viewed along *a*, *b*, and *c* axis.

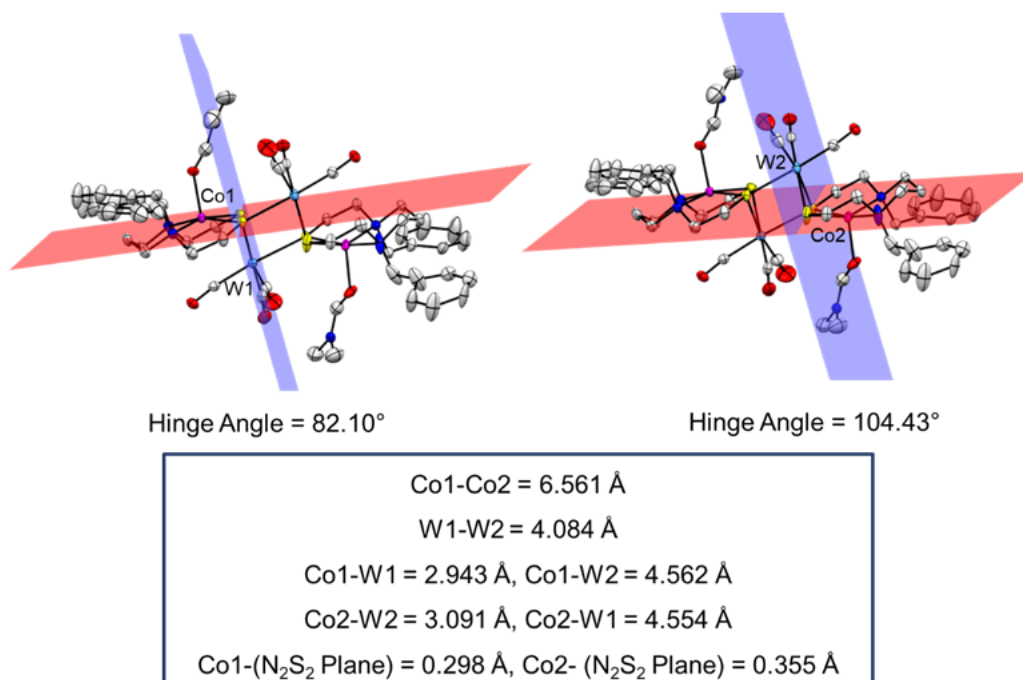


Figure S28. Hinge Angle, displacement of Co from N₂S₂ plane and the M-M distances for Complex 4.

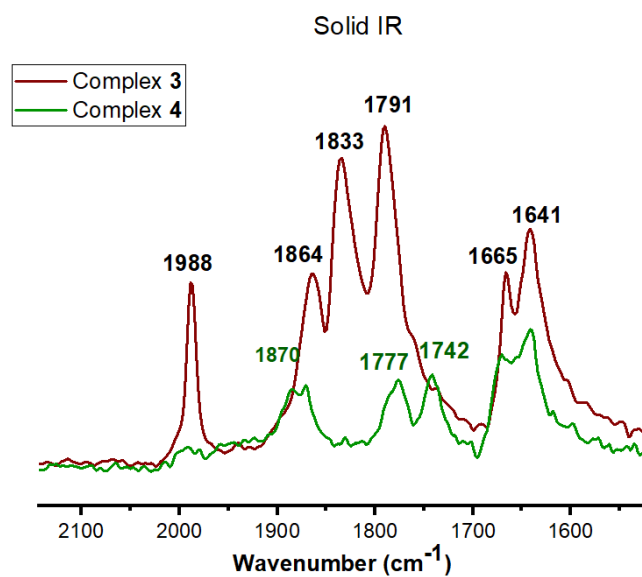


Figure S29: Solid IR (ATR) of complex 3 (brown) and 4 (green). The absorption band at ca. 1641 cm^{-1} is for the coordinated DMF molecule and the band at ca. 1665 cm^{-1} is for the free DMF molecule.

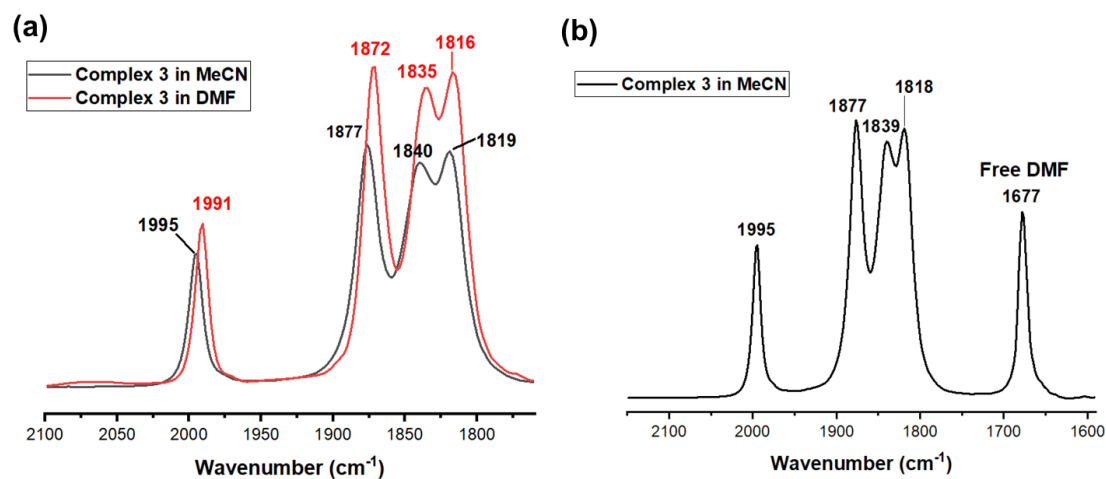


Figure S30: (a) IR spectrum of complex 3 in MeCN (black line) and DMF (red line) solution. (b) In MeCN, the compound loses the coordinated DMF molecule as evident from the IR spectrum (only one band at ca. 1677 cm^{-1} for the free DMF molecule).

Table S5: The $\nu(\text{CO})$ absorption bands for previously reported⁹ C_{2V} symmetric Fe, Co and Ni complexes as well as the complex **3**.

Compound	$\nu(\text{CO})$ (cm^{-1})			
	$\nu(A_1^1)$	$\nu(B_1)$	$\nu(A_1^2)$	$\nu(B_2)$
[Co-1'(NO)]W(CO) ₄	1997	1878	1851	1824
[Fe-1'(NO)]W(CO) ₄	1998	1880	1854	1827
[(bme-daco)Ni]W(CO) ₄	1996	1873	1852	1817
[((ema)Ni)W(CO) ₄] ₂ (Et ₄ N) ₂	1986	1853	1837	1791
(pip) ₂ W(CO) ₄	2000	1863	1852	1809
Complex 3 (DMF)	1991	1872	1835	1816
Complex 3 (MeCN)	1995	1877	1840	1819
Complex 3 (ATR)	1988	1864	1833	1791

Table S6: The $\nu(\text{CO})$ absorption bands for previously reported pseudo C_{3V} symmetric W complexes¹⁰ as well as the complex **4**.

Compound	$\nu(\text{CO})$ (cm^{-1})		
	$\nu(A_1^1)$	Split $\nu(E)$	
fac-[W(CO) ₃ (dppm)(MeCN)]	1930	1837	1823
mer-[W(CO) ₃ (dppm)(PPh ₃)]	1998	1880	1854
mer-[W(CO) ₃ (dppm)(Ph ₂ PCH ₂ -P(O)Ph ₂)]	1996	1873	1852
Complex 4 (DMF)	1885	1784	--
Complex 4 (ATR)	1870	1777	1742

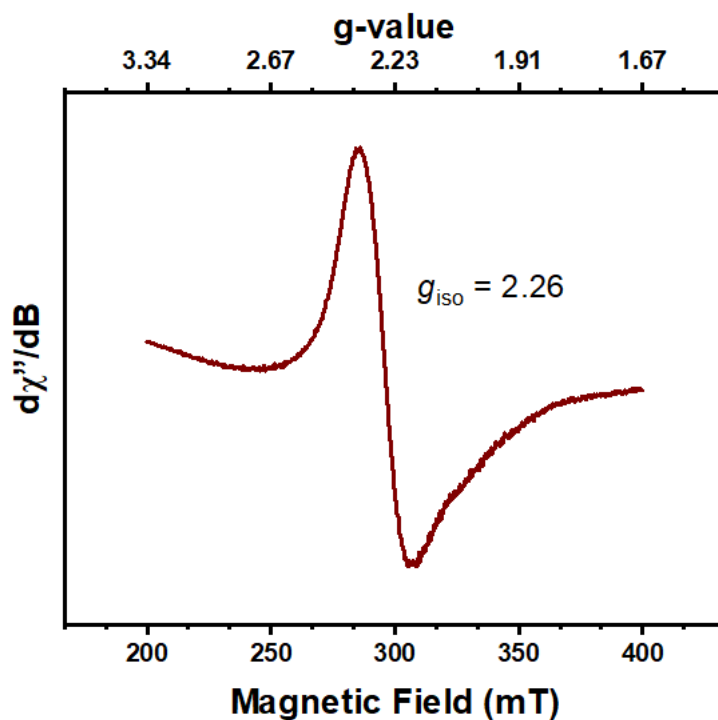


Figure S31: X-band EPR spectrum of Sample 3 in frozen CH_3CN solution at 6 K (Microwave frequency 9.353 GHz). 1 G modulation amplitude; 100 kHz modulation frequency; 39.06 ms conversion time; 6.325 mW microwave power.

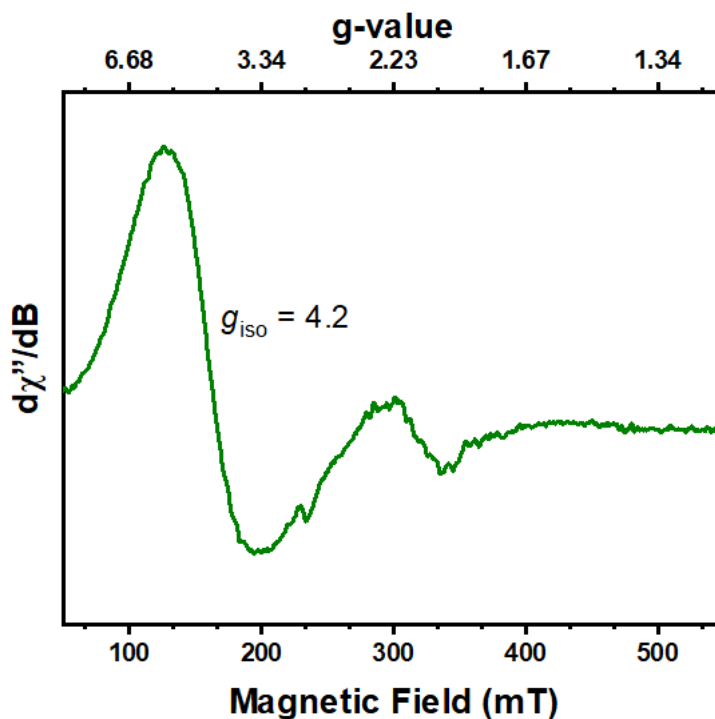


Figure S32: X-band EPR spectrum of Sample 4 in frozen DMF solution at 6 K (Microwave frequency 9.353 GHz). 1 G modulation amplitude; 100 kHz modulation frequency; 39.06 ms conversion time; 6.325 mW microwave power.

Theoretical Computations

Computational methodology. Density functional theory (DFT) calculations were performed in Gaussian 16 Revision B.01¹¹ with the TPSSSTPSS¹² functional. Triple- ζ basis set 6-311++ G(d,p) basis set for Complex 1-3.^{12,13} TPSSSTPSS functional and 6-31G basis set was used for Complex 4. For simplicity of calculation the benzyl groups in complex 4 was replaced with methyl groups. For tungsten an Effective Core Potential (ECP) and a triple- ζ quality basis set (ccpVTZ-PP VTZ-PP) was used for core and valence electrons, respectively.¹⁴ The crystal structure of all the complexes were imported to use as the starting coordinates for gas phase optimization and frequency calculations using GaussView 6.0.16.¹⁵ For calculation of hypothetical tetrahedral complex 1, the coordinates of tetrahedral Zn crystal structure were used as starting point for geometry optimization. The crystal structure of complex 1 was modified by methylene groups between N-to-N connector and was used as starting point for geometry optimization of hypothetical dimeric complex 2. All species were confirmed to be minimum energy structures by the absence of imaginary frequencies.

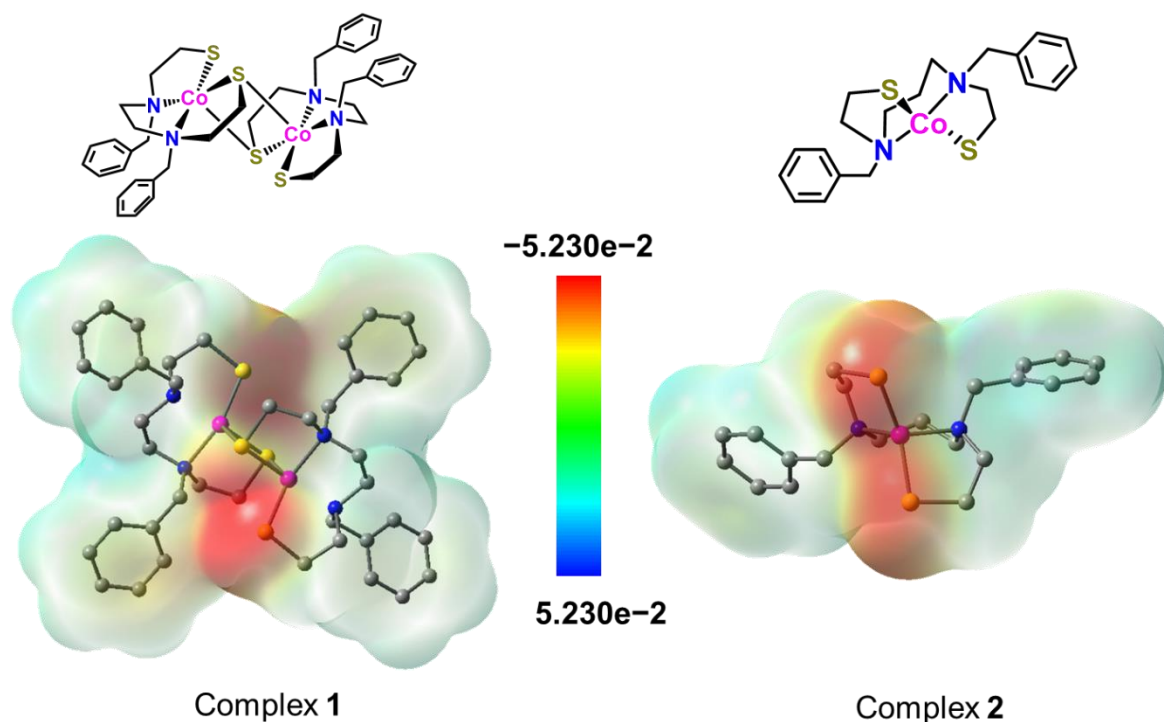


Figure S33. ESP map for Complex 1 (left) and Complex 2 (right) calculated using TPSSSTPSS functional and 6-311++G(d,p) basis set (in gas phase).

Comparison between spin states for hypothetical tetrahedral structure of Complex 1

The hypothetical tetrahedral structure for complex 1 shows quartet as the ground state. The energy difference (E_e) between the quartet and doublet spin state is found to be 10.05 kcal/mol in favour of the quartet ground state in smd model (solvent = *N,N'*-Dimethylformamide). Also, the doublet spin state displays a much larger \angle S-Co-S angle of ca. 149° .

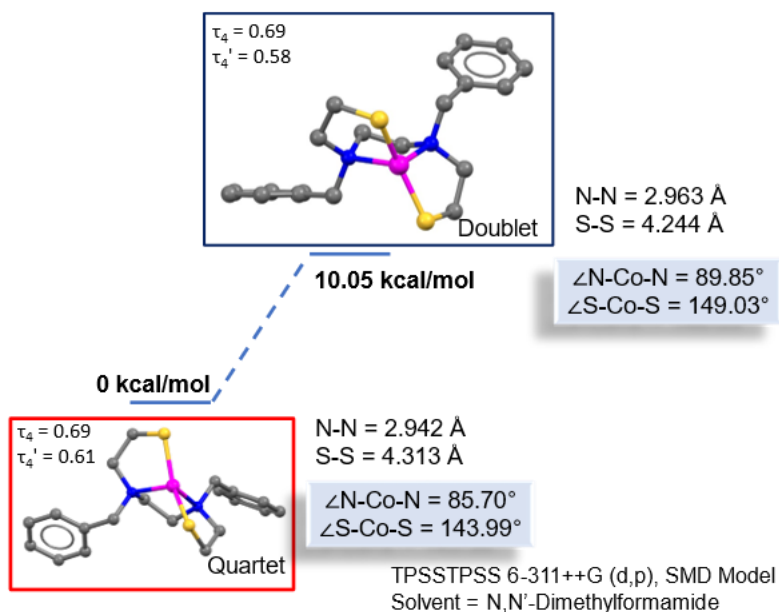


Figure S34: Electronic energy difference (as obtained from DFT) between doublet and quartet spin states for hypothetical tetrahedral structure of complex **1**.

Comparison between spin states for tetrahedral structure of Complex 2

The tetrahedral structure for complex **2** shows quartet spin state as the ground state. The energy difference (E_e) between the quartet and doublet spin state is found to be 7.2 kcal/mol in favour of the quartet ground state (in the SMD solvent model, solvent = DCM).

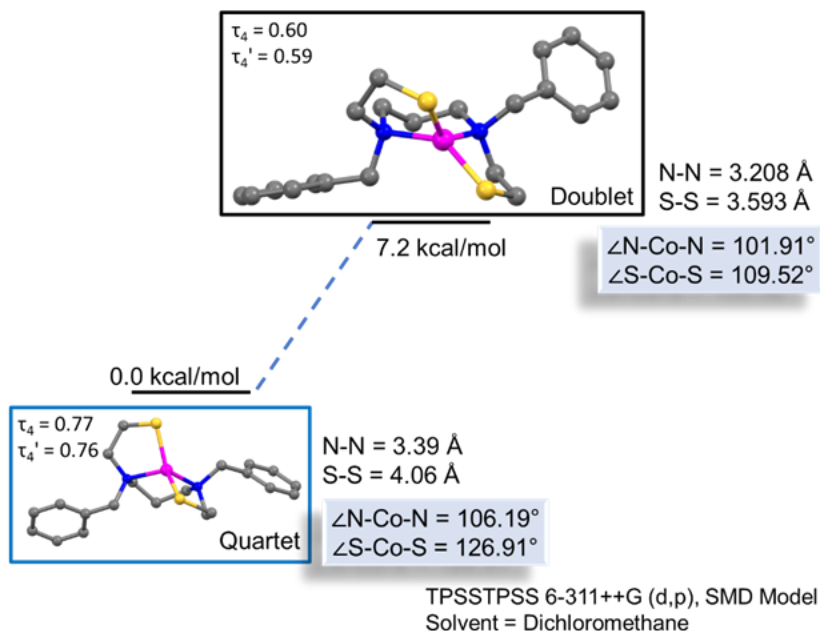


Figure S35: Electronic energy difference (as obtained from DFT) between doublet and quartet spin states for tetrahedral structure of complex **2**.

DFT computation on Complex 3:

DFT optimized structure of complex **3** suggests that doublet is the ground state. The energy difference between doublet and quartet spin state is found to be 6.56 kcal/mol (in smd solvent model, solvent = *N,N'*-dimethylformamide) in favour of the doublet spin state.

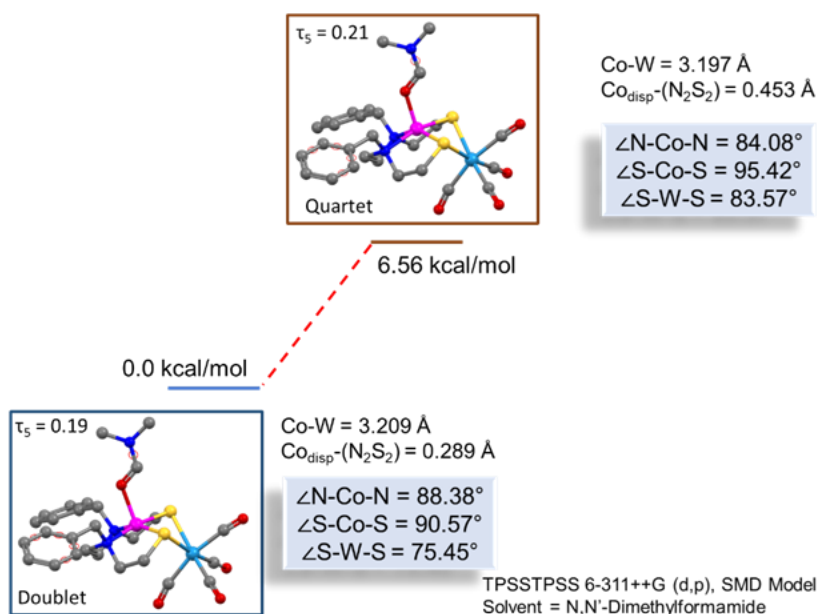


Figure S36: Electronic energy difference (as obtained from DFT) between doublet and quartet spin states for complex **3**.

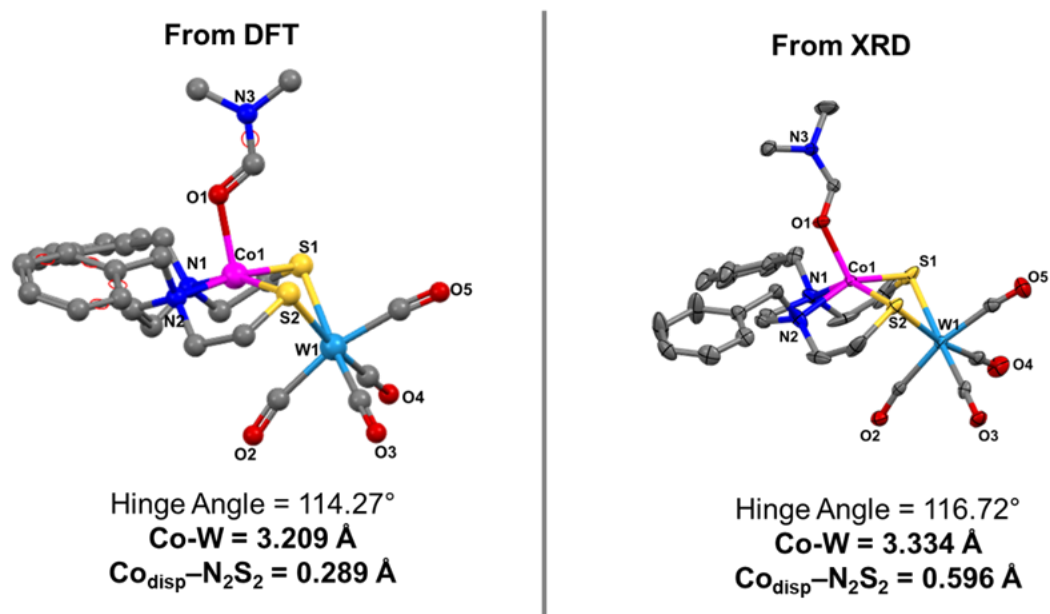


Figure S37: DFT optimized structure (on left) and experimentally determined X-ray structure (on right) of complex **3**.

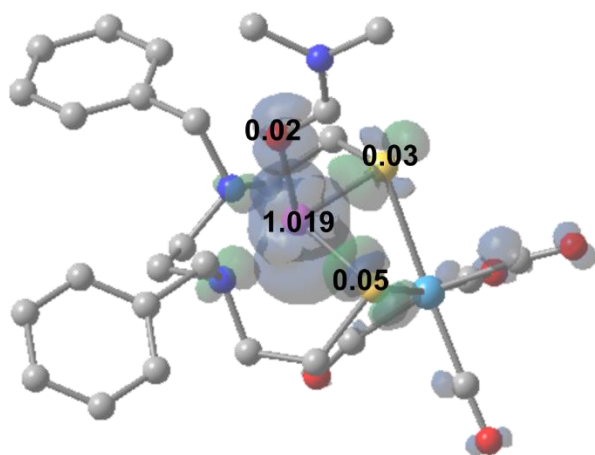
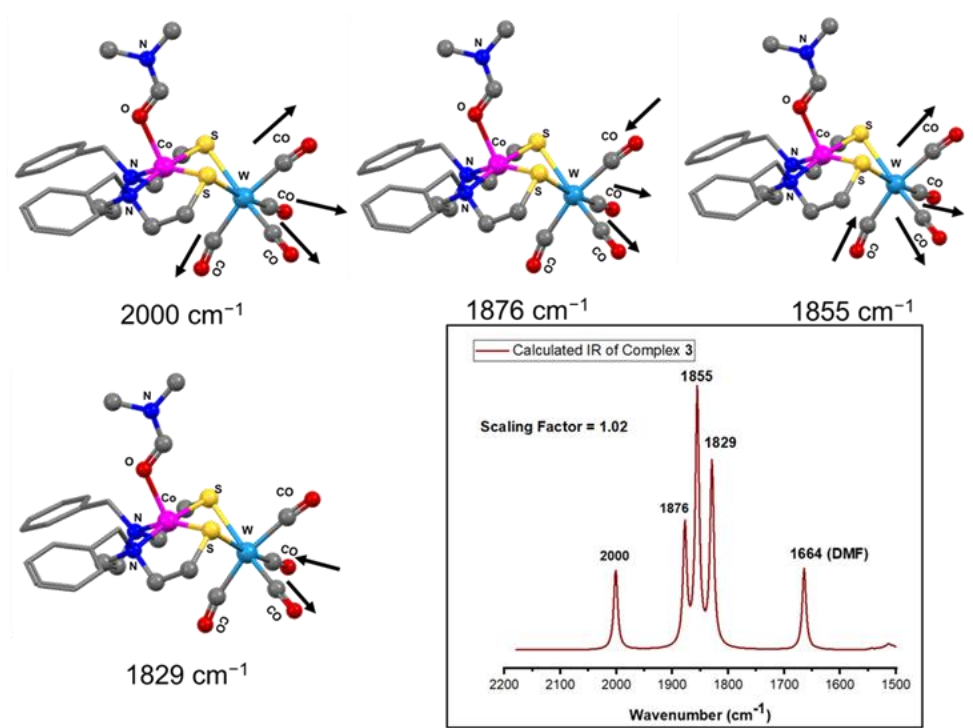


Figure S38. Spin density plot for complex **3**, showing most of the spins are localized on the Co center (iso value = 0.001).



	$\nu(\text{CO})$ (cm^{-1})			
Complex 3	A_1^1	B_1	A_1^2	B_2
Experimental (DMF)	1991	1872	1835	1816
Experimental (Solid)	1988	1864	1833	1791
Calculated (DMF)	2000	1876	1855	1829

Figure S39: $\nu(\text{CO})$ IR stretching frequency of complex **3** obtained from frequency calculation in the SMD solvent model using DMF as a solvent (Scaling factor = 1.02).

DFT Computations on Complex 4:

The crystal structure of complex **4** was imported to use as the starting coordinates for gas phase optimization and frequency calculations using GaussView 6.0.16.¹⁵ Density functional theory (DFT) calculations were performed in Gaussian 16 Revision B.01.09 with the TPSSSTPSS¹¹ functional and 6-31G basis set for Complex **4**. For simplicity of calculation the benzyl groups in complex **4** was replaced with methyl groups. For tungsten an Effective Core Potential (ECP) and a triple- ζ quality basis set (ccpVTZ-PP VTZ-PP) was used for core and valence electrons, respectively.¹⁴ All species were confirmed to be minimum energy structures by the absence of imaginary frequencies.

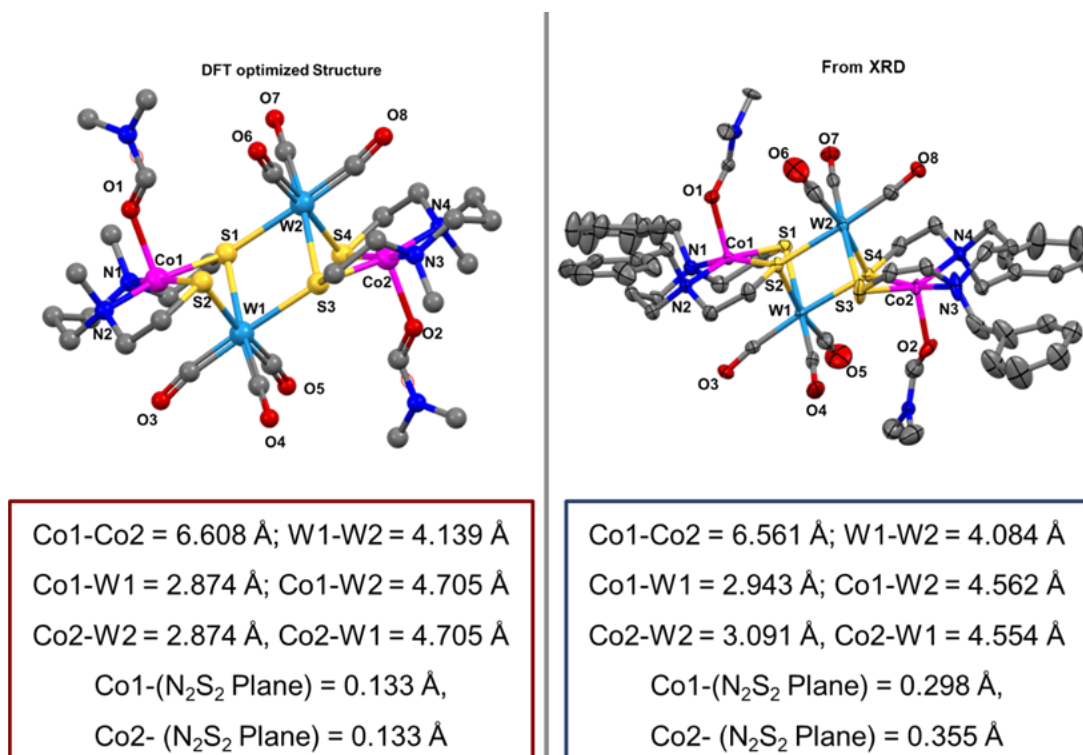
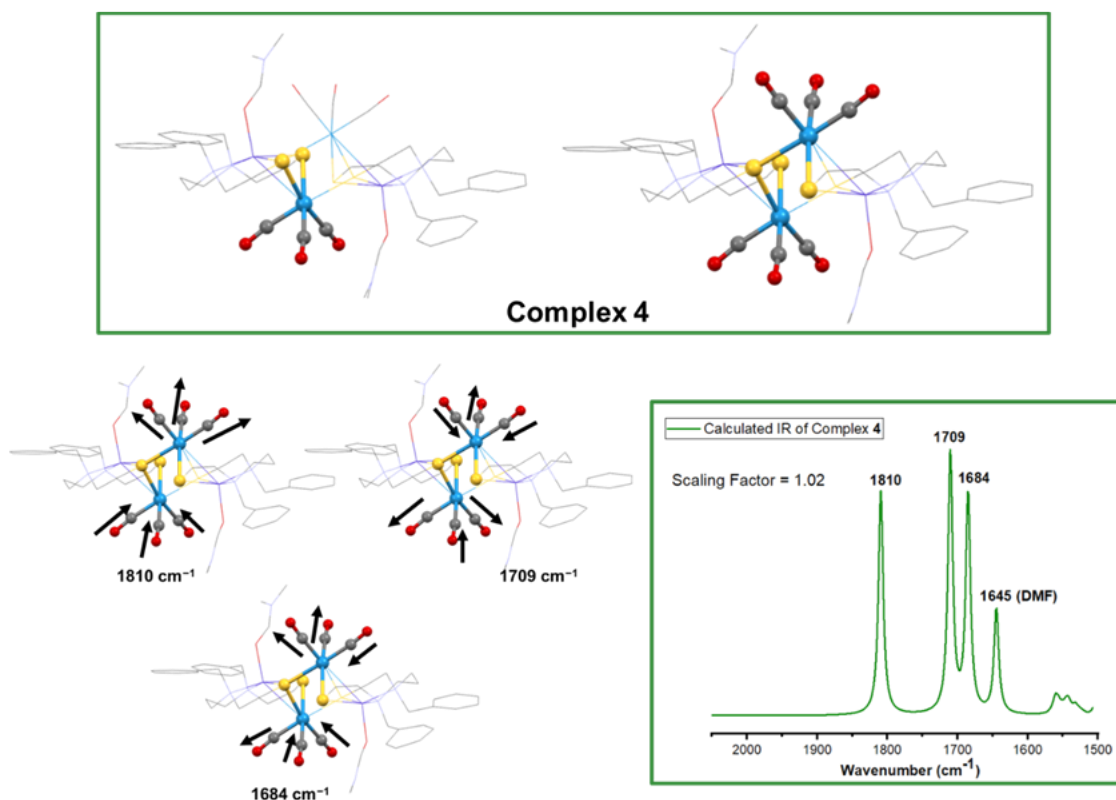


Figure S40: DFT optimized structure (on left) and experimentally determined X-ray structure (on right) of complex **4**.



$\nu(\text{CO})$ (cm^{-1})			
	A_1	Split E	
Experimental IR (DMF)	1870	1784	--
Experimental IR (Solid)	1870	1777	1742
Calculated IR	1810	1709	1684

Figure S41: $\nu(\text{CO})$ IR stretching frequency of complex 4 obtained from frequency calculation in the SMD solvent model using DMF as a solvent (Scaling factor = 1.02). The separation between the peaks (experimental) match with the calculated $\nu(\text{CO})$ IR spectrum.

Coordinates for Complex 1.

0 1

Co	6.99550000	8.03810000	5.91450000
S	6.38930000	5.82620000	5.04100000
S	6.00910000	9.25820000	4.27590000
N	8.94880000	7.18290000	6.22130000
N	8.18350000	9.96040000	6.37800000
C	9.95270000	8.28740000	5.95110000
H	10.85420000	7.98750000	6.22960000
H	9.97990000	8.47710000	4.97950000
C	8.00140000	5.05990000	5.24080000
H	8.02480000	4.56650000	6.09920000
H	8.14670000	4.40810000	4.51060000
C	9.59470000	9.52540000	6.68610000
H	10.22330000	10.24900000	6.43390000
H	9.68590000	9.36760000	7.65860000
C	7.61770000	10.80850000	7.46820000
H	7.64410000	10.29720000	8.31610000
H	6.66720000	10.99880000	7.26350000
C	10.38820000	6.13170000	8.06100000
C	6.79550000	10.88350000	4.53180000
H	6.84760000	11.37090000	3.67150000
H	6.25600000	11.42300000	5.16200000
C	8.19530000	10.68170000	5.09330000
H	8.73670000	10.17230000	4.44030000
H	8.62390000	11.56450000	5.22160000
C	10.59690000	4.78320000	7.89510000
H	9.94150000	4.25280000	7.45720000
C	8.34740000	12.12970000	7.67060000
C	9.13170000	6.09760000	5.22510000
H	9.99180000	5.63930000	5.40480000
H	9.18840000	6.49770000	4.32070000
C	11.36130000	6.86110000	8.71510000
H	11.23340000	7.79490000	8.83740000
C	9.41720000	12.25100000	8.51140000
H	9.71120000	11.48570000	8.99230000
C	9.04220000	6.71660000	7.62490000
H	8.34580000	6.02800000	7.76920000
H	8.83110000	7.47930000	8.21890000
C	12.49650000	6.28300000	9.18770000
H	13.14290000	6.81430000	9.63810000
C	11.77720000	4.18870000	8.37040000
H	11.91520000	3.25870000	8.23810000
C	12.72380000	4.91810000	9.01670000
H	13.51700000	4.51030000	9.34240000
C	10.09670000	13.45910000	8.68770000
H	10.87170000	13.49970000	9.23460000
C	7.91590000	13.24910000	7.01640000
H	7.18900000	13.18670000	6.40880000
C	9.62980000	14.57850000	8.06620000
H	10.05330000	15.41850000	8.20280000
C	8.52960000	14.47220000	7.22930000
H	8.19100000	15.24830000	6.79760000
Co	5.27850000	5.59690000	7.14180000
S	5.88470000	7.80880000	8.01530000
S	6.26490000	4.37680000	8.78040000

N	3.32520000	6.45210000	6.83500000
N	4.09050000	3.67460000	6.67830000
C	2.32130000	5.34760000	7.10520000
H	1.41980000	5.64750000	6.82670000
H	2.29400000	5.15790000	8.07680000
C	4.27260000	8.57510000	7.81550000
H	4.24920000	9.06850000	6.95710000
H	4.12730000	9.22690000	8.54570000
C	2.67930000	4.10960000	6.37020000
H	2.05070000	3.38600000	6.62240000
H	2.58800000	4.26740000	5.39770000
C	4.65620000	2.82650000	5.58810000
H	4.62990000	3.33780000	4.74020000
H	5.60670000	2.63620000	5.79270000
C	1.88580000	7.50330000	4.99530000
C	5.47850000	2.75150000	8.52440000
H	5.42640000	2.26410000	9.38480000
H	6.01790000	2.21200000	7.89430000
C	4.07860000	2.95330000	7.96300000
H	3.53730000	3.46270000	8.61600000
H	3.65010000	2.07050000	7.83460000
C	1.67710000	8.85180000	5.16110000
H	2.33250000	9.38220000	5.59910000
C	3.92660000	1.50530000	5.38570000
C	3.14230000	7.53740000	7.83120000
H	2.28220000	7.99570000	7.65140000
H	3.08560000	7.13730000	8.73550000
C	0.91260000	6.77390000	4.34120000
H	1.04050000	5.84010000	4.21890000
C	2.85680000	1.38400000	4.54490000
H	2.56280000	2.14930000	4.06400000
C	3.23180000	6.91840000	5.43140000
H	3.92820000	7.60700000	5.28710000
H	3.44290000	6.15570000	4.83740000
C	-0.22250000	7.35200000	3.86860000
H	-0.86890000	6.82070000	3.41810000
C	0.49680000	9.44630000	4.68590000
H	0.35880000	10.37630000	4.81820000
C	-0.44980000	8.71690000	4.03960000
H	-1.24300000	9.12470000	3.71380000
C	2.17720000	0.17590000	4.36860000
H	1.40230000	0.13530000	3.82170000
C	4.35810000	0.38590000	6.03980000
H	5.08490000	0.44830000	6.64750000
C	2.64420000	-0.94350000	4.99010000
H	2.22070000	-1.78350000	4.85350000
C	3.74440000	-0.83720000	5.82700000
H	4.08300000	-1.61330000	6.25870000

Coordinates for hypothetical tetrahedral structure of Complex **1**.

0 4

S	5.42090000	-1.72720000	6.12770000
N	7.81260000	0.33950000	6.39080000
C	7.46100000	-0.48290000	7.57920000
H	6.78660000	-0.00030000	8.12000000
H	8.26800000	-0.60570000	8.13940000
C	9.01060000	2.11920000	7.75910000

C	6.90790000	-1.84860000	7.19370000
H	6.67690000	-2.34860000	8.01640000
H	7.60870000	-2.35860000	6.71540000
C	9.02230000	-0.18700000	5.70740000
H	9.04900000	-1.17250000	5.79770000
H	9.83230000	0.18250000	6.14040000
C	7.93720000	1.79170000	6.74400000
H	7.06650000	2.10450000	7.09630000
H	8.12310000	2.30090000	5.91550000
C	10.29740000	2.46810000	7.34950000
H	10.49350000	2.51340000	6.42100000
C	8.74490000	2.09140000	9.13320000
H	7.86890000	1.88460000	9.43730000
C	11.02090000	2.68880000	9.63210000
H	11.70430000	2.86990000	10.26670000
C	11.29900000	2.75100000	8.27080000
H	12.16970000	2.98570000	7.97190000
C	9.74640000	2.36250000	10.05910000
H	9.55440000	2.32340000	10.98870000
S	5.42090000	1.72720000	3.80860000
N	7.81260000	-0.33950000	3.54550000
C	7.46100000	0.48290000	2.35710000
H	6.78660000	0.00030000	1.81630000
H	8.26800000	0.60570000	1.79690000
C	9.01060000	-2.11920000	2.17720000
C	6.90790000	1.84860000	2.74260000
H	6.67690000	2.34860000	1.91990000
H	7.60870000	2.35860000	3.22090000
C	9.02230000	0.18700000	4.22890000
H	9.04900000	1.17250000	4.13860000
H	9.83230000	-0.18250000	3.79590000
C	7.93720000	-1.79170000	3.19230000
H	7.06650000	-2.10450000	2.84000000
H	8.12310000	-2.30090000	4.02080000
C	10.29740000	-2.46810000	2.58680000
H	10.49350000	-2.51340000	3.51530000
C	8.74490000	-2.09140000	0.80310000
H	7.86890000	-1.88460000	0.49900000
C	11.02090000	-2.68880000	0.30420000
H	11.70430000	-2.86990000	-0.33040000
C	11.29900000	-2.75100000	1.66550000
H	12.16970000	-2.98570000	1.96440000
C	9.74640000	-2.36250000	-0.12280000
H	9.55440000	-2.32340000	-1.05240000
Co	6.24280000	0.00000000	4.96820000

Coordinates for Complex 2.

0 4

Co	7.31610000	10.34590000	8.89510000
S	9.54280000	10.22580000	9.13320000
S	6.15730000	10.28670000	6.96740000
N	6.31640000	12.06860000	9.54390000
N	7.01070000	8.95650000	10.43500000
C	6.68620000	14.60400000	9.45940000
C	7.21420000	13.21040000	9.16710000
H	7.40410000	13.14820000	8.19750000
H	8.07430000	13.09870000	9.64440000

C	5.84480000	17.22940000	9.94950000
H	5.55940000	18.11920000	10.12110000
C	5.03990000	12.08890000	8.78100000
H	4.60070000	12.96720000	8.90760000
H	4.43550000	11.39270000	9.14180000
C	5.82360000	15.25720000	8.57600000
H	5.52170000	14.80640000	7.79630000
C	5.55780000	7.04860000	11.27870000
C	5.40130000	16.55840000	8.82310000
H	4.80760000	16.98760000	8.21810000
C	7.12800000	15.28790000	10.58300000
H	7.72110000	14.86310000	11.19150000
C	6.78190000	9.74610000	11.67540000
H	7.61890000	10.22530000	11.89840000
H	6.59480000	9.11590000	12.41560000
C	5.24750000	11.84580000	7.29230000
H	5.75350000	12.60420000	6.90640000
H	4.36630000	11.80800000	6.84290000
C	5.86360000	8.01340000	10.15560000
H	6.07310000	7.49310000	9.33990000
H	5.05210000	8.54880000	9.96870000
C	6.70760000	16.59230000	10.82340000
H	7.01640000	17.05050000	11.59620000
C	6.27660000	5.85620000	11.40140000
H	6.91750000	5.61820000	10.74190000
C	6.03150000	12.11030000	11.00960000
H	5.29570000	12.75260000	11.17120000
H	6.83420000	12.45020000	11.47890000
C	8.28070000	8.17900000	10.55420000
H	8.32030000	7.51980000	9.81660000
H	8.26610000	7.67510000	11.40620000
C	5.64640000	10.76550000	11.61360000
H	4.90530000	10.38100000	11.08140000
H	5.30770000	10.91710000	12.53140000
C	9.53780000	9.03260000	10.51380000
H	10.32690000	8.44050000	10.43080000
H	9.61920000	9.52710000	11.36750000
C	6.05500000	5.02160000	12.48400000
H	6.55740000	4.21960000	12.56810000
C	4.58720000	7.34370000	12.22950000
H	4.06930000	8.13540000	12.14290000
C	5.10980000	5.34080000	13.44620000
H	4.97490000	4.77190000	14.19510000
C	4.36770000	6.49370000	13.30360000
H	3.70100000	6.70770000	13.94560000

Coordinates for hypothetical dimeric Complex 2

0 1

Co	-1.39770000	0.19510000	0.98970000
S	0.80000000	-0.32290000	1.27140000
S	-1.25440000	1.42280000	2.83000000
N	-3.39680000	0.83210000	0.82350000
N	-1.81650000	-2.00910000	1.12520000
C	-2.86440000	2.32680000	2.78090000
H	-3.55330000	1.93720000	3.54050000
H	-2.68440000	3.38180000	3.01890000
C	-4.29740000	-1.51450000	1.34130000
H	-5.18280000	-1.94510000	1.83040000

H	-4.43360000	-1.69310000	0.26800000
C	-4.29760000	-0.01880000	1.66980000
H	-5.32070000	0.38170000	1.59420000
H	-3.95850000	0.10600000	2.70200000
C	-3.45540000	2.23590000	1.38030000
H	-4.50130000	2.58540000	1.36540000
H	-2.86640000	2.85750000	0.69690000
C	0.66860000	-2.17160000	1.43880000
H	0.87010000	-2.62430000	0.46090000
H	1.42870000	-2.51540000	2.15150000
C	-3.89260000	0.86750000	-0.61250000
H	-3.20130000	1.52450000	-1.14300000
H	-3.75070000	-0.13470000	-1.02330000
C	-1.83510000	-2.65530000	-0.24390000
H	-2.62040000	-2.15000000	-0.81410000
H	-0.88750000	-2.39610000	-0.72830000
C	-0.70470000	-2.54010000	1.97350000
H	-0.79820000	-3.63470000	2.08440000
H	-0.83050000	-2.08040000	2.95990000
C	-3.07750000	-2.26540000	1.87620000
H	-2.89370000	-1.93540000	2.90570000
H	-3.28320000	-3.34810000	1.90640000
Co	1.39780000	-0.19530000	-0.98970000
S	-0.79990000	0.32240000	-1.27140000
S	1.25470000	-1.42320000	-2.82990000
N	3.39710000	-0.83200000	-0.82340000
N	1.81630000	2.00890000	-1.12530000
C	2.86490000	-2.32680000	-2.78080000
H	3.55380000	-1.93700000	-3.54030000
H	2.68520000	-3.38180000	-3.01880000
C	4.29730000	1.51470000	-1.34120000
H	5.18270000	1.94540000	-1.83020000
H	4.43330000	1.69340000	-0.26790000
C	4.29770000	0.01900000	-1.66970000
H	5.32090000	-0.38130000	-1.59400000
H	3.95870000	-0.10590000	-2.70190000
C	3.45590000	-2.23570000	-1.38020000
H	4.50180000	-2.58510000	-1.36520000
H	2.86690000	-2.85750000	-0.69680000
C	-0.66880000	2.17120000	-1.43920000
H	-0.87050000	2.62400000	-0.46140000
H	-1.42880000	2.51470000	-2.15210000
C	3.89290000	-0.86730000	0.61260000
H	3.20160000	-1.52440000	1.14310000
H	3.75070000	0.13480000	1.02340000
C	1.83480000	2.65520000	0.24390000
H	2.62000000	2.15010000	0.81410000
H	0.88710000	2.39590000	0.72820000
C	0.70450000	2.53980000	-1.97370000
H	0.79790000	3.63440000	-2.08470000
H	0.83050000	2.08010000	-2.96010000
C	3.07740000	2.26540000	-1.87620000
H	2.89370000	1.93540000	-2.90570000
H	3.28280000	3.34810000	-1.90640000
C	-2.05640000	-4.15950000	-0.28300000
C	-0.97060000	-5.05210000	-0.24200000
C	-3.35070000	-4.70000000	-0.38660000
C	-1.17100000	-6.43570000	-0.27750000
H	0.04260000	-4.65700000	-0.20590000
C	-3.55780000	-6.08270000	-0.42400000

H	-4.20640000	-4.02990000	-0.45740000
C	-2.46680000	-6.95610000	-0.36260000
H	-0.31530000	-7.10710000	-0.25060000
H	-4.56810000	-6.47740000	-0.50990000
H	-2.62410000	-8.03180000	-0.39510000
C	2.05590000	4.15940000	0.28280000
C	0.97000000	5.05200000	0.24140000
C	3.35010000	4.70000000	0.38670000
C	1.17030000	6.43550000	0.27680000
H	-0.04320000	4.65680000	0.20490000
C	3.55710000	6.08280000	0.42410000
H	4.20580000	4.03000000	0.45790000
C	2.46610000	6.95610000	0.36230000
H	0.31460000	7.10700000	0.24950000
H	4.56740000	6.47750000	0.51030000
H	2.62340000	8.03180000	0.39470000
C	5.32050000	-1.33960000	0.84750000
C	5.59320000	-2.69770000	1.09140000
C	6.39400000	-0.43270000	0.88920000
C	6.89580000	-3.13970000	1.34140000
H	4.77340000	-3.41410000	1.09830000
C	7.69930000	-0.86880000	1.13900000
H	6.20650000	0.62890000	0.73970000
C	7.95510000	-2.22600000	1.35990000
H	7.08220000	-4.19470000	1.53040000
H	8.51360000	-0.14820000	1.17010000
H	8.96860000	-2.56680000	1.55820000
C	-5.32020000	1.34000000	-0.84730000
C	-5.59280000	2.69810000	-1.09110000
C	-6.39380000	0.43320000	-0.88890000
C	-6.89530000	3.14030000	-1.34100000
H	-4.77290000	3.41430000	-1.09810000
C	-7.69910000	0.86950000	-1.13870000
H	-6.20650000	-0.62850000	-0.73950000
C	-7.95470000	2.22670000	-1.35960000
H	-7.08160000	4.19520000	-1.53010000
H	-8.51350000	0.14900000	-1.16970000
H	-8.96830000	2.56760000	-1.55780000

Coordinates for Complex 3

0 2

W	0.06020000	0.77020000	12.29770000
Co	1.16090000	2.84830000	9.93420000
S	1.38000000	2.98800000	12.26080000
S	1.22270000	0.51590000	9.99440000
O	2.69340000	3.63330000	8.87720000
O	-2.85360000	1.63190000	11.42230000
O	-1.18660000	1.13070000	15.13350000
N	0.08270000	4.72470000	10.10180000
O	-1.07670000	-2.11750000	11.99730000
N	-0.19200000	2.57090000	8.22420000
N	4.50400000	3.54610000	7.53940000
O	2.51810000	-0.54350000	13.82260000
C	3.62450000	3.01120000	8.35130000
H	3.70830000	2.08580000	8.55040000
C	0.42570000	7.24910000	10.13580000
C	-1.74880000	1.38500000	11.67320000

C	-0.69520000	1.00420000	14.07690000
C	1.03650000	5.86700000	10.05340000
H	1.55240000	5.80580000	9.21080000
H	1.67850000	5.76690000	10.80090000
C	-0.66440000	-1.03910000	12.12780000
C	0.22110000	7.88120000	11.33670000
H	0.42740000	7.43220000	12.14700000
C	0.59730000	2.53460000	6.95880000
H	1.29930000	1.84150000	7.04750000
H	1.05370000	3.40630000	6.84970000
C	0.26350000	4.40060000	12.55200000
H	-0.29550000	4.21090000	13.34640000
H	0.80600000	5.20470000	12.74820000
C	-0.28680000	9.17760000	11.37250000
H	-0.40970000	9.60900000	12.21090000
C	-0.19810000	2.25120000	5.70240000
C	4.46400000	4.94990000	7.18430000
H	3.67720000	5.36830000	7.59200000
H	4.41260000	5.03910000	6.20940000
H	5.27520000	5.39250000	7.51010000
C	1.68200000	-0.04650000	13.21780000
C	-0.63940000	4.69130000	11.37250000
H	-1.34320000	3.99680000	11.32600000
H	-1.08400000	5.56420000	11.51430000
C	-0.61060000	9.83740000	10.22350000
H	-0.95220000	10.72310000	10.25690000
C	-0.01300000	0.14820000	8.71460000
H	0.45330000	-0.10730000	7.87960000
H	-0.55800000	-0.62580000	9.00540000
C	-0.33660000	0.94900000	5.23700000
H	0.11540000	0.24040000	5.67960000
C	-0.91250000	1.29200000	8.43360000
H	-1.54020000	1.39940000	9.19200000
H	-1.44660000	1.08930000	7.62610000
C	-0.81240000	3.27860000	4.99900000
H	-0.69610000	4.17870000	5.27900000
C	0.09980000	7.92780000	8.98490000
H	0.24490000	7.51230000	8.14250000
C	-1.12990000	0.67580000	4.13270000
H	-1.22800000	-0.21740000	3.82640000
C	5.57800000	2.78310000	6.95170000
H	5.54290000	1.86010000	7.28080000
H	6.43750000	3.18450000	7.19800000
H	5.48510000	2.78460000	5.97570000
C	-0.63910000	4.86420000	8.74330000
H	-1.52840000	5.25090000	8.94000000
H	-0.14100000	5.55260000	8.23430000
C	-0.43970000	9.21250000	9.02960000
H	-0.68730000	9.65240000	8.22510000
C	-1.59760000	2.99670000	3.88930000
H	-2.01600000	3.70290000	3.41110000
C	-1.76980000	1.69890000	3.48300000
H	-2.33730000	1.50770000	2.74640000
C	-0.81170000	4.03150000	8.04700000
H	-0.52120000	4.34990000	7.15550000
H	-1.79300000	3.91220000	7.99520000

Coordinates for complex 4

0 3

W	-0.76330000	3.30110000	10.81170000
Co	-0.19150000	3.87690000	7.95100000
S	-2.27120000	4.30950000	8.98900000
S	-0.38280000	1.68020000	8.82300000
O	-0.89200000	3.71330000	5.98320000
O	0.87930000	1.70910000	12.90400000
O	1.78590000	5.05840000	10.84200000
O	-1.38040000	5.46790000	12.95420000
N	-0.08660000	6.10900000	7.80620000
N	1.88040000	3.39680000	7.54120000
C	1.33230000	6.56910000	7.94280000
H	1.61370000	6.45610000	8.88600000
H	1.37710000	7.53400000	7.72940000
N	-2.61350000	3.99150000	4.55560000
C	1.86740000	2.74980000	6.17190000
H	1.25390000	1.87350000	6.19730000
H	1.47400000	3.43990000	5.45510000
C	0.84720000	4.36340000	10.73360000
C	-0.69100000	6.61160000	6.50320000
H	-0.15440000	6.19440000	5.67680000
H	-1.71750000	6.31480000	6.44830000
C	-1.22950000	4.60820000	12.11690000
C	-0.85670000	6.64850000	8.95870000
H	-0.89090000	7.63530000	8.88620000
H	-0.37810000	6.42440000	9.79550000
C	-2.27550000	6.11280000	9.04500000
H	-2.81070000	6.46730000	8.29150000
H	-2.69390000	6.41750000	9.88940000
C	-2.07820000	3.61420000	5.69810000
H	-2.65600000	3.23560000	6.35060000
C	2.84370000	4.51750000	7.61950000
H	3.66450000	4.26990000	7.12320000
H	3.09580000	4.65780000	8.56640000
C	2.29970000	5.82590000	7.05330000
H	3.06470000	6.42270000	6.85650000
H	1.84750000	5.62990000	6.19470000
C	0.24490000	2.27820000	12.09690000
C	2.28630000	2.41920000	8.55720000
H	2.33750000	2.87960000	9.43210000
H	3.19610000	2.09720000	8.33680000
C	1.37010000	1.21110000	8.70170000
H	1.62630000	0.70430000	9.51300000
H	1.49250000	0.61520000	7.92080000
C	-1.80800000	4.60180000	3.51160000
H	-0.88730000	4.70250000	3.82500000
H	-2.17630000	5.49060000	3.29740000
H	-1.82840000	4.04260000	2.71150000
C	-4.02760000	3.83730000	4.31870000
H	-4.16370000	3.26120000	3.53430000
H	-4.43350000	4.70850000	4.16170000
H	-4.44280000	3.41410000	5.10270000
W	-4.51340000	3.03250000	9.26610000
Co	-5.08520000	2.45680000	12.12680000
S	-3.00550000	2.02410000	11.08880000
S	-4.89390000	4.65350000	11.25480000
O	-4.38470000	2.62030000	14.09460000
O	-6.15600000	4.62450000	7.17380000

O	-7.06260000	1.27530000	9.23580000
O	-3.89630000	0.86570000	7.12360000
N	-5.19010000	0.22460000	12.27150000
N	-7.15700000	2.93690000	12.53660000
C	-6.60900000	-0.23550000	12.13500000
H	-6.89040000	-0.12250000	11.19170000
H	-6.65380000	-1.20030000	12.34840000
N	-2.66320000	2.34210000	15.52210000
C	-7.14410000	3.58390000	13.90590000
H	-6.53060000	4.46020000	13.88050000
H	-6.75070000	2.89380000	14.62280000
C	-6.12390000	1.97020000	9.34420000
C	-4.58570000	-0.27790000	13.57460000
H	-5.12230000	0.13940000	14.40090000
H	-3.55910000	0.01890000	13.62940000
C	-4.04710000	1.72540000	7.96080000
C	-4.42000000	-0.31490000	11.11910000
H	-4.38580000	-1.30170000	11.19160000
H	-4.89860000	-0.09070000	10.28230000
C	-3.00120000	0.22090000	11.03270000
H	-2.46600000	-0.13360000	11.78630000
H	-2.58280000	-0.08390000	10.18840000
C	-3.19850000	2.71940000	14.37970000
H	-2.62070000	3.09800000	13.72720000
C	-8.12040000	1.81610000	12.45830000
H	-8.94120000	2.06380000	12.95460000
H	-8.37250000	1.67590000	11.51130000
C	-7.57640000	0.50770000	13.02450000
H	-8.34140000	-0.08900000	13.22130000
H	-7.12420000	0.70370000	13.88310000
C	-5.52160000	4.05550000	7.98090000
C	-7.56300000	3.91440000	11.52060000
H	-7.61420000	3.45400000	10.64570000
H	-8.47280000	4.23650000	11.74100000
C	-6.64680000	5.12260000	11.37610000
H	-6.90300000	5.62930000	10.56480000
H	-6.76920000	5.71850000	12.15700000
C	-3.46870000	1.73180000	16.56620000
H	-4.38940000	1.63120000	16.25280000
H	-3.10040000	0.84300000	16.78040000
H	-3.44820000	2.29100000	17.36630000
C	-1.24910000	2.49640000	15.75910000
H	-1.11300000	3.07240000	16.54350000
H	-0.84320000	1.62520000	15.91610000
H	-0.83390000	2.91950000	14.97510000
H	-0.62600000	7.67910000	6.46820000
H	2.86510000	2.47890000	5.89590000
H	-4.65070000	-1.34530000	13.60970000
H	-8.14180000	3.85480000	14.18180000

References

1. D. K. Mills, I. Font, P. J. Farmer, Y.-M. Hsiao, T. Tuntulani, R. M. Buonomo, D. C. Goodman, G. Musie, C. A. Grapperhaus, M. J. Maguire, C.-H. Lai, M. L. Hatley, J. J. Smee, J. A. Bellefeuille, M. Y. Darensbourg, R. D. Hancock, S. Eng and A. E. Martell, in *Inorganic Syntheses*, John Wiley & Sons, Ltd, 1998, pp. 89–98.
2. D. J. Darensbourg and R. L. Kump, *Inorg. Chem.*, 1978, **17**, 2680–2682.
3. Bruker (2019). *APEX3* (v2019.1-0) Bruker AXS Inc., Madison, Wisconsin, USA.
4. Sheldrick, G. M. (2016). *SADABS*. University of Göttingen, Germany.
5. Sheldrick, G., SHELXT - Integrated space-group and crystal-structure determination. *Acta Crystallographica Section A* 2015, **71**, 3-8.
6. Sheldrick, G. M., Crystal structure refinement with SHELXL. *Acta Crystallographica Section C* 2015, **71**, 3-8.
7. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H., OLEX2: a complete structure solution, refinement and analysis program. *Journal of Applied Crystallography* 2009, **42**, 339-341.
8. C. F. Macrae, I. Sovago, S. J. Cottrell, P. T. A. Galek, P. McCabe, E. Pidcock, M. Platings, G. P. Shields, J. S. Stevens, M. Towler and P. A. Wood, *J. Appl. Cryst.*, 2020, **53**, 226-235
9. J. L. Hess, H. L. Conder, K. N. Green and M. Y. Darensbourg, *Inorg. Chem.*, 2008, **47**, 2056–2063.
10. D. J. Darensbourg, D. J. Zalewski, C. Plepys and C. Campana, *Inorg. Chem.*, 1987, **26**, 3727–3732.
11. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, Williams, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, Gaussian Inc., Wallingford, CT, 2016.
12. J. Tao, J. P. Perdew, V. N. Staroverov and G. E. Scuseria, *Phys. Rev. Lett.*, 2003, **91**, 146401.
13. R. Krishnan, J. S. Binkley, R. Seeger and J. A. Pople, *The Journal of Chemical Physics*, 2008, **72**, 650–654.
14. K. A. Peterson, D. Figgen, M. Dolg and H. Stoll, *The Journal of Chemical Physics*, 2007, **126**, 124101.
15. R. Dennington, T. Keith, and J. Millam, Semichem Inc., Shawnee Mission, KS, 2019.