

Supporting Information

Sulfur Insertion into Group 12 Metal Dithiolate Complexes: Metal-Dependent Equilibria

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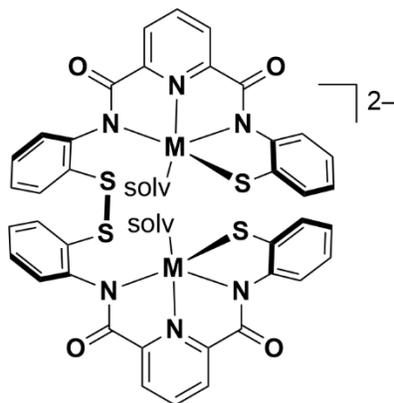
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Experimental Section

General Considerations. Unless otherwise indicated, all commercial chemicals were used without further purification. S_8 was purchased from Beantown Chemicals. 2-Aminothiophenol, Iodomethane (MeI) and tetraethylammonium chloride (Et_4NCl) were purchased from TCI America. $ZnCl_2$, $CdCl_2$, were purchased from Strem Chemicals, and $PbCl_2$ was purchased from J.T. Baker Chemicals Co. and dried under vacuum at 110 °C. $HgCl_2$ was purchased from Mallinckrodt Chemicals and purified by recrystallization.¹ Sodium bis(trimethylsilyl)amide ($NaHMDS$) and ferrocene were purchased from Aldrich. 2,6-lutidine, Johnson Matthey Company, triflic acid, Oakwood Chemicals, Ferrocenium triflate ($FcOTf$),² 2,6-lutidinium triflate,³ H_4L ligand,⁴ and $[Et_4N]_2[1-Zn]$ ⁵ were synthesized according to literature procedures.

UV-vis spectra were obtained using an Agilent Cary 60 spectrophotometer in 1 cm quartz cuvettes. Cyclic voltammetry was performed using a Princeton Applied Research VersaSTAT 4 potentiostat, with voltammograms recorded using a glassy carbon working electrode, a platinum wire counter electrode, and an $Ag/AgNO_3$ reference electrode with 0.1 M TBAPF₆ electrolyte in CH_3CN . Potentials were referenced to the ferrocenium/ferrocene (Fc^+/Fc) couple. A scan rate of 0.1 V/s was used unless otherwise indicated.

Synthetic Procedures



$[Et_4N]_2[5-M(solv)]$ (proposed)

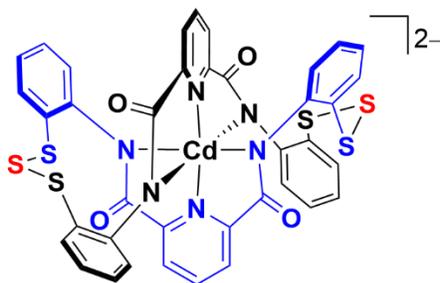
solv = CH_3CN , DMSO

Synthesis of $[Et_4N]_2[5-M]$ ($M = Cd, Hg$). In a representative procedure, in the glovebox, a 20 mL scintillation vial equipped with a stir bar was charged with $[Et_4N]_2[1-Cd]$ (0.200 g, 0.27 mmol, 1 equiv) and CH_3CN (10 mL). A solution of $FcOTf$ (0.089 g, 0.27 mmol, 1 equiv) in CH_3CN (1 mL) was added dropwise to the reaction mixture. During addition, the reaction mixture formed a yellow precipitate. After 30 min, the solvent was removed under vacuum and the residue was washed with THF and cold CH_3CN , then dried in vacuo to yield the product as a yellow solid.

$[Et_4N]_2[5-Cd(solv)]$. Yield: 0.120 g (72%). ¹H NMR (400 MHz, $DMSO-d_6$) δ 8.72 (d, $J = 8.0$ Hz, 2H), 8.30 – 8.09 (m, 6H), 7.47 (d, $J = 7.7$ Hz, 2H), 7.34 (d, $J = 7.7$, 2H), 7.08 (t, $J = 7.7$ Hz, 6H), 6.70 (t, $J = 7.0$ Hz, 2H), 6.52 (t, $J = 7.0$ Hz, 2H), 3.16 (q, $J = 7.2$ Hz, 16H), 1.15 (t, $J = 7.2$

Hz, 24H). ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) δ 163.60, 161.27, 152.05, 149.25, 145.77, 140.70, 138.78, 132.01, 130.61, 125.66, 122.78, 122.46, 121.84, 121.83, 121.25, 119.57, 51.38, 7.03.

$[\text{Et}_4\text{N}]_2[\mathbf{5}\text{-Hg(solv)}]$. Yield: 0.98 g (59%). ^1H NMR (500 MHz, $\text{DMSO-}d_6$) δ 8.78 (d, $J = 8.2$ Hz, 1H), 8.33 – 8.26 (m, 2H), 8.25 – 8.13 (m, 4H), 7.51 (d, $J = 7.8$, 2H), 7.35 (t, $J = 7.8$, 2H), 7.22 (d, $J = 7.0$, 2H), 7.22 (d, $J = 7.0$ Hz, 2H), 6.80 (m, 4H), 3.16 (d, $J = 7.2$ Hz, 16H), 1.12 (t, $J = 7.2$ Hz, 24H). ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) δ 164.13, 162.49, 152.17, 148.93, 147.51, 145.15, 141.18, 131.91, 131.06, 130.29, 127.23, 126.92, 126.06, 124.83, 124.30, 123.51, 123.07, 122.34, 52.11, 7.75.



$[\text{Et}_4\text{N}]_2[\mathbf{7}]$

Synthesis of $[\text{Et}_4\text{N}]_2[\mathbf{7}]$. In the glovebox, a 20 mL scintillation vial equipped with a stir bar was charged with $[\text{Et}_4\text{N}]_2[\mathbf{1}\text{-Cd}]$ (0.427 g, 0.569 mmol, 1 equiv) and CH_3CN (10 mL). S_8 (0.91 g, 2.85 mmol S, 5 S atom equiv) was added to the solution. The vial was removed from the glovebox and the reaction mixture was stirred at 80 °C for 1 h; the color changed from yellow to orange. After 1 h, the mixture was filtered using a fritted glass funnel, and the filtrate was concentrated under vacuum to a volume of 2 mL. The product was crystallized by vapor diffusion of Et_2O into this solution. The yellow crystals were collected by filtration, washed with Et_2O and THF, then dried in vacuo. Yield: 0.240 g (72%). ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 8.08 – 7.90 (m, 6H), 7.56 (dd, $J = 7.8$, 4H), 7.01 (dd, $J = 7.5$, 4H), 6.73 (t, $J = 7.5$ Hz, 4H), 6.62 (t, $J = 7.5$ Hz, 4H), 3.16 (q, $J = 7.2$ Hz, 16H), 1.13 (t, $J = 7.2$ Hz, 24H). ^{13}C NMR (101 MHz, DMSO) δ 162.12, 154.17, 150.56, 139.08, 132.48, 130.90, 130.88, 127.06, 122.87, 121.89, 121.52, 51.40, 7.04. Anal. Calcd. for $\text{C}_{54}\text{H}_{62}\text{N}_8\text{O}_4\text{S}_6\text{Cd}_2$: C, 54.42; H, 5.24; N, 9.40. Found: C, 54.26; H, 5.29; N, 9.45.

NMR Spectra

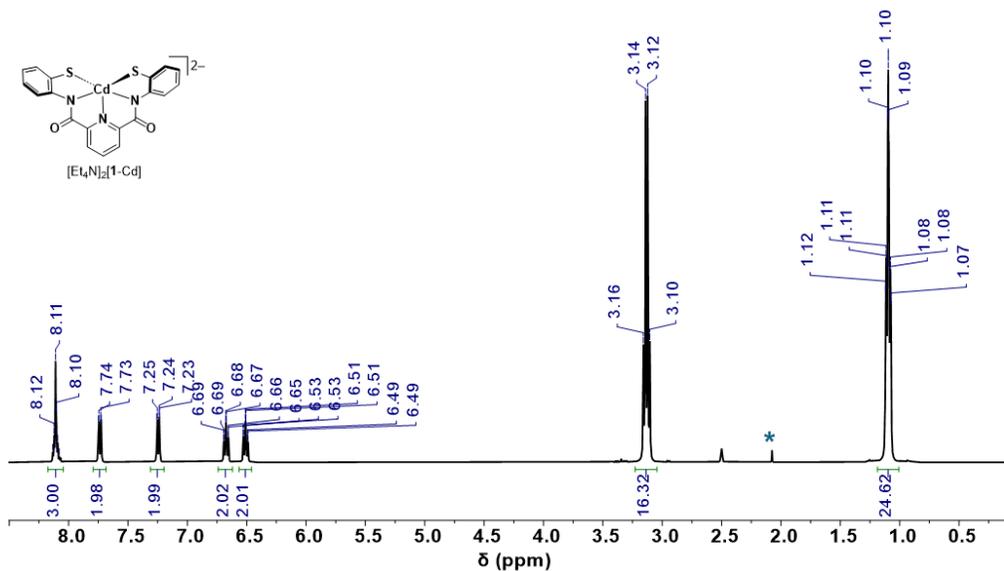


Figure S1. ^1H NMR spectrum of DMSO- d_6 solution of $[\text{Et}_4\text{N}]_2[\mathbf{1}\text{-Cd}]$ at 25 °C. Residual CH_3CN indicated with *.

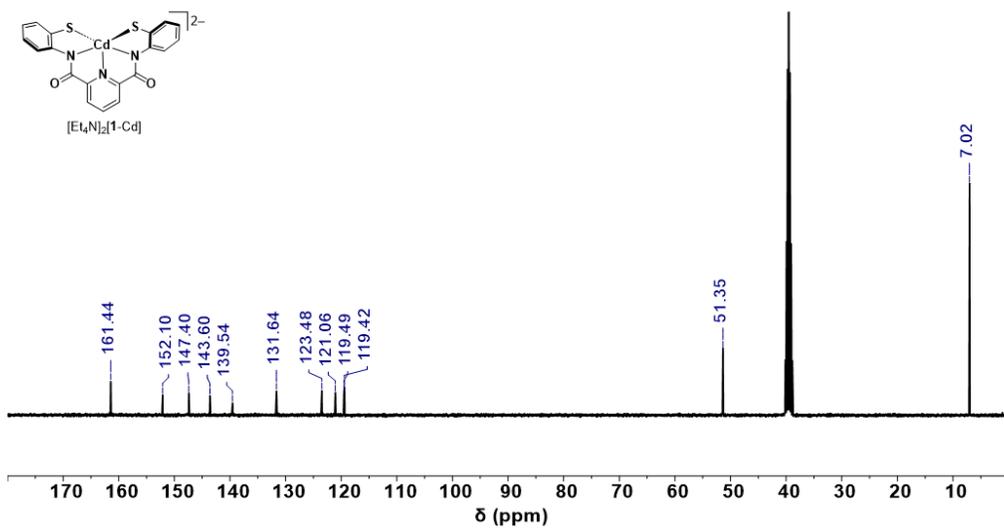


Figure S2. ^{13}C NMR spectrum of a DMSO- d_6 solution of $[\text{Et}_4\text{N}]_2[\mathbf{1}\text{-Cd}]$ at 25 °C.

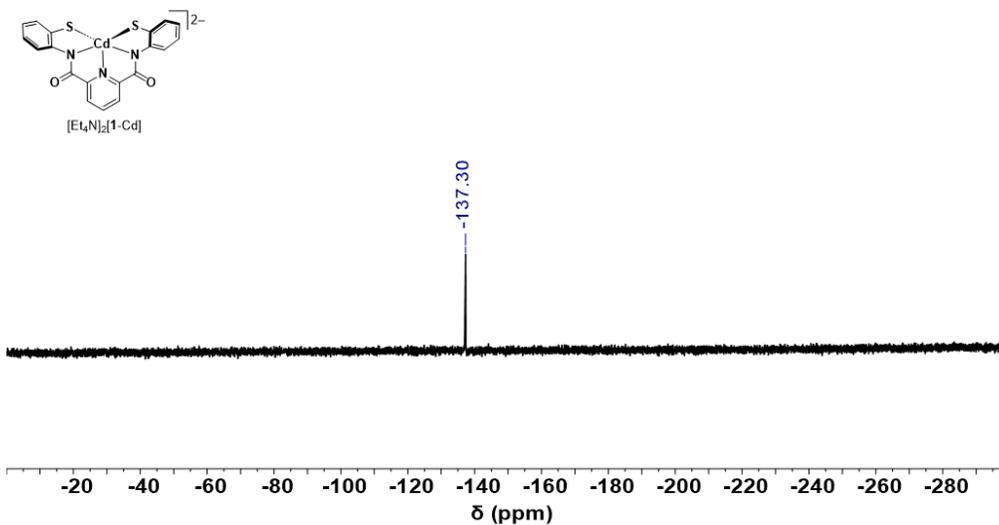


Figure S3. ^{113}Cd NMR spectrum of a $\text{DMSO-}d_6$ solution of $[\text{Et}_4\text{N}]_2[\mathbf{1-Cd}]$ at 25°C .

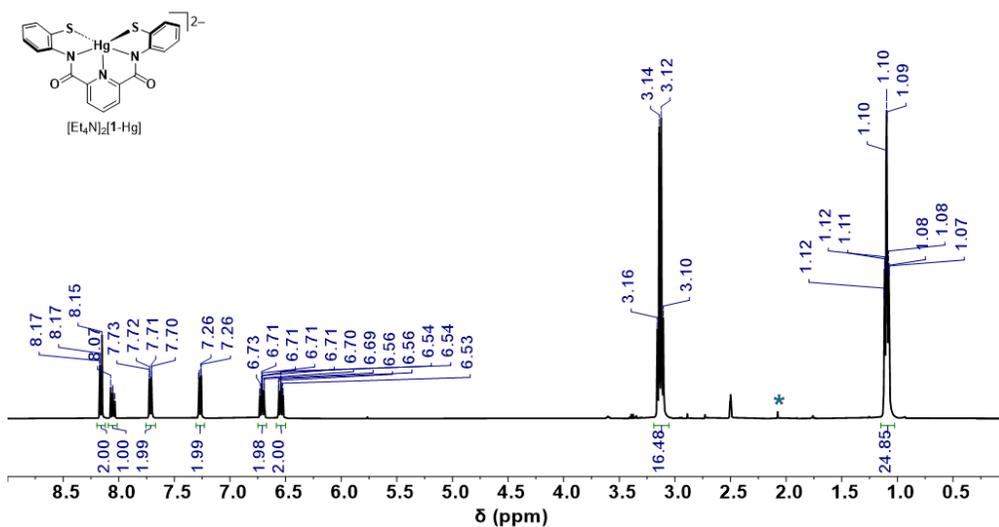


Figure S4. ^1H NMR spectrum of a $\text{DMSO-}d_6$ solution of $[\text{Et}_4\text{N}]_2[\mathbf{1-Hg}]$ at 25°C . Residual CH_3CN indicated with *.

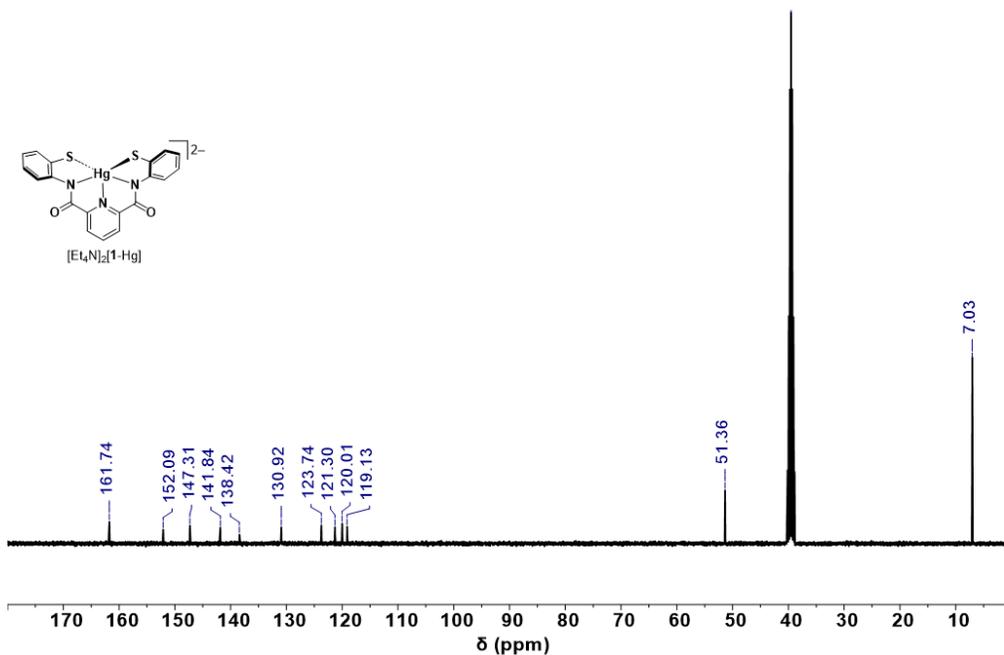


Figure S5. ^{13}C NMR spectrum of a $\text{DMSO-}d_6$ solution of $[\text{Et}_4\text{N}]_2[\mathbf{1}\text{-Hg}]$ at 25°C .

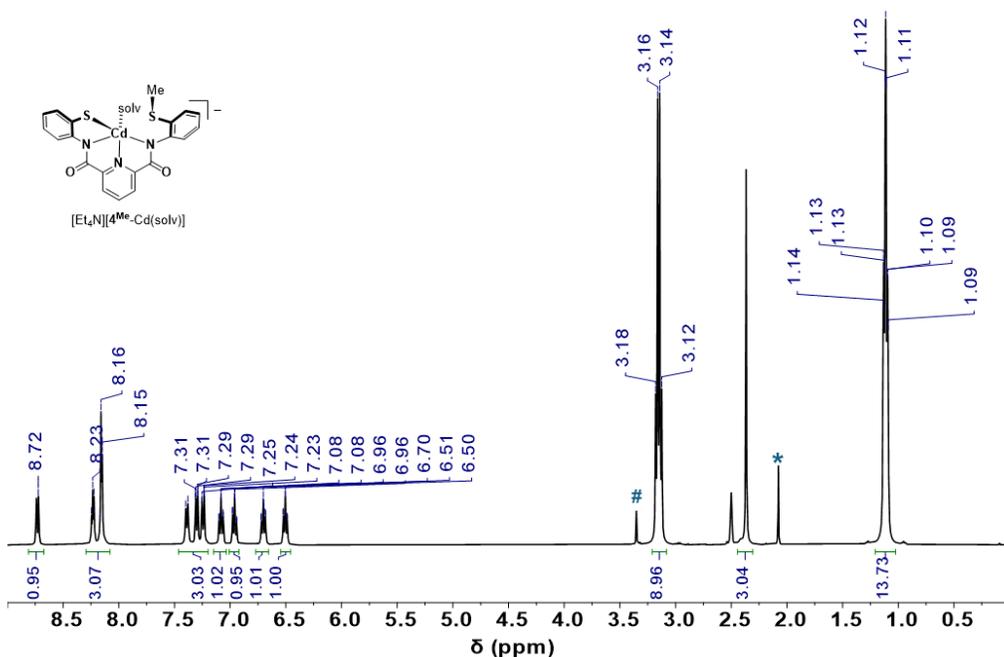


Figure S6. ^1H NMR spectrum of a $\text{DMSO-}d_6$ solution of $[\text{Et}_4\text{N}][\mathbf{4}^{\text{Me}}\text{-Cd}(\text{solv})]$ at 25°C . Residual CH_3CN (*) and H_2O (#) are indicated.

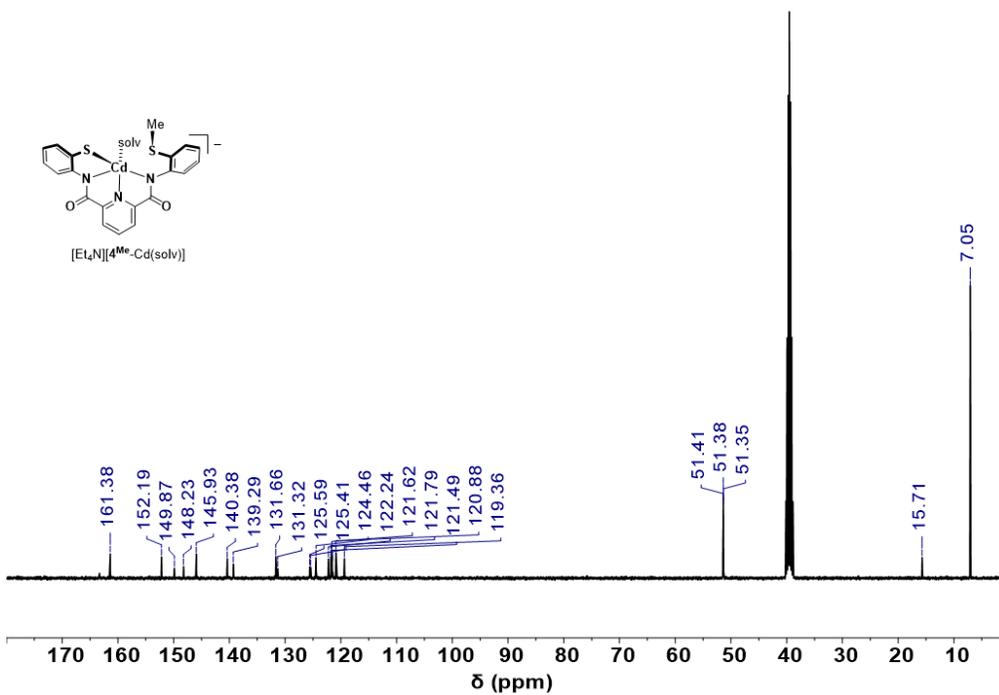


Figure S7. ^{13}C NMR spectrum of a DMSO- d_6 solution of $[\text{Et}_4\text{N}][4^{\text{Me}}\text{-Cd(solv)}]$ at 25 °C.

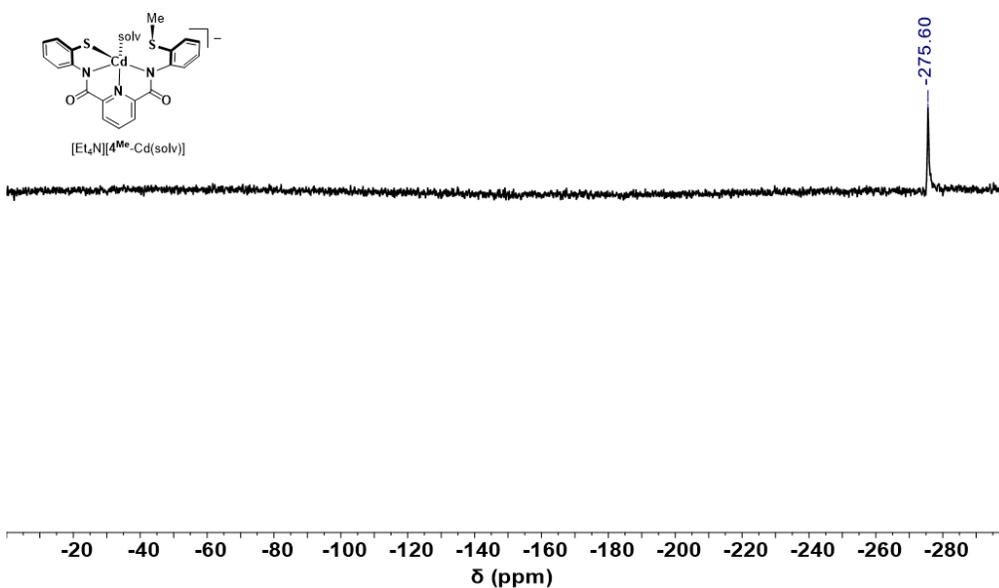


Figure S8. ^{113}Cd NMR spectrum of a DMSO- d_6 solution of $[\text{Et}_4\text{N}][4^{\text{Me}}\text{-Cd(solv)}]$ at 25 °C.

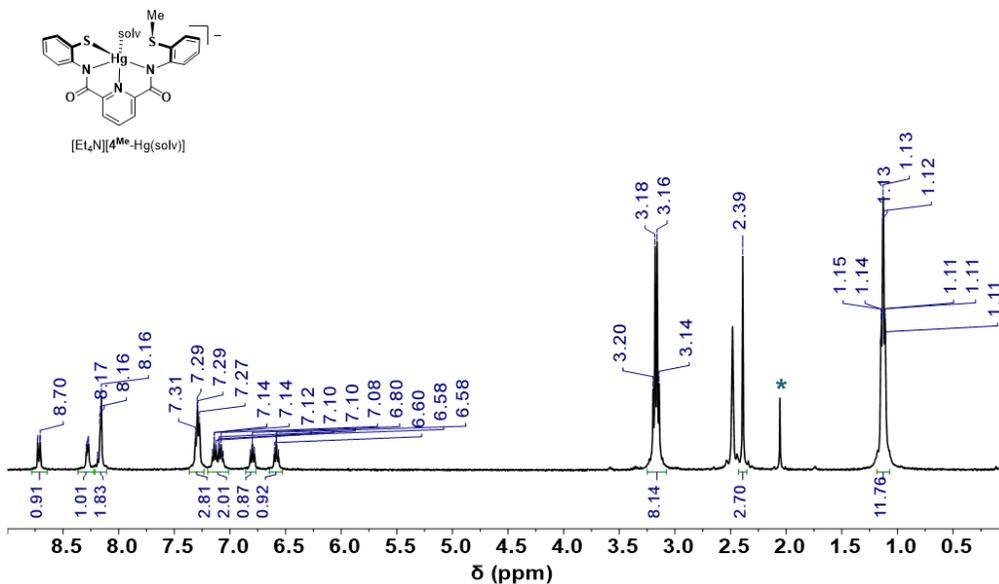


Figure S9. ^1H NMR spectrum of a DMSO- d_6 solution of $[\text{Et}_4\text{N}][4^{\text{Me}}\text{-Hg(solvs)}]$ at 25 °C. Residual CH_3CN (*) is indicated.

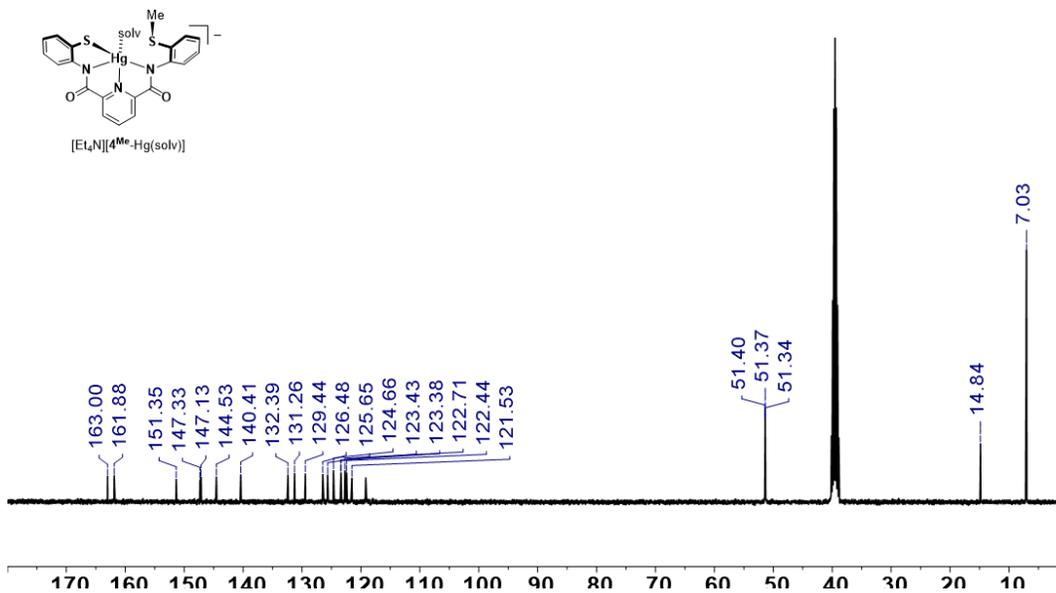


Figure S10. ^{13}C NMR spectrum of a DMSO- d_6 solution of $[\text{Et}_4\text{N}][4^{\text{Me}}\text{-Hg(solvs)}]$ at 25 °C.

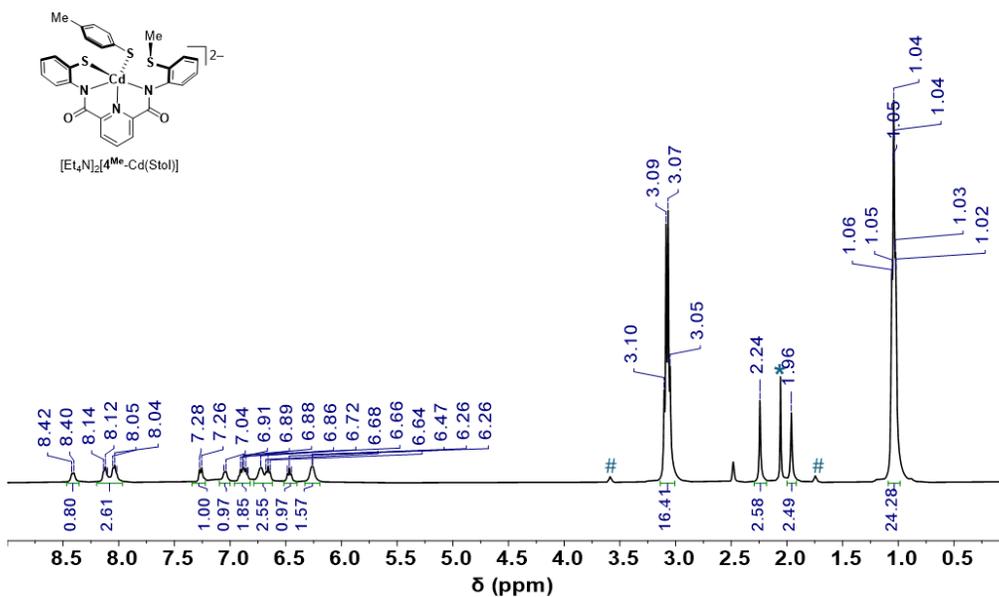


Figure S11. ^1H NMR spectrum of a DMSO- d_6 solution of $[\text{Et}_4\text{N}]_2[4^{\text{Me}}\text{-Cd}(\text{Stol})]$ at 25 °C. Residual CH_3CN (*) and Et_2O (#) are indicated.

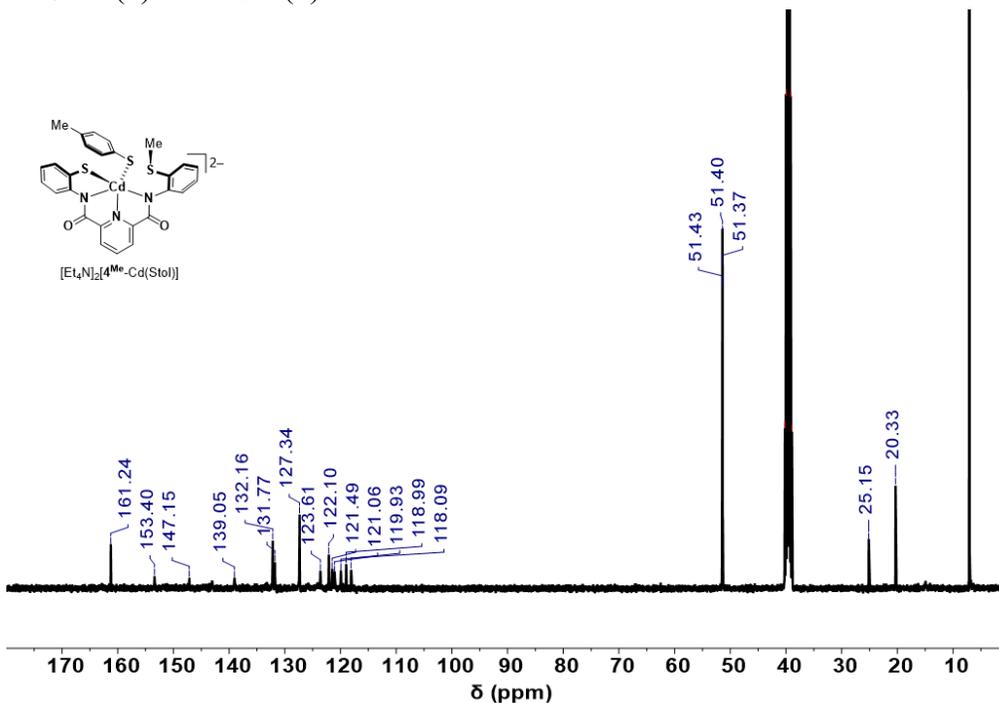


Figure S12. ^{13}C NMR spectrum of a DMSO- d_6 solution of $[\text{Et}_4\text{N}]_2[4^{\text{Me}}\text{-Cd}(\text{Stol})]$ at 25 °C.

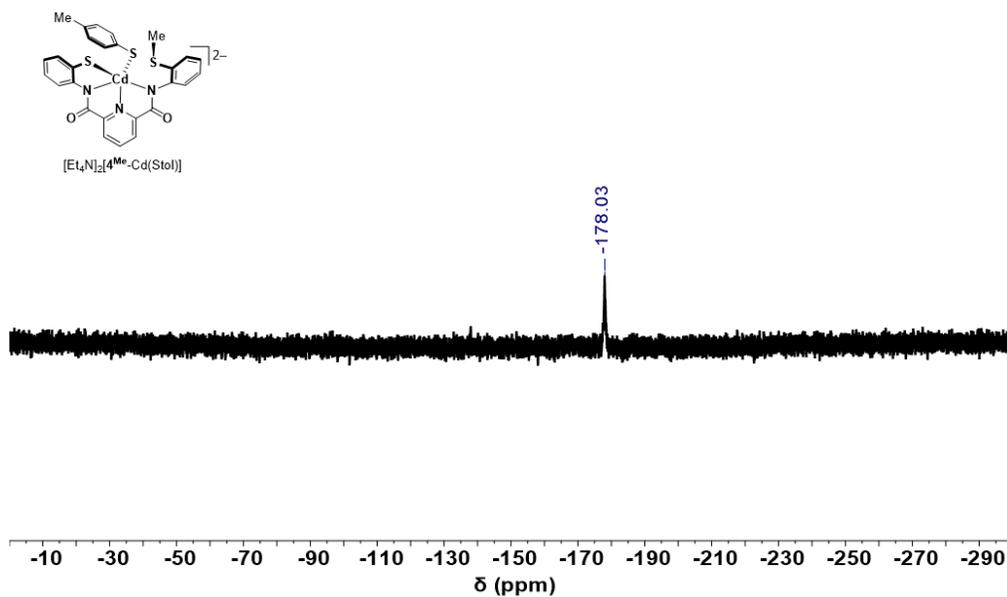


Figure S13. ^{113}Cd NMR spectrum of a DMSO- d_6 solution of $[\text{Et}_4\text{N}]_2[4^{\text{Me}}\text{-Cd(Stol)}]$ at 25 °C.

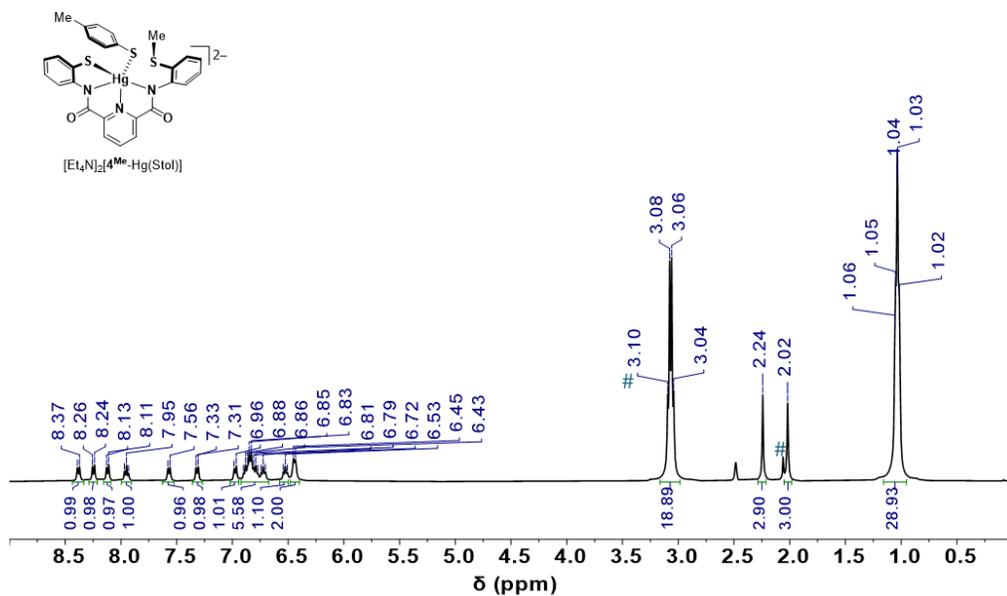


Figure S14. ^1H NMR spectrum of a DMSO- d_6 solution of $[\text{Et}_4\text{N}]_2[4^{\text{Me}}\text{-Hg(Stol)}]$ at 25 °C. Residual CH_3CN (#) is indicated.

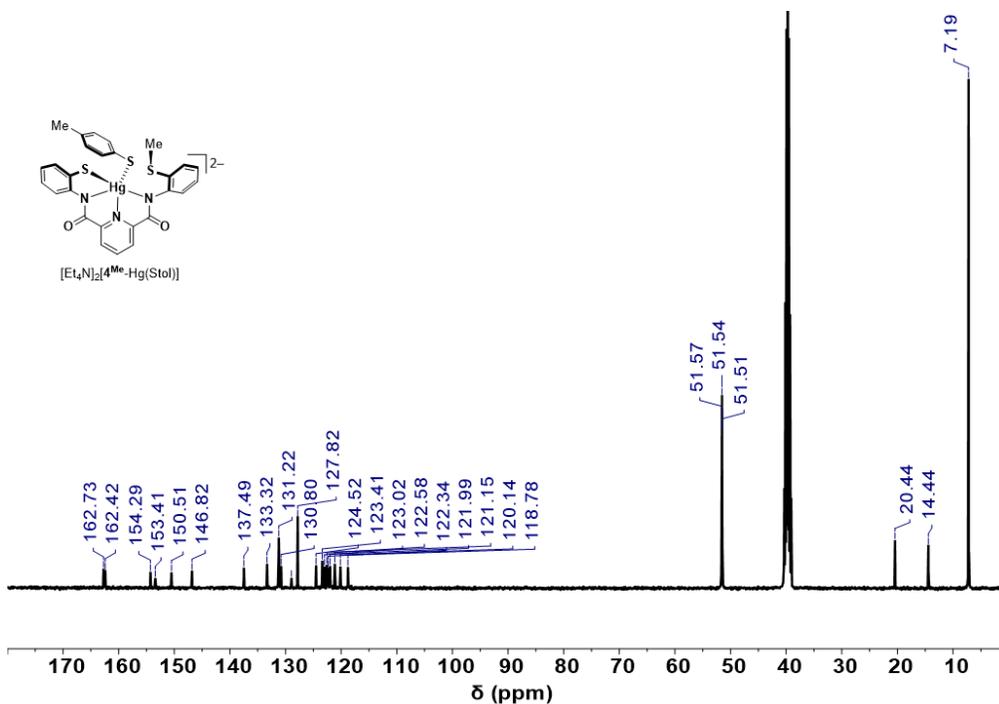


Figure S15. ^{13}C NMR spectrum of a $\text{DMSO-}d_6$ solution of $[\text{Et}_4\text{N}]_2[4^{\text{Me}}\text{-Hg}(\text{Stol})]$ at 25 °C.

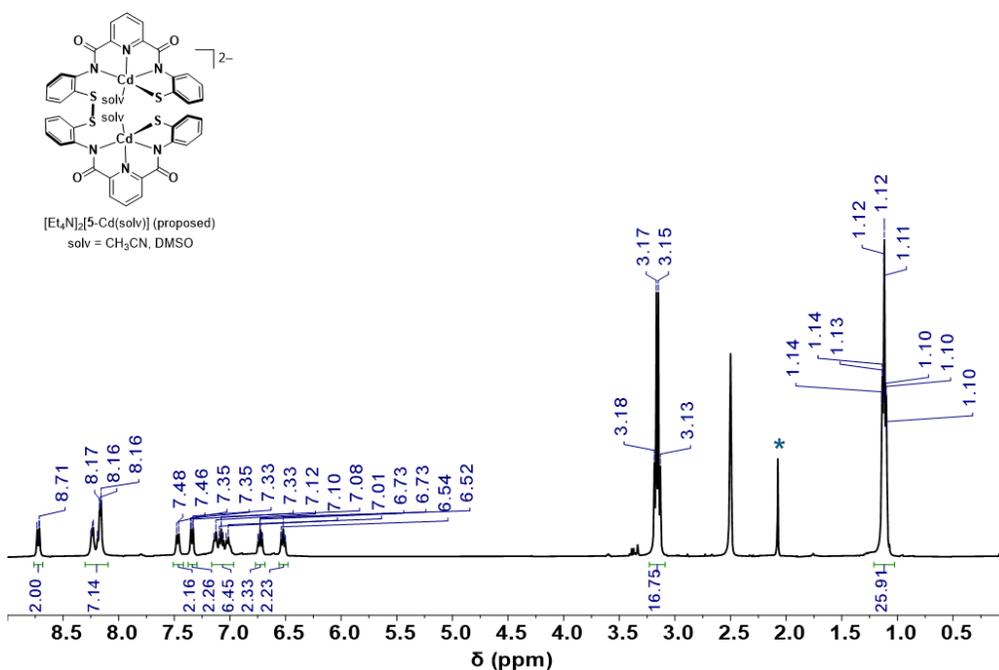


Figure S16. ^1H NMR spectrum of a $\text{DMSO-}d_6$ solution of $[\text{Et}_4\text{N}]_2[5\text{-Cd}(\text{sol})]$ at 25 °C. Residual CH_3CN (*) is indicated.

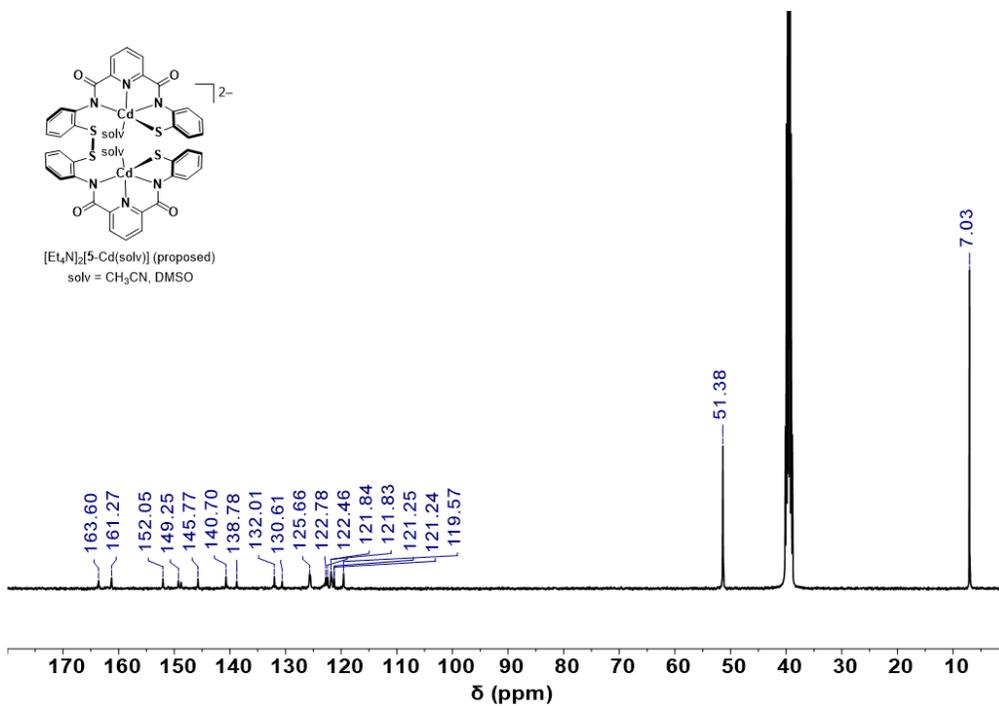


Figure S17. ^{13}C NMR spectrum of a DMSO- d_6 solution of $[\text{Et}_4\text{N}]_2[\text{5-Cd}(\text{solv})]$ at 25 °C.

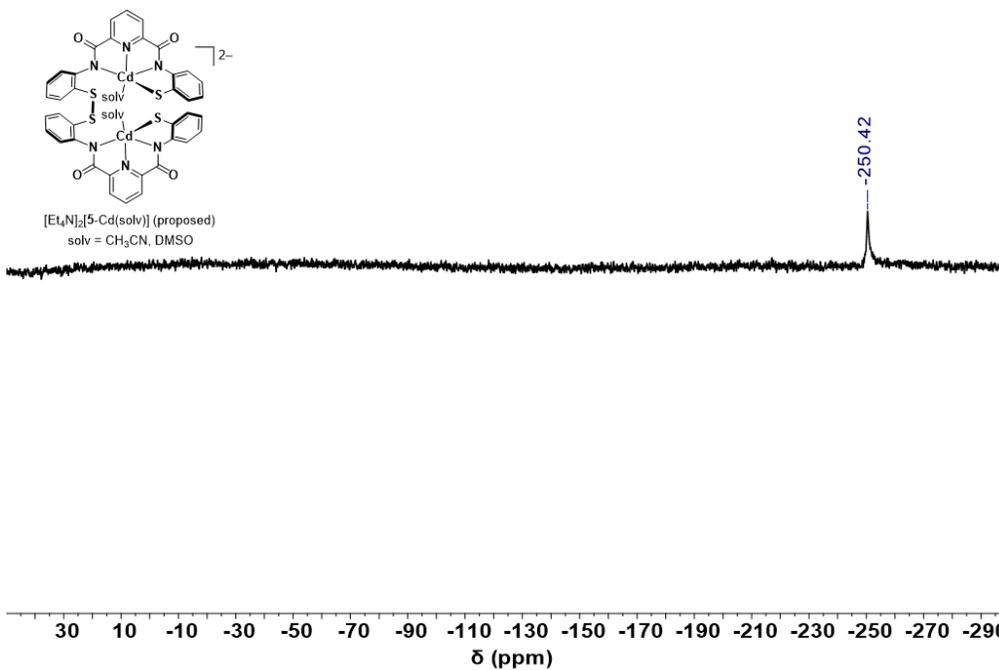


Figure S18. ^{113}Cd NMR spectrum of a DMSO- d_6 solution of $[\text{Et}_4\text{N}]_2[\text{5-Cd}(\text{solv})]$ at 25 °C.

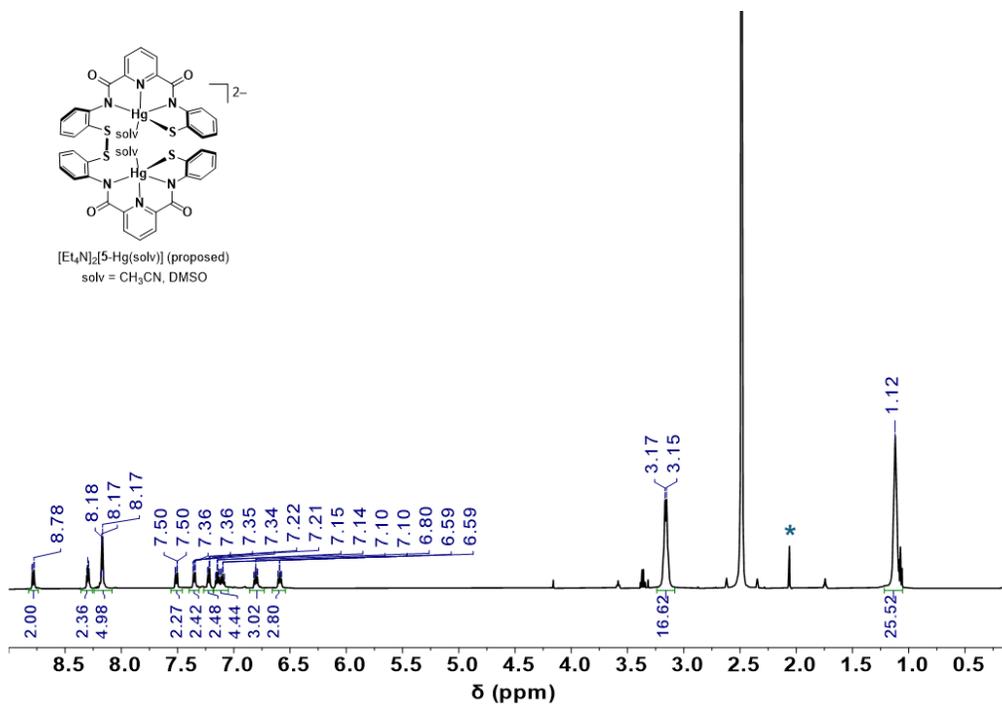


Figure S19. ^1H NMR spectrum of a $\text{DMSO-}d_6$ solution of $[\text{Et}_4\text{N}]_2[\text{5-Hg}(\text{solv})_2]$ at 25°C . Residual CH_3CN (*) is indicated.

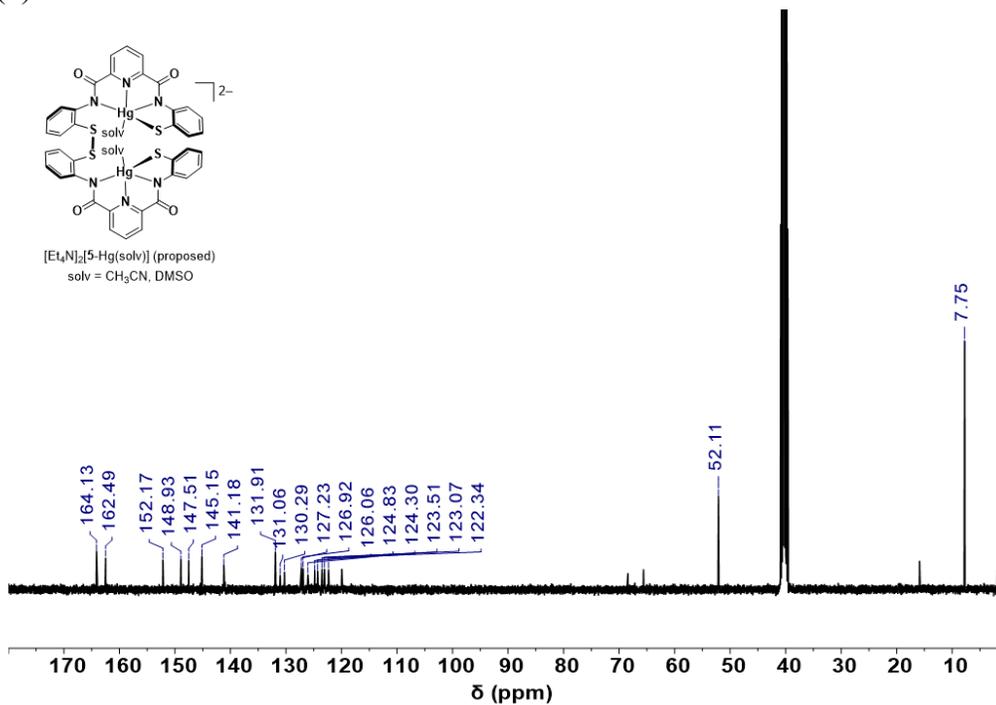


Figure S20. ^{13}C NMR spectrum of a $\text{DMSO-}d_6$ solution of $[\text{Et}_4\text{N}]_2[\text{5-Hg}(\text{solv})_2]$ at 25°C .

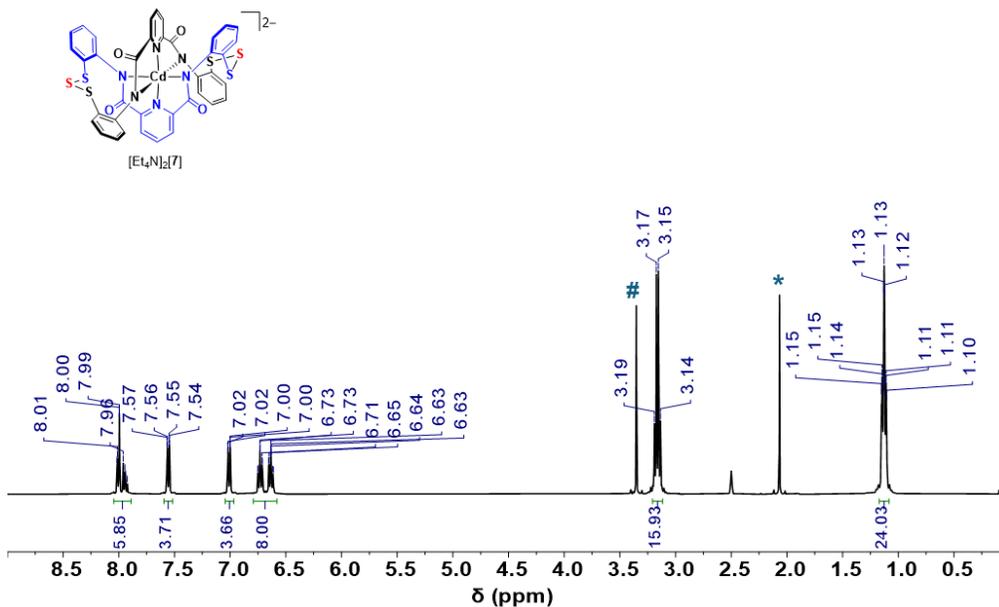


Figure S21. ^1H NMR spectrum of a $\text{DMSO-}d_6$ solution of $[\text{Et}_4\text{N}]_2[7]$ at 25 °C. Residual CH_3CN (*) and H_2O (#) are indicated.

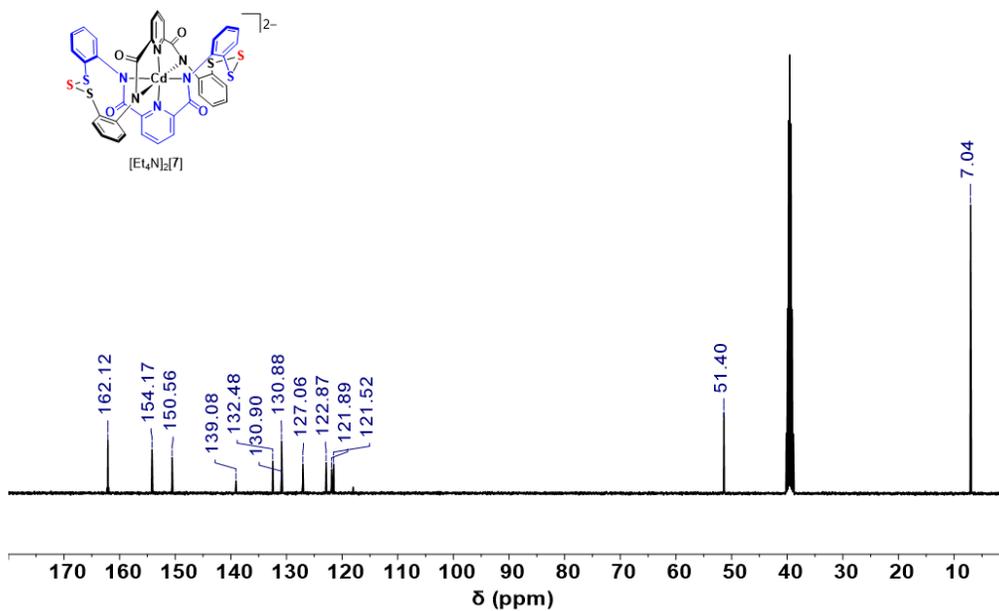


Figure S22. ^{13}C NMR spectrum of a $\text{DMSO-}d_6$ solution of $[\text{Et}_4\text{N}]_2[7]$ at 25 °C.

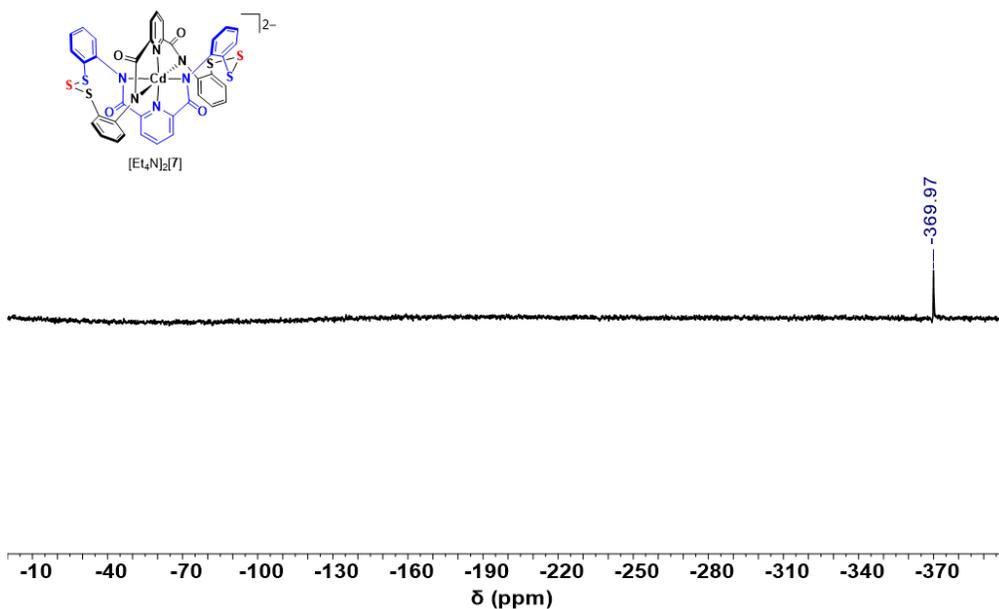


Figure S23. ^{113}Cd NMR spectrum of a DMSO- d_6 solution of $[\text{Et}_4\text{N}]_2[\mathbf{7}]$ at 25 °C.

Alkylation Competition Studies

Competition experiments were performed in screw-cap NMR tubes equipped with septum-lined caps. In a typical experiment, in the glovebox, a 0.5 mL 1:1 mixture of two metal dithiolate complexes $[\text{Et}_4\text{N}]_2[\mathbf{1-Zn}]$ (0.025 g, 0.036 mmol, 1.0 equiv) and $[\text{Et}_4\text{N}]_2[\mathbf{1-Cd}]$ (0.027 g, 0.036 mmol, 1.0 equiv) in DMSO- d_6 (0.5 mL) was added to the NMR tube. MeI (2.2 μL , 0.036 mmol, 1.0 equiv) was then added by microsyringe, and the reaction mixture was measured by ^1H NMR spectroscopy.

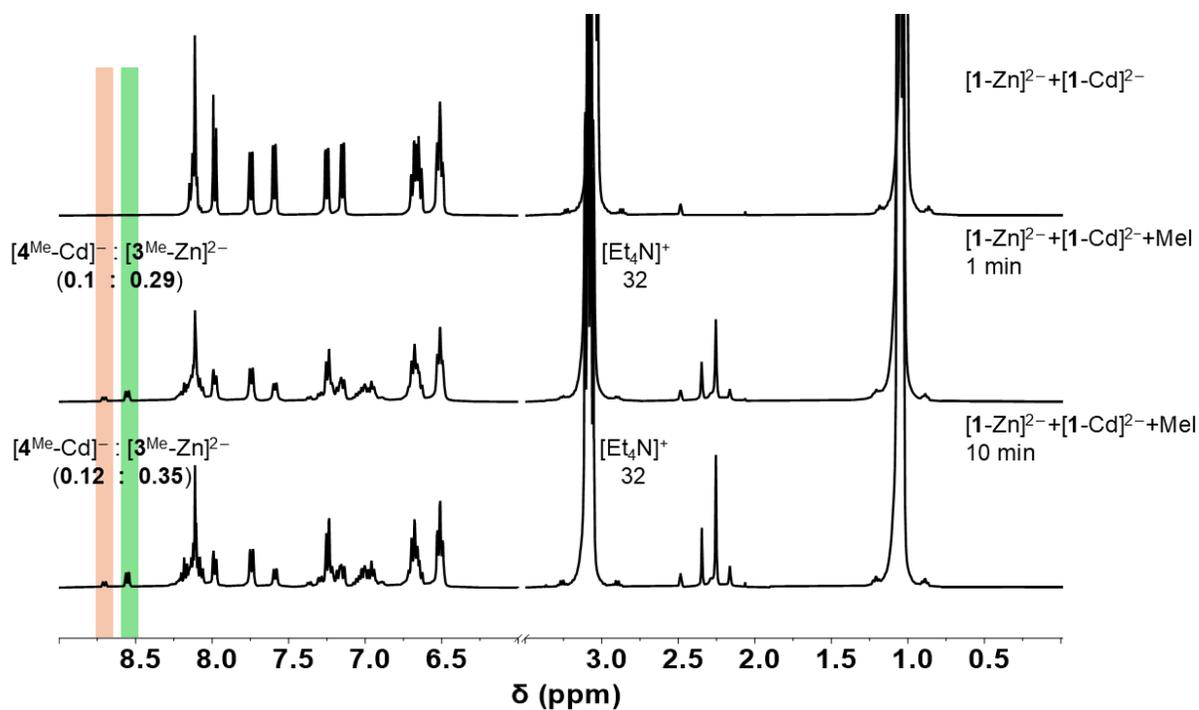


Figure S24. ^1H NMR spectra of a 1:1 mixture of $[\text{1-Zn}]^{2-}$ and $[\text{1-Cd}]^{2-}$ before (top) and after addition of MeI (middle, bottom).

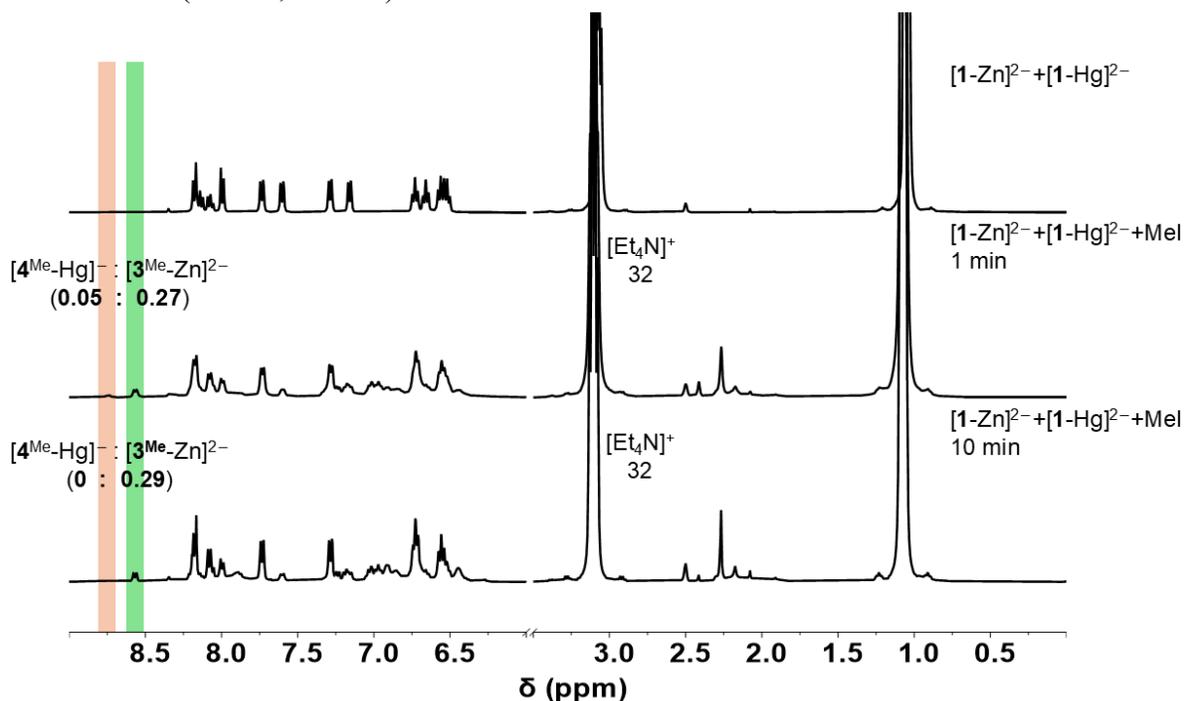


Figure S25. ^1H NMR spectra of a 1:1 mixture of $[\text{1-Zn}]^{2-}$ and $[\text{1-Hg}]^{2-}$ before (top) and after addition of MeI (middle, bottom).

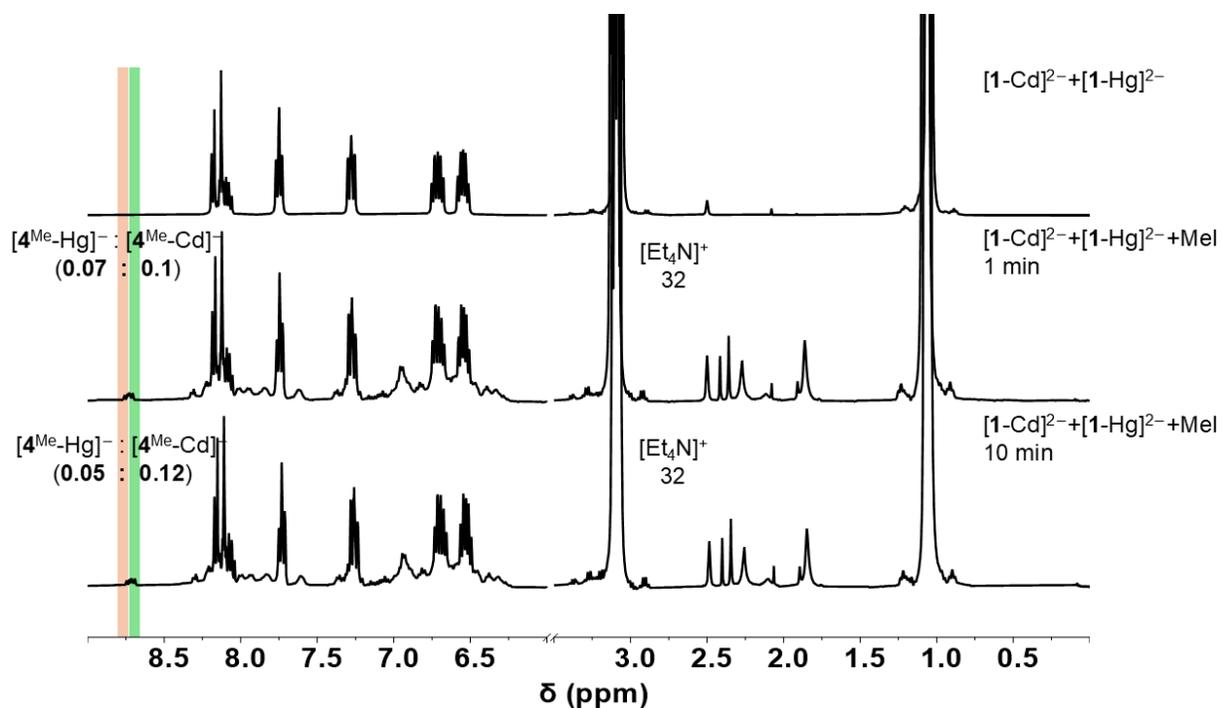


Figure S26. ^1H NMR spectra of a 1:1 mixture of $[\text{1-Cd}]^{2-}$ and $[\text{1-Hg}]^{2-}$ before (top) and after addition of MeI (middle, bottom).

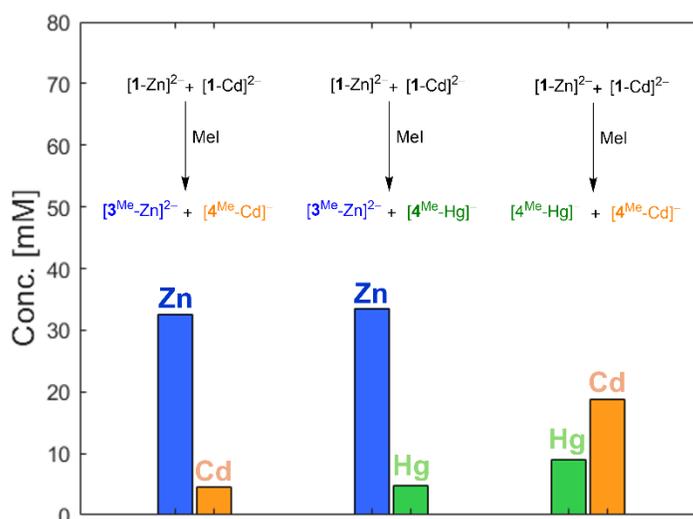


Figure S27. Concentrations of methylated products measured by ^1H NMR spectroscopy after addition of MeI (0.072 M) to 1:1 mixture of metal dithiolate complexes in $\text{DMSO-}d_6$.

Metal Cation Exchange

Metal cation exchange studies reactions were performed in screw-cap NMR tubes equipped with septum-lined caps. In a representative procedure, in the glovebox, a solution of $[\text{Et}_4\text{N}]_2[\text{1-Cd}]$ (0.032 g, 0.043 mmol, 1.0 equiv) was prepared in $\text{DMSO-}d_6$ (0.4 mL), and MeI (2.7 μL , 0.043

mmol, 1.0 equiv) was then injected by microsyringe. $[\text{Et}_4\text{N}]_2[\mathbf{1}\text{-Zn}]$ (0.030 g, 0.043 mmol, 1.0 equiv) in $\text{DMSO-}d_6$ (0.3 mL) was injected by syringe.

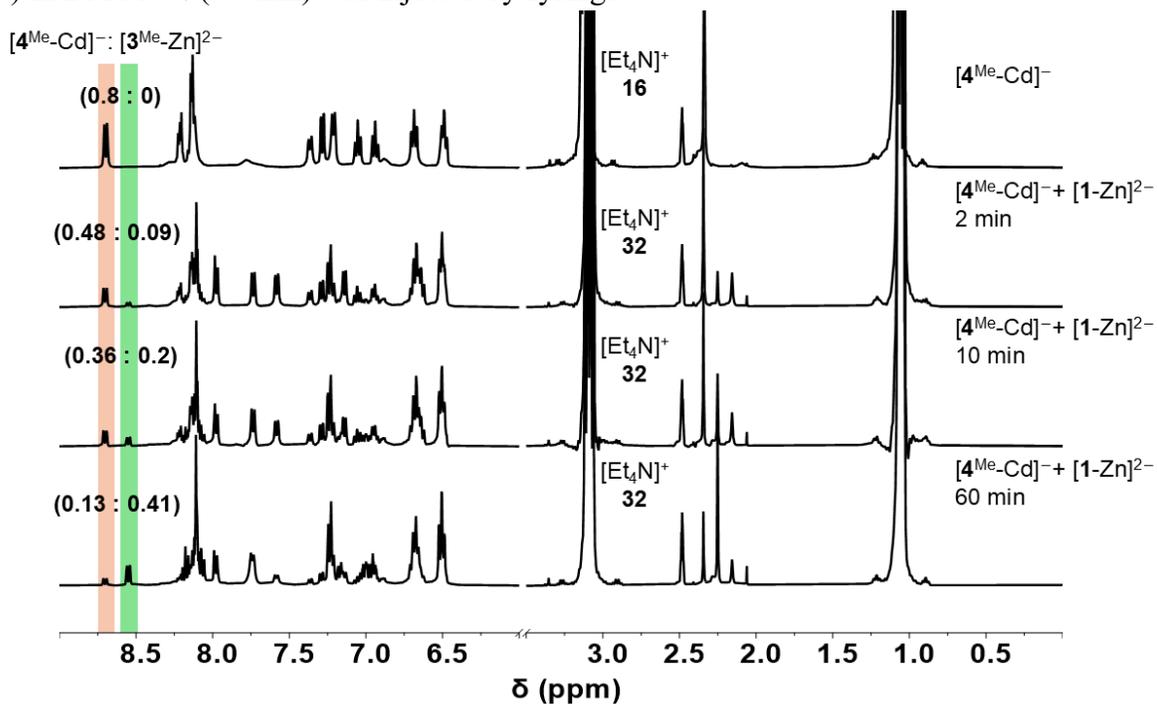


Figure S28. ^1H NMR spectra of a $\text{DMSO-}d_6$ mixture of $[\mathbf{1}\text{-Zn}]^{2-}$ and $[\mathbf{4}^{\text{Me}}\text{-Cd}(\text{solv})]^-$ over time.

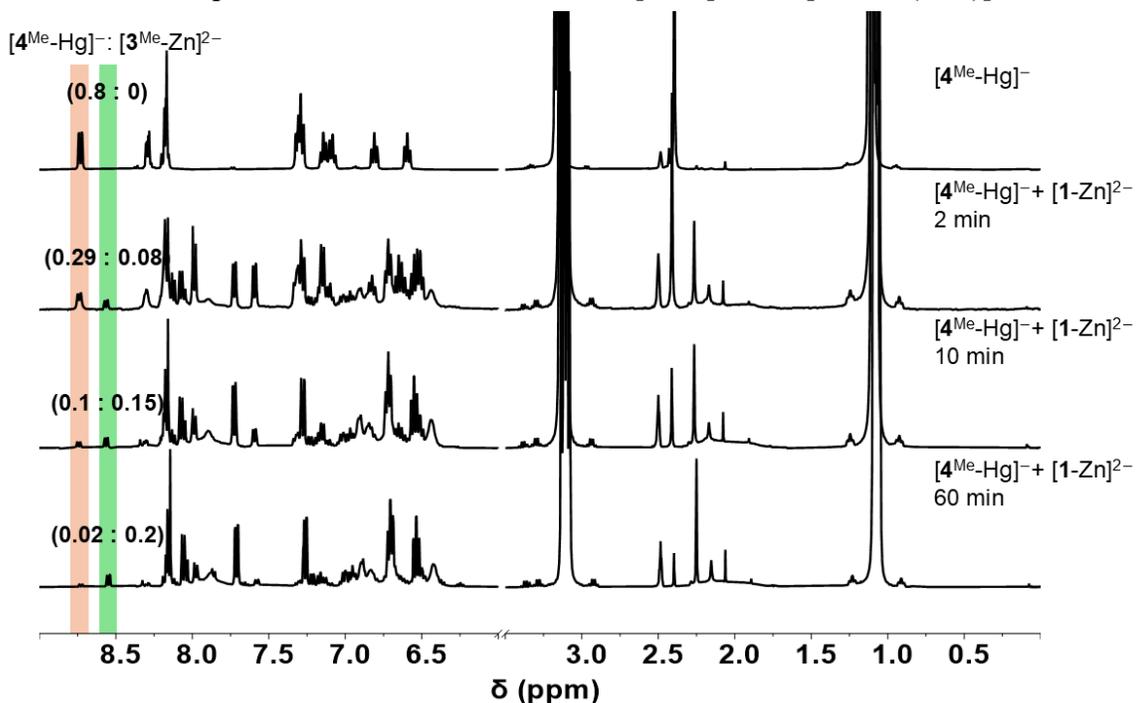


Figure S29. ^1H NMR spectra of a $\text{DMSO-}d_6$ mixture of $[\mathbf{1}\text{-Zn}]^{2-}$ and $[\mathbf{4}^{\text{Me}}\text{-Hg}(\text{solv})]^-$ over time.

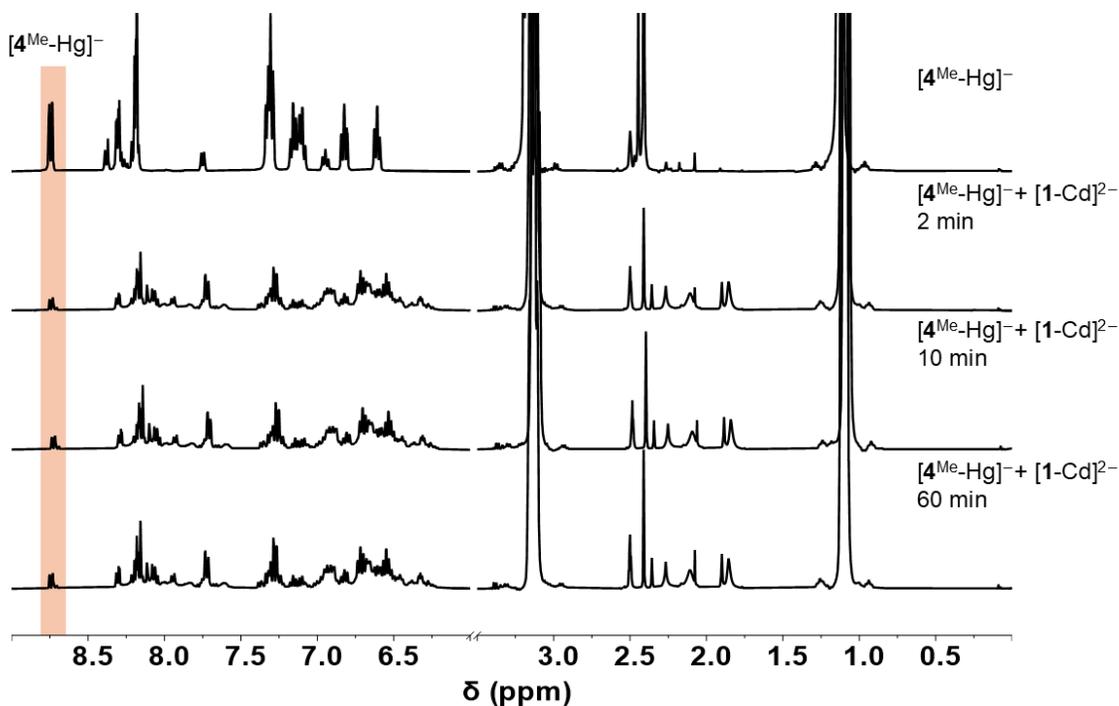


Figure S30. ^1H NMR spectra of a $\text{DMSO-}d_6$ mixture of $[\text{1-Cd}]^{2-}$ and $[\text{4}^{\text{Me}}\text{-Hg}(\text{solv})]^-$ over time.

Sulfur Insertion Reactions

Sulfur insertion into $[\text{Et}_4\text{N}]_2[\text{1-Cd}]$

In the glovebox, a 20 mL scintillation vial equipped with a stir bar was charged with $[\text{Et}_4\text{N}]_2[\text{1-Cd}]$ (0.100 g, 0.133 mmol, 1 equiv) and CH_3CN (5 mL). S_8 (0.021 g, 0.66 mmol S, 5 S atom equiv) was added as a solid to the solution, and the reaction mixture was stirred at room temperature for 5 min, during which the color gradually changed from orange-yellow to yellow. After completion, the solvent was removed under reduced pressure to afford an orange oil. The residue was washed sequentially with diethyl ether, toluene, and THF and dried under vacuum to give as an orange oil. ^1H NMR spectroscopy suggests the formation of two species, $[\text{Et}_4\text{N}]_2[\text{2-Cd}]$ and $[\text{Et}_4\text{N}]_2[\text{6-Cd}]$, which could not be separated.

Sulfur insertion into $[\text{Et}_4\text{N}]_2[\text{1-Hg}]$

In the glovebox, a 20 mL scintillation vial equipped with a magnetic stir bar was charged with $[\text{Et}_4\text{N}]_2[\text{1-Hg}]$ (0.100 g, 0.12 mmol, 1 equiv) and CH_3CN (5 mL). S_8 (0.019 g, 0.6 mmol S, 5 S atom equiv) was added as a solid, and the reaction mixture was stirred at room temperature for 5 min, during which the color gradually changed from orange-yellow to yellow. The solvent was removed under reduced pressure to afford as an orange oil. The residue was washed with diethyl ether, toluene, and THF and dried under vacuum to afford a yellow oil. ^1H NMR spectroscopy suggests formation of two species, $[\text{Et}_4\text{N}]_2[\text{2-Hg}]$ and $[\text{Et}_4\text{N}]_2[\text{6-Hg}]$.

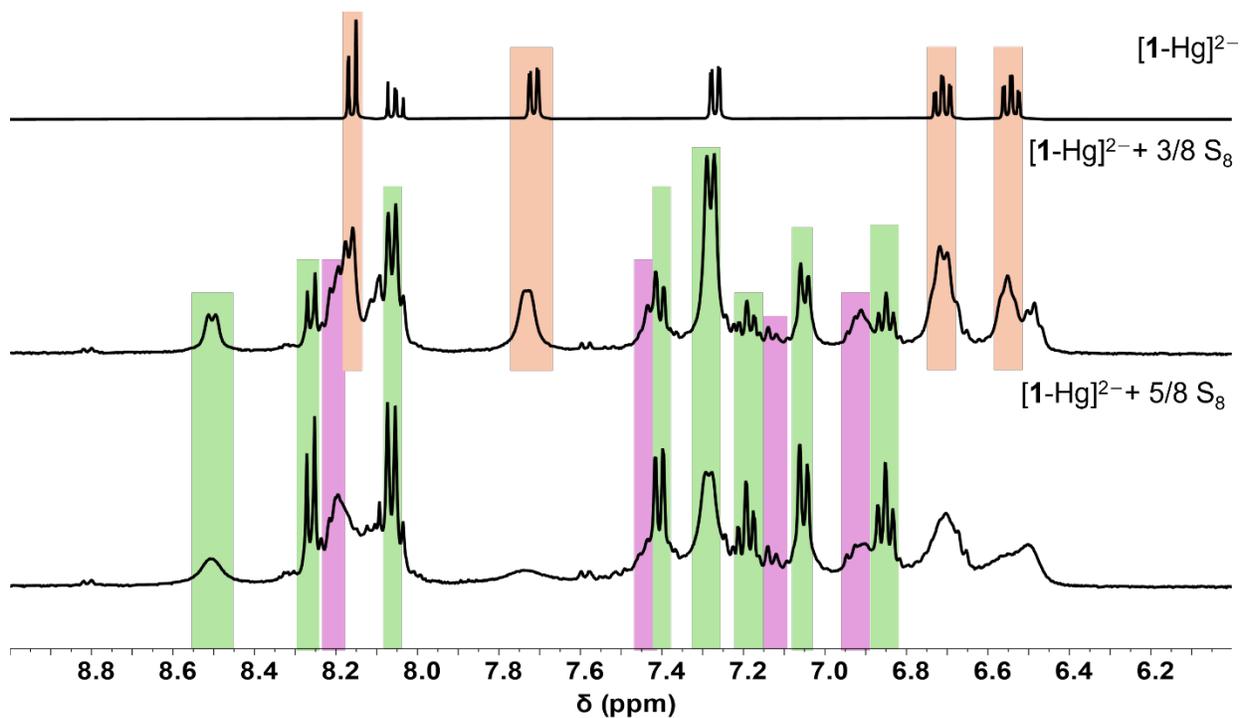


Figure S31. ^1H NMR spectra of a DMSO- d_6 solution of $[\mathbf{1}\text{-Hg}]^{2-}$ before (top), after addition of S_8 ($3/8$ equiv, middle), and ($5/8$ equiv, bottom).

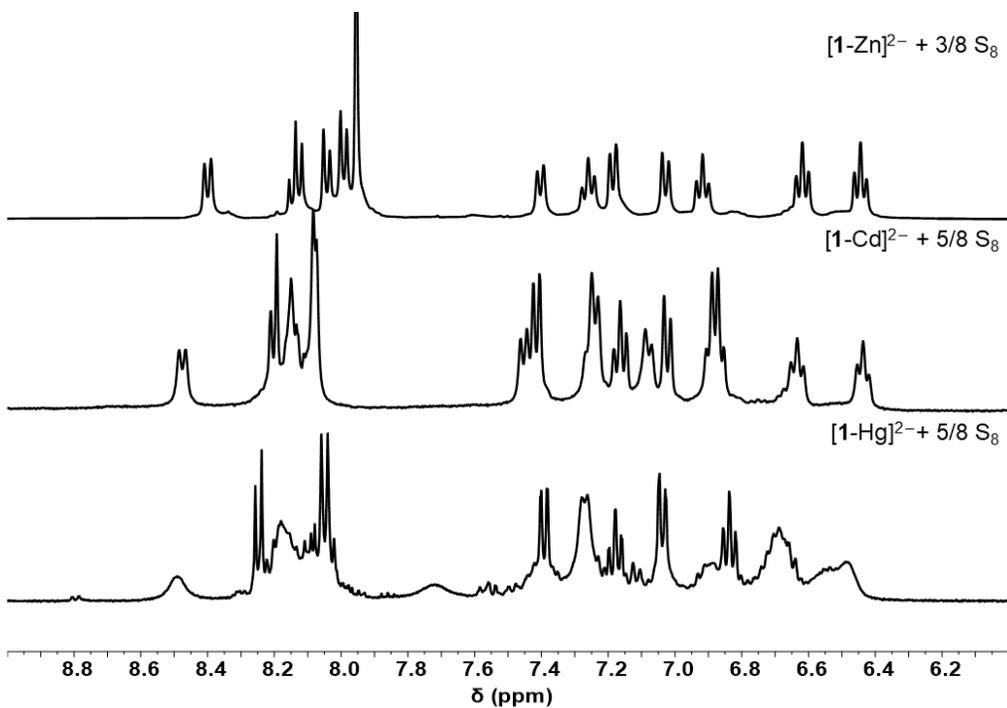


Figure S32. ^1H NMR spectra of DMSO- d_6 solutions of $[\mathbf{1}\text{-Zn}]^{2-}$ with $3/8 \text{S}_8$, $[\mathbf{2}\text{-Cd}]^{2-}$ and $[\mathbf{2}\text{-Hg}]^{2-}$ with $5/8 \text{S}_8$.

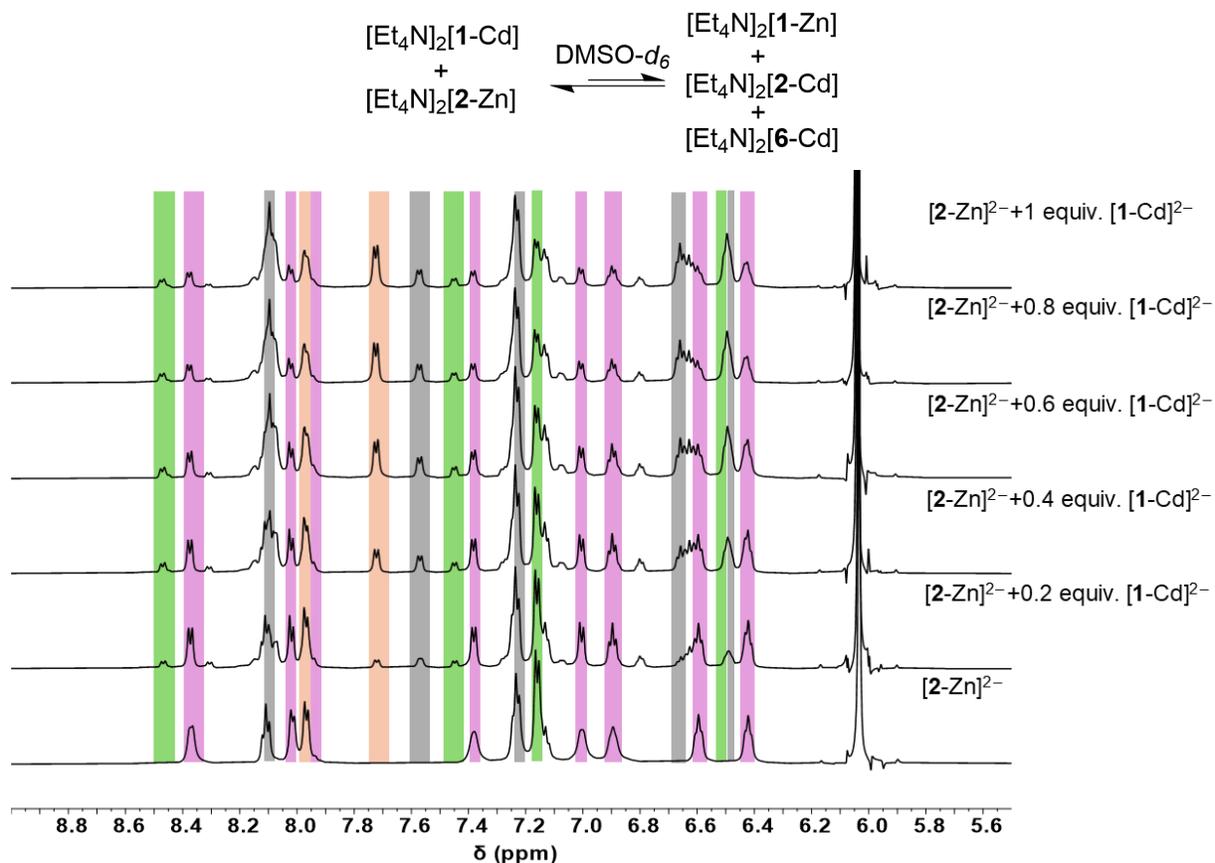


Figure S33. ^1H NMR spectra of a $\text{DMSO-}d_6$ solution of $[\text{Et}_4\text{N}]_2[\mathbf{2}\text{-Zn}]$ (bottom) with increasing amounts of added $[\text{Et}_4\text{N}]_2[\mathbf{1}\text{-Cd}]$. ^1H NMR resonances corresponding to $[\mathbf{1}\text{-Cd}]^{2-}$ (gray), $[\mathbf{2}\text{-Cd}]^{2-}$ (green), $[\mathbf{2}\text{-Zn}]^{2-}$ (purple), and $[\mathbf{1}\text{-Zn}]^{2-}$ (orange) are indicated.

K_{eq} Calculations

In a representative experiment, in the glovebox, a screw-cap NMR tube was charged with a $\text{DMSO-}d_6$ solution of $[\text{Et}_4\text{N}]_2[\mathbf{1}\text{-Cd}]$ (0.045 g, 0.14 mmol, 1.0 equiv). $2/8 \text{ S}_8$ (0.036 g, 0.028 mmol, $2/8$ equiv) was added, and the components were quantified by integration of the ^1H NMR spectrum, with $d_1 = 20$ s. The experiment was repeated with $3/8$ and $4/8$ equiv S_8 . The equilibrium constants for the formation of $[\mathbf{2}\text{-M}]^{2-}$ (K_1) and $[\mathbf{6}\text{-M}]^{2-}$ (K_2 , $\text{M} = \text{Cd, Hg}$) were calculated by integration of the ^1H NMR spectra of mixtures containing $[\mathbf{1}\text{-M}]^{2-}$, $[\mathbf{2}\text{-M}]^{2-}$, and $[\mathbf{6}\text{-M}]^{2-}$,

Where

$$K_1^{\text{M}} = \frac{[\mathbf{2}\text{-M}]}{[\mathbf{1}\text{-M}][\text{S}_8]^{\frac{3}{8}}} \quad \text{and} \quad K_2^{\text{M}} = \frac{[\mathbf{6}\text{-M}]}{[\mathbf{2}\text{-M}][\text{S}_8]^{\frac{3}{8}}} .$$

DOSY ^1H NMR Data

Table S1. Diffusion coefficients of complexes measured by DOSY NMR.

Compound	Average D ($\times 10^{-10}$ m ² /s)
[Et ₄ N] ₂ [1 -Zn]	2.04 ⁵
[Et ₄ N] ₂ [1 -Cd]	1.71
[Et ₄ N] ₂ [1 -Hg]	1.66
[Et ₄ N] ₂ [3 ^{Me} -Zn]	1.62 ⁵
[Et ₄ N][4 ^{Me} -Cd(sol _v)]	1.84
[Et ₄ N][4 ^{Me} -Hg(sol _v)]	1.88
[Et ₄ N] ₂ [L ^{SS} -Zn]	1.31 ⁵
[Et ₄ N] ₂ [5 -Cd(sol _v)]	1.23
[Et ₄ N] ₂ [5 -Hg(sol _v)]	1.28

UV-Vis Spectra

Electronic absorption measurements were recorded using an Agilent Cary 60 UV-Vis spectrophotometer with 1 cm quartz cuvettes.

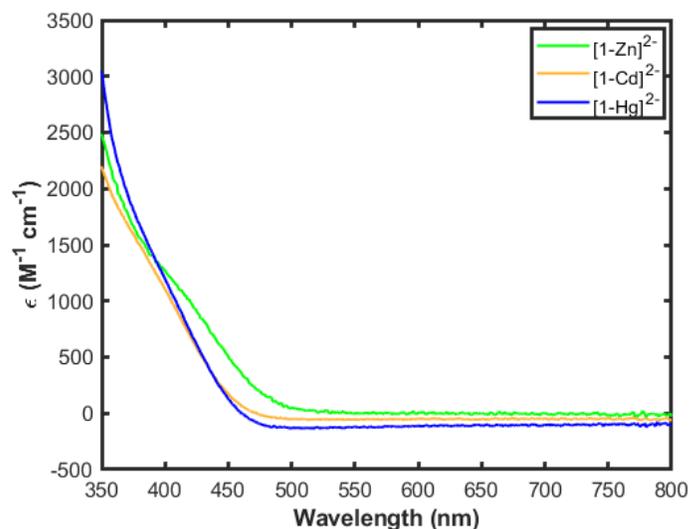


Figure S34. UV-vis spectra of CH₃CN solutions of [Et₄N]₂[**1**-Zn] (0.0000616 M), [Et₄N]₂[**1**-Cd] (0.0000947 M), and [Et₄N]₂[**1**-Hg] (0.000146 M).

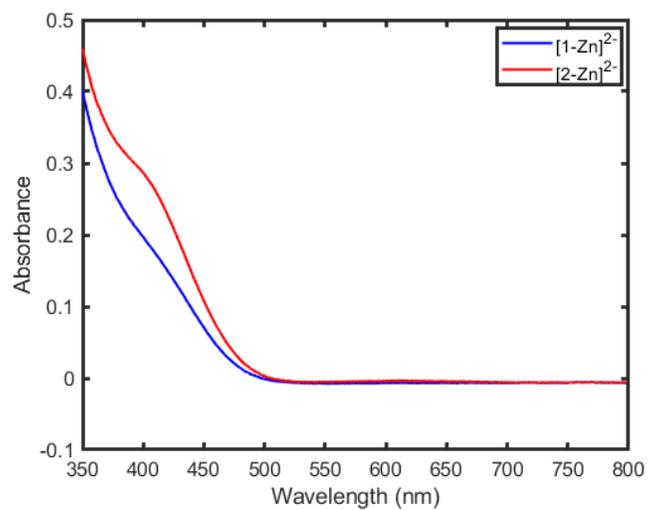


Figure S35. UV-vis spectra of CH₃CN solutions of [Et₄N]₂[1-Zn] (blue) and [Et₄N]₂[2-Zn] (red).

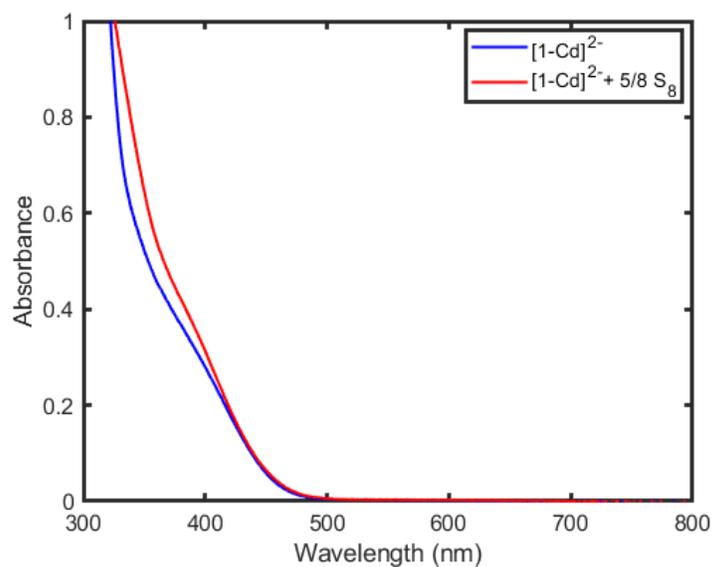


Figure S36. UV-vis spectra of CH₃CN solutions of [Et₄N]₂[1-Cd] (blue) and with 5/8 S₈ (red).

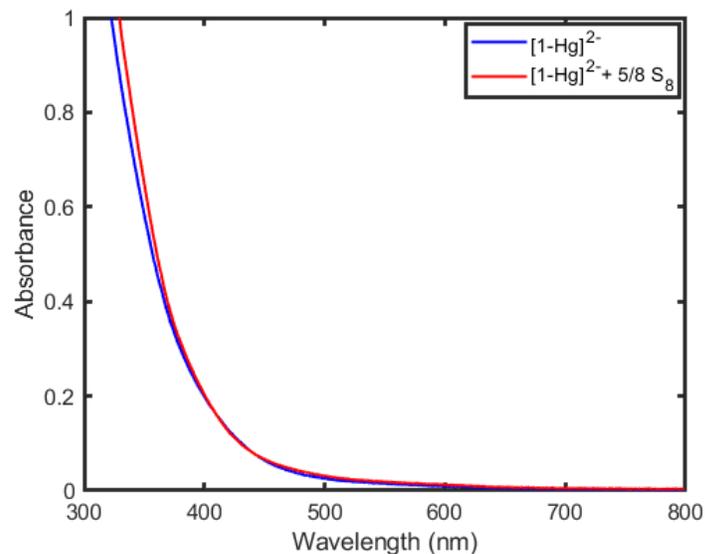


Figure S37. UV-vis spectra of CH₃CN solutions of [Et₄N]₂[1-Hg] (blue) and with 5/8 S₈ (red).

Oxidation Data

Cyclic voltammetry was performed using a Princeton Applied Research VersaSTAT 4 potentiostat, with voltammograms recorded using a glassy carbon working electrode, a platinum wire counter electrode, and an AgNO₃/Ag reference electrode with 0.1 M ⁿBu₄NPF₆ electrolyte. Potentials were referenced to the ferrocenium/ferrocene (Fc⁺/Fc) couple. A scan rate of 0.1 V/s was used unless otherwise indicated.

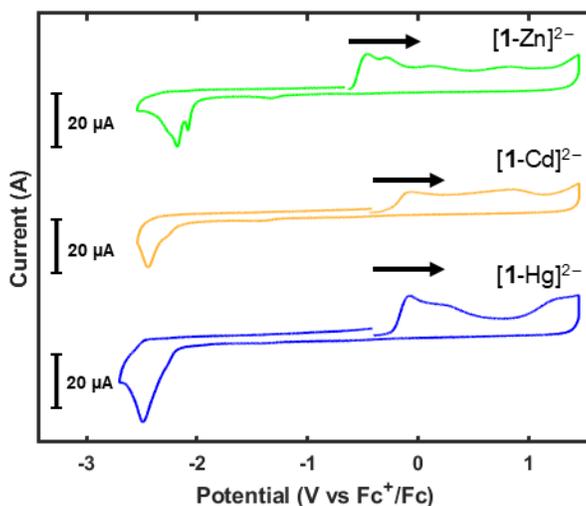


Figure S38. Cyclic voltammograms of 0.01 M solutions of [Et₄N]₂[1-Zn], [Et₄N]₂[1-Cd], and [Et₄N]₂[1-Hg].

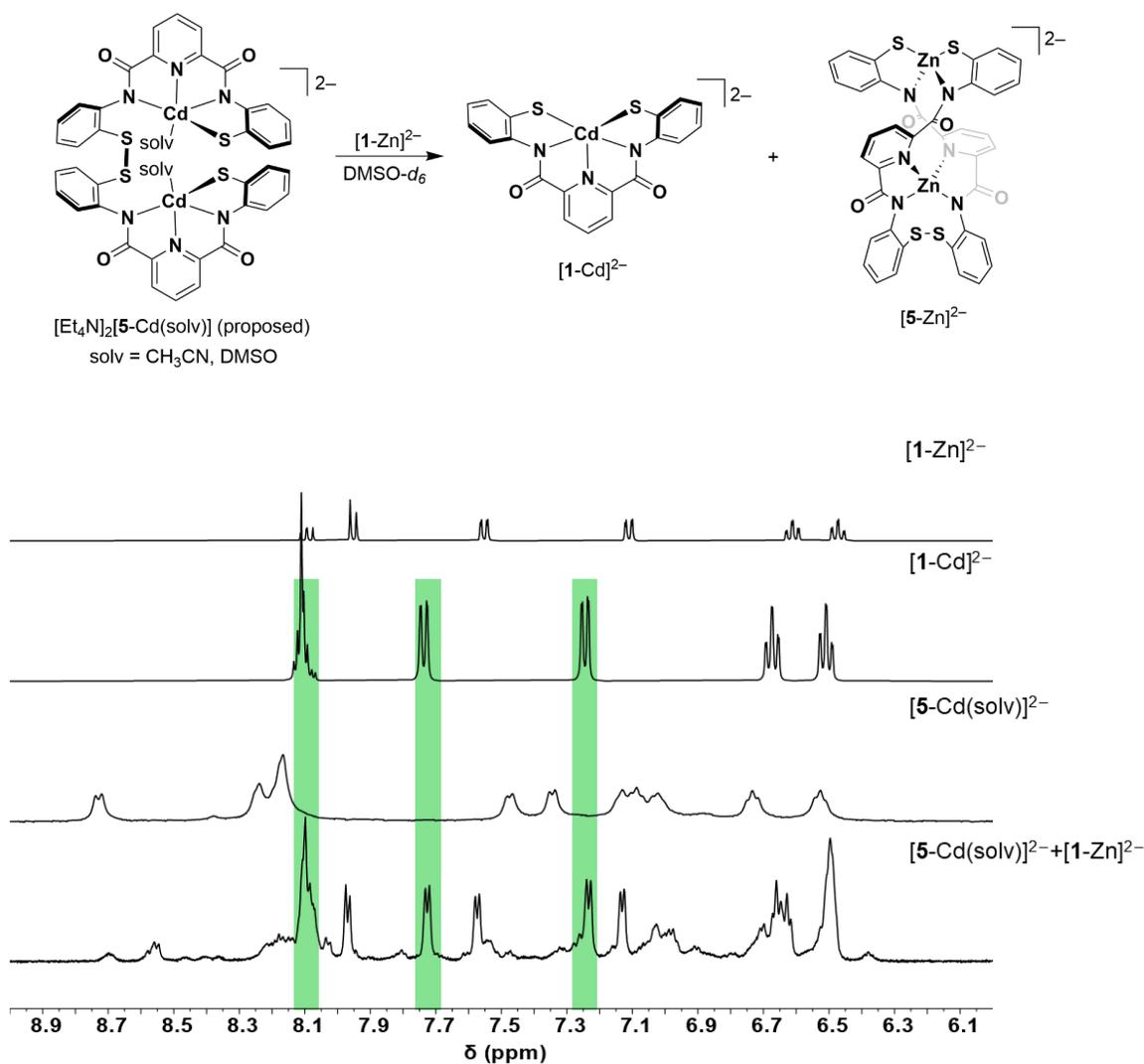


Figure S39. 1H NMR spectra of the reaction between $[Et_4N]_2[5-Cd(solv)]$ and $[Et_4N]_2[1-Zn]$ in DMSO- d_6 at 25 °C, showing reduction of $[5-Cd(solv)]^{2-}$ and oxidation of $[1-Zn]^{2-}$.

PXRD Data

Powder X-ray diffraction (PXRD) data were collected on a Bruker D8 Advance diffractometer equipped with a Cu anode ($K_{\alpha 1} = 1.54060 \text{ \AA}$, $K_{\alpha 2} = 1.54443 \text{ \AA}$, $K_{\alpha 2}/K_{\alpha 1} = 0.50000$), a variable divergence filter set to a 6 mm illumination length on the sample, and a LYNXEYE detector. The instrument was operated in Bragg–Brentano geometry with a step size of 0.2° in 2θ .

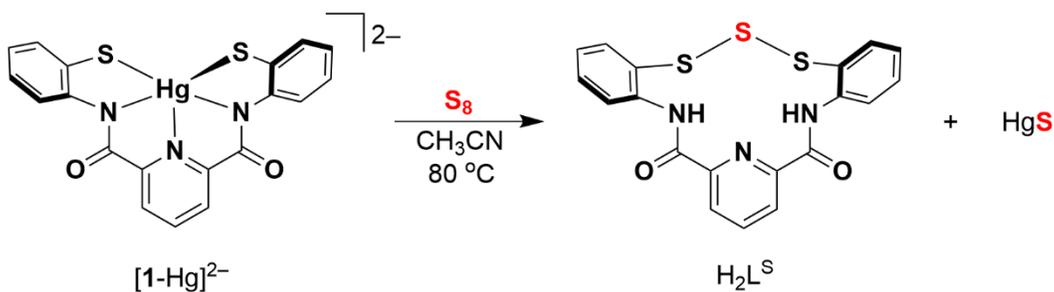


Figure S40. Scheme for the reaction of $[\text{Et}_4\text{N}]_2[1\text{-Hg}]$ with $5/8 \text{S}_8$ at 80°C for 1 h forms $\text{H}_2\text{L}^{\text{S}}$ and HgS .

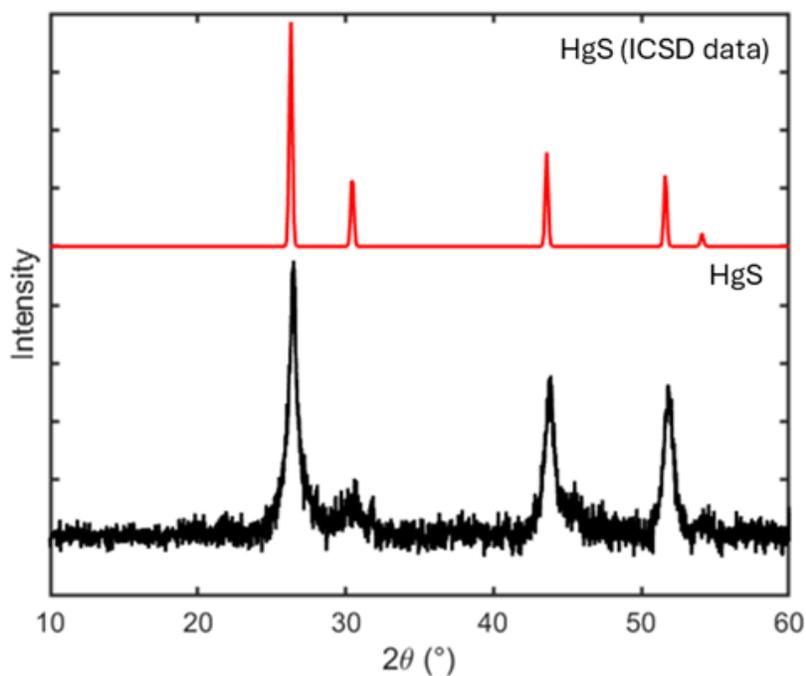


Figure S41. PXRD patterns of HgS formed from heating of a mixture of $[\text{Et}_4\text{N}]_2[1\text{-Hg}]$ and S_8 at 80°C for 1 h (black). The PXRD pattern of authentic HgS (ICSD 24094) is shown for comparison (red).

Mass Spectrometry Data

Electrospray ionization mass spectrometry (ESI-MS) data were collected of samples as DMSO solutions at the University of Notre Dame Spectrometry & Proteomics Facility using a Bruker micro TOF-Q II instrument in negative ion mode.

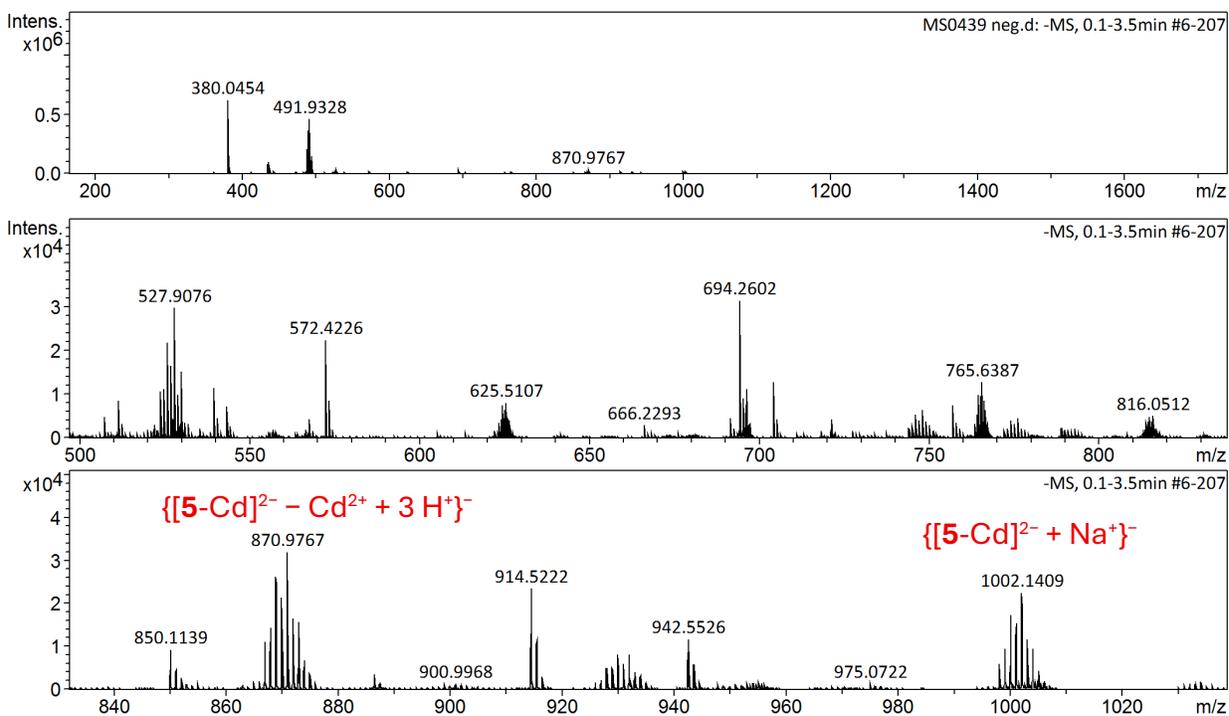


Figure S42. ESI-MS data for $[Et_4N]_2[5-Cd(solv)]$.

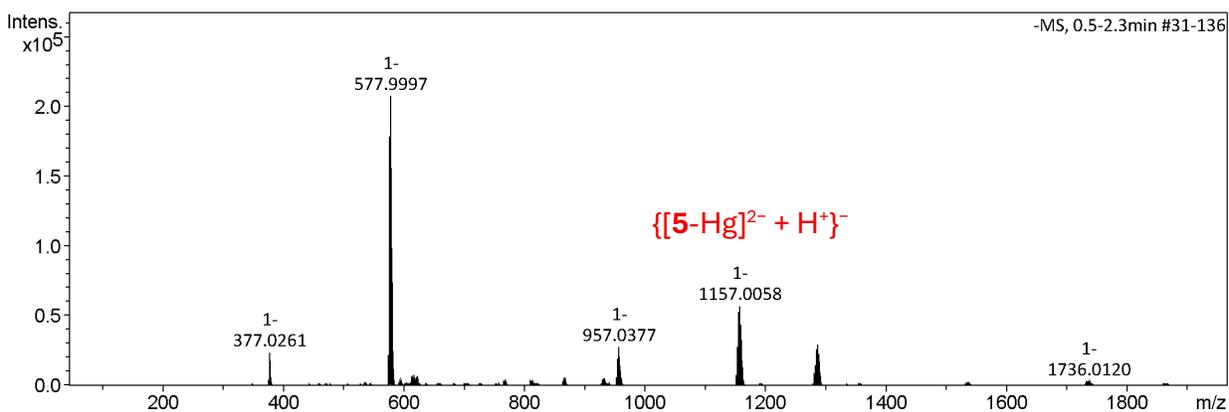


Figure S43. ESI-MS data for $[Et_4N]_2[5-Hg(solv)]$.

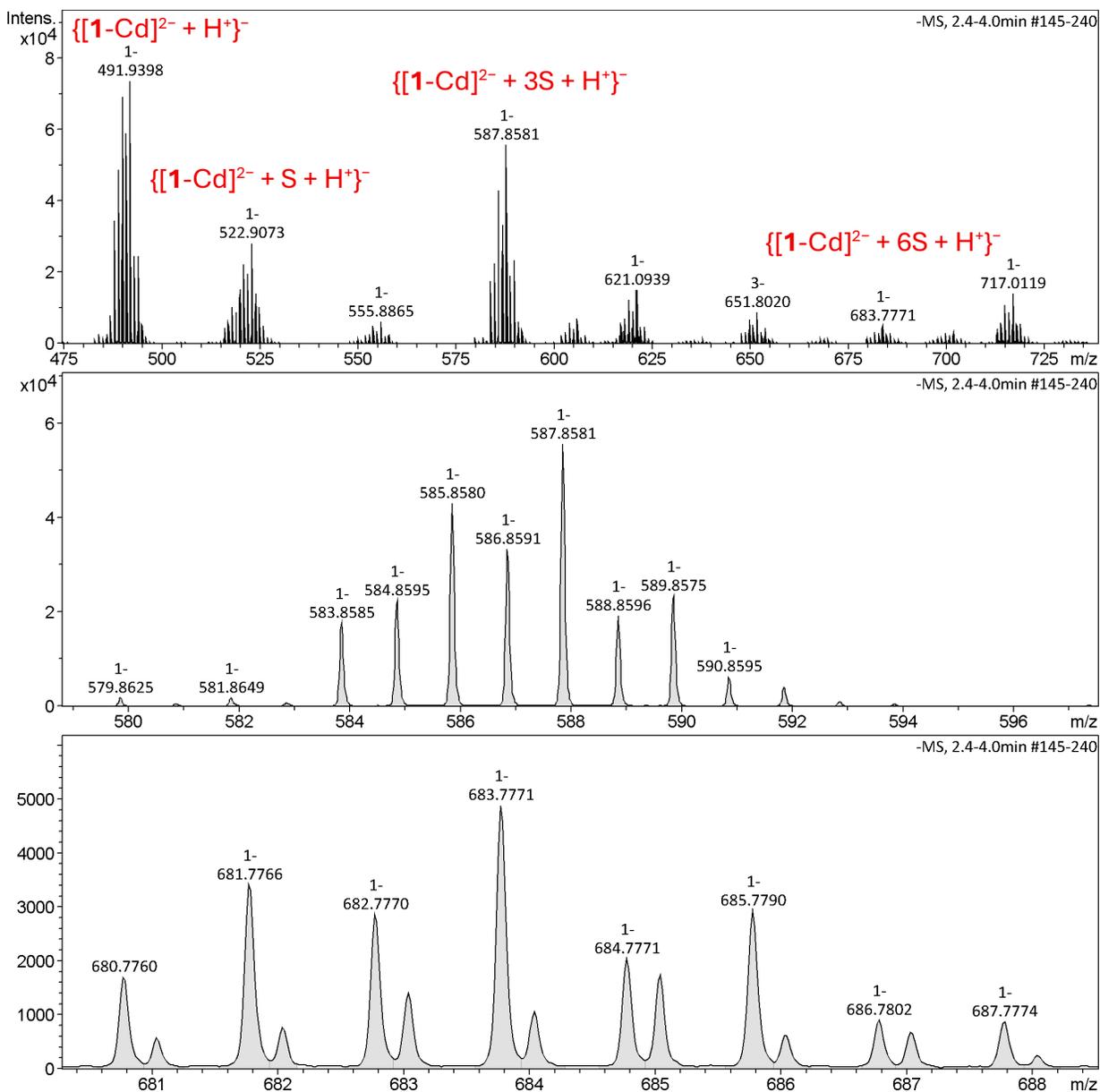


Figure S44. ESI-MS data for $[\text{Et}_4\text{N}]_2[1\text{-Cd}]$ with added S_8 (5/8 equiv).

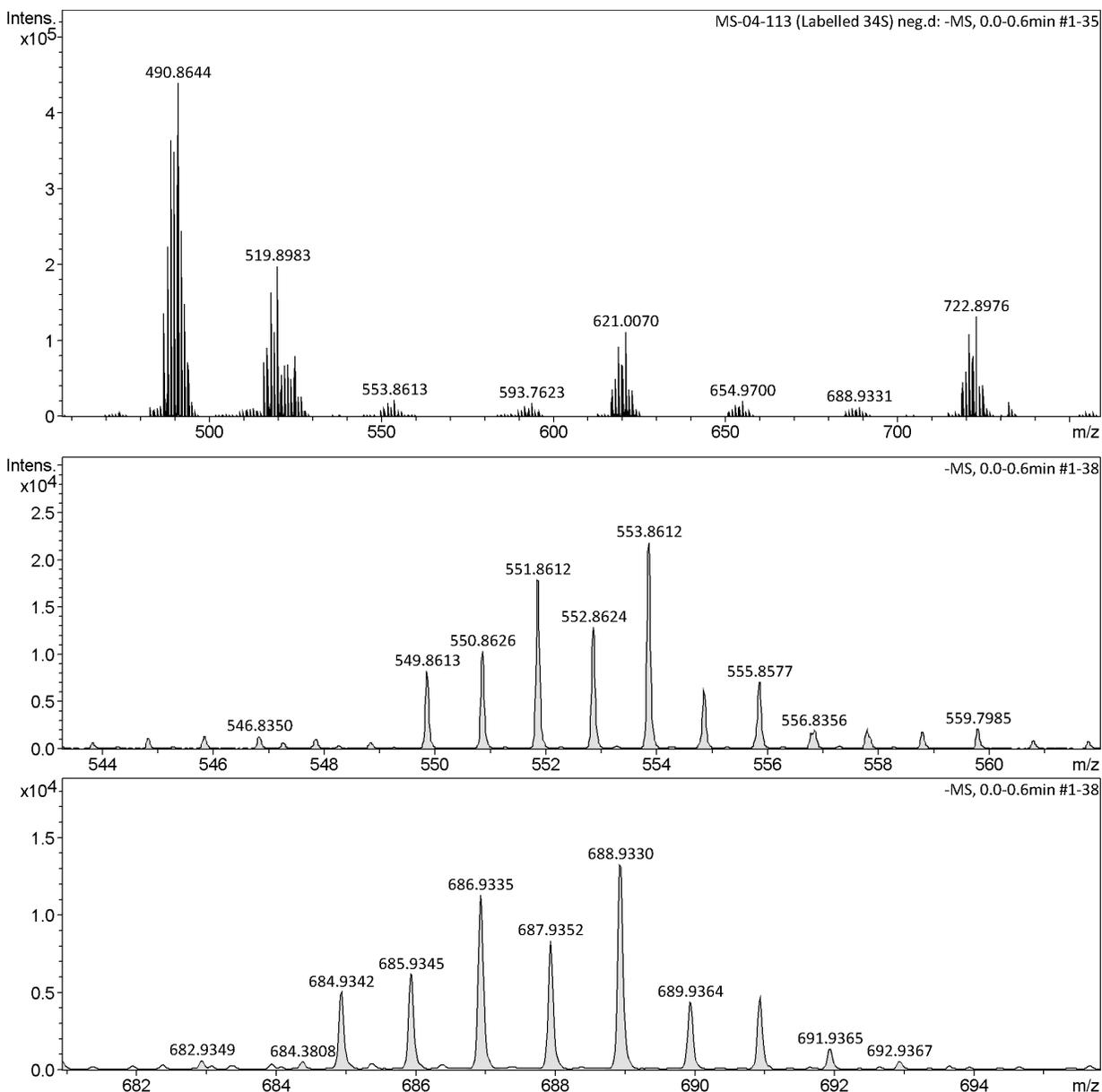


Figure S45. ESI-MS data for $[\text{Et}_4\text{N}]_2[1\text{-Cd}]$ with added $^{34}\text{S}_8$.

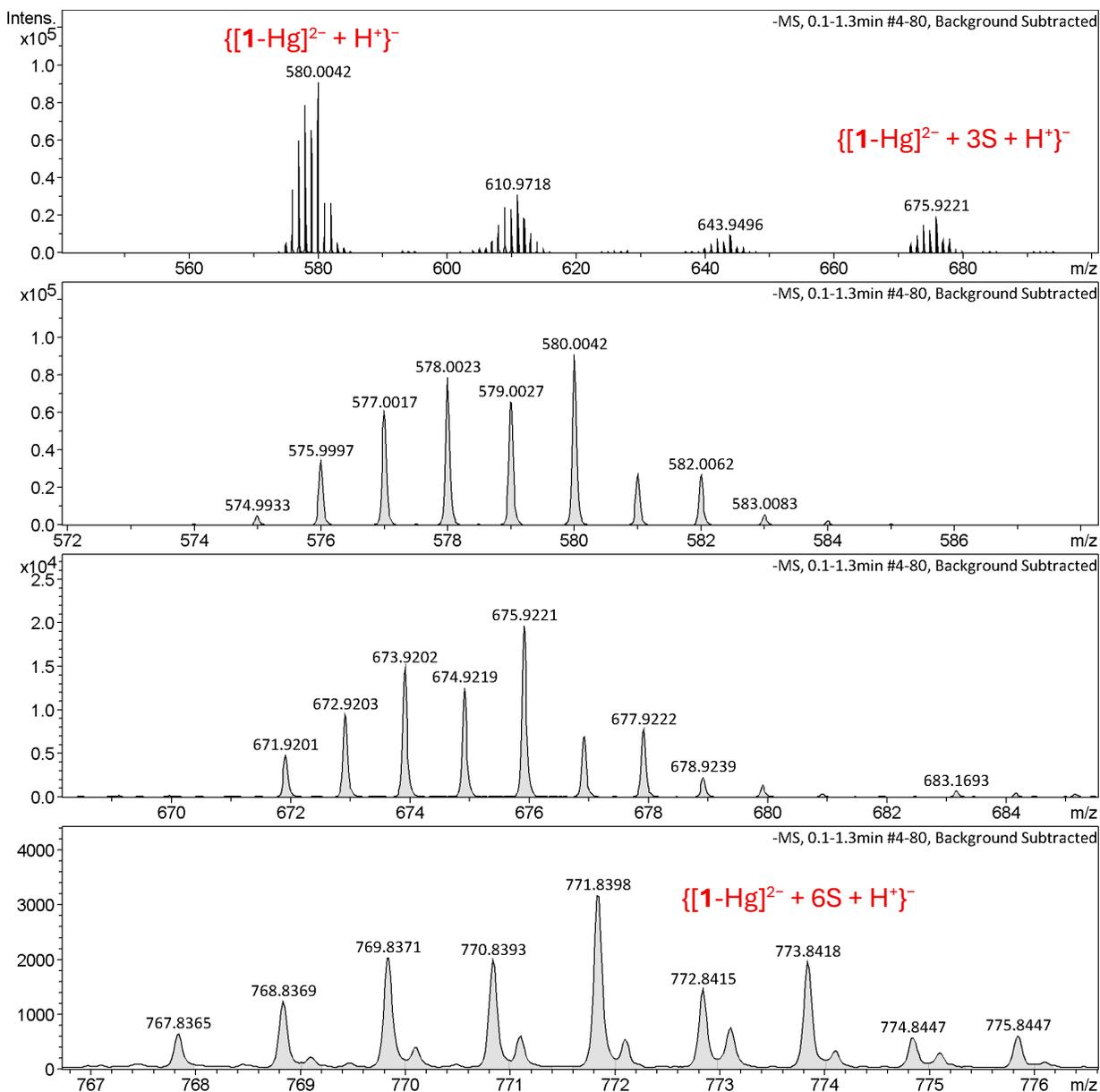


Figure S46. ESI-MS data for $[\text{Et}_4\text{N}]_2[\text{1-Hg}]$ with added S_8 (5/8 equiv).

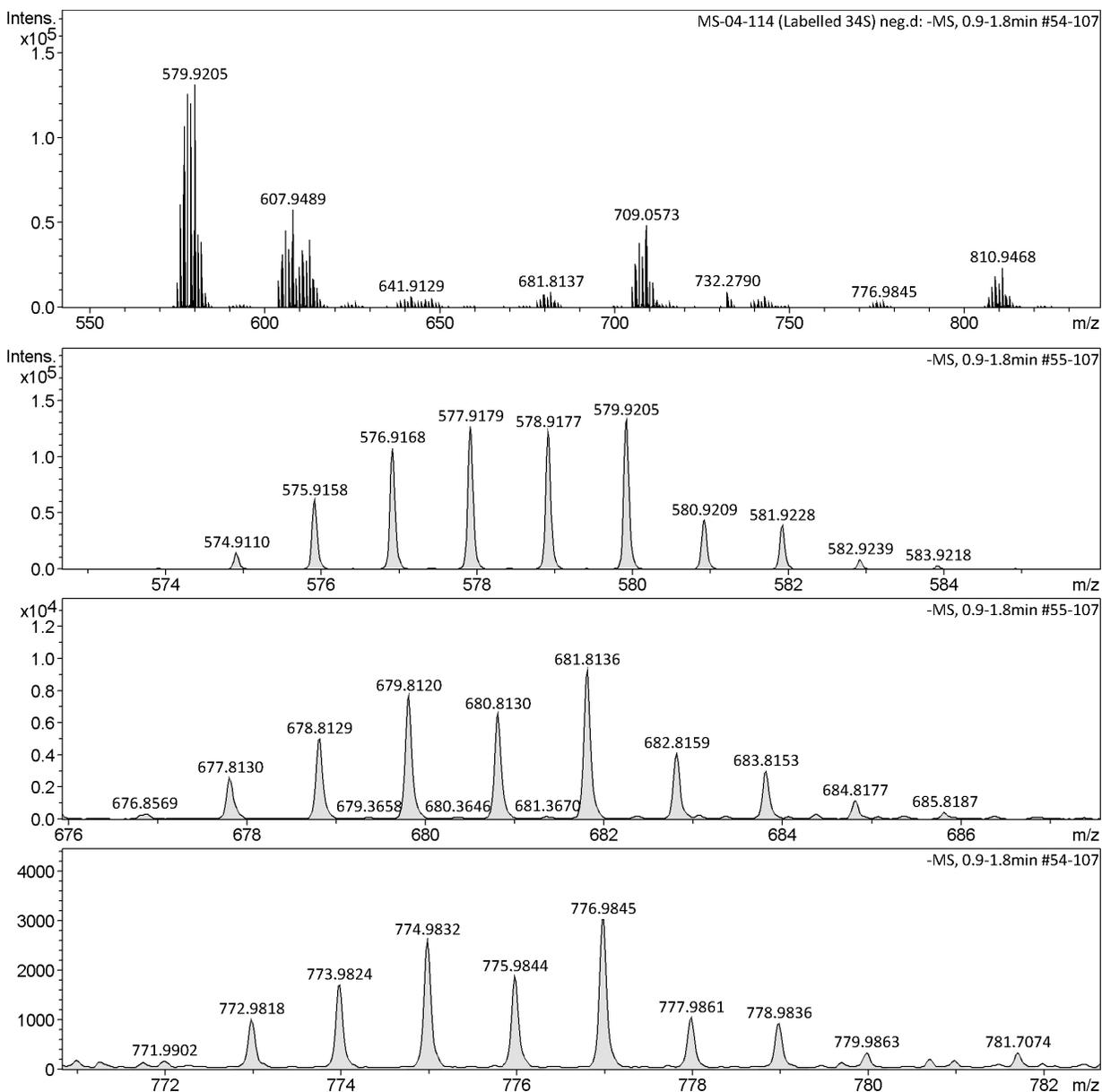


Figure S47. ESI-MS data for $[\text{Et}_4\text{N}]_2[1\text{-Hg}]$ with added $^{34}\text{S}_8$.

Crystallographic Information

CCDC 2521016–2521020 contain the supplementary crystallographic data for this paper. These data can be obtained free from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Refinement and instrument Details. Crystals were mounted on a MiTeGen loop using Paratone oil and placed on the diffractometer under a cold nitrogen stream on a Bruker D8 Quest diffractometer using a combination of ω - and ϕ -scans of 0.5° .⁶ Data were corrected for absorption and polarization effects and analyzed for space group determination.⁷ The structure was solved by dual-space methods and expanded routinely.⁸ The model was refined by full-matrix least-squares

analysis of F^2 against all reflections.⁹ All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. Unless otherwise noted, hydrogen atoms were included in calculated positions. Atomic displacement parameters for the hydrogens were tied to the equivalent isotropic displacement parameter of the atom to which they are bonded ($U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl, $1.2U_{\text{eq}}(\text{C})$ for all others).

[Et₄N]₂[1-Cd]. Crystals of [Et₄N]₂[1-Cd] were grown from vapor diffusion of diethyl ether into a concentrated solution of [Et₄N]₂[1-Cd] in CH₃CN. An arbitrary sphere of data was collected on a yellow rectangular prism-like crystal, having approximate dimensions of 0.174 × 0.104 × 0.088 mm.

[Et₄N]₂[1-Hg]. Crystals of [Et₄N]₂[1-Hg] were grown from vapor diffusion of diethyl ether into a concentrated solution of [Et₄N]₂[1-Hg] in CH₃CN. An arbitrary sphere of data was collected on an orange/yellow rectangular prism-like crystal, having approximate dimensions of 0.175 × 0.125 × 0.119 mm.

Table S2. Crystal and refinement data for [Et₄N]₂[1-Cd] and [Et₄N]₂[1-Hg].

Compound	[Et ₄ N] ₂ [1-Cd]	[Et ₄ N] ₂ [1-Hg]
Identification	ms0281_a	ms0293c
Empirical formula	C ₃₅ H ₅₁ CdN ₅ O ₂ S ₂	C ₃₅ H ₅₁ N ₅ O ₂ S ₂ Hg
Formula weight	750.32	838.51
Crystal system	120	120
Space group	monoclinic	monoclinic
a/Å	P2 ₁ /n	P2 ₁ /n
b/Å	9.5567(6)	9.5352(6)
c/Å	15.4561(11)	15.4127(8)
α/°	24.0658(16)	24.2083(15)
β/°	90	90
γ/°	90.072(2)	90.247(2)
Volume/Å ³	90	90
Z	3554.7(4)	3557.7(4)
ρ _{calc} /cm ³	4	4
μ/mm ⁻¹	1.402	1.565
F(000)	0.77	4.482
Crystal size/mm ³	1568	1696
Radiation	0.174 × 0.104 × 0.088	0.175 × 0.125 × 0.119
2θ range for data collection/°	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
Index ranges	4.29 to 46.512	4.278 to 56.712
Reflections collected	-10 ≤ h ≤ 10, -17 ≤ k ≤ 17, -26 ≤ l ≤ 26	-12 ≤ h ≤ 12, -20 ≤ k ≤ 20, -32 ≤ l ≤ 32
Independent reflections	141686	318181
Data/restraints/parameters	5107 [R _{int} = 0.3186, R _{sigma} = 0.0731]	8874 [R _{int} = 0.2110, R _{sigma} = 0.0427]

Goodness-of-fit on F ²	5107/88/409	8874/54/499
Final R indexes [I>=2σ (I)]	1.082	1.023
Final R indexes [all data]	R ₁ = 0.0508, wR ₂ = 0.0876	R ₁ = 0.0319, wR ₂ = 0.0526
Largest diff. peak/hole / e Å ⁻³	R ₁ = 0.0910, wR ₂ = 0.1008	R ₁ = 0.0557, wR ₂ = 0.0588

[Et₄N]₂[7]. Crystals of [Et₄N]₂[7] were grown from vapor diffusion of diethyl ether into a concentrated solution of [Et₄N]₂[7]. An arbitrary sphere of data was collected on a yellow rectangular prism-like crystal, having approximate dimensions of 0.262 × 0.132 × 0.122 mm.

[Et₄N]₂[4^{Me}-Cd(Stol)]. Crystals of [Et₄N]₂[4^{Me}-Cd(Stol)] were grown from vapor diffusion of diethyl ether into a concentrated solution of [Et₄N]₂[4^{Me}-Cd(Stol)] in CH₃CN at -30 °C. An arbitrary sphere of data was collected on a yellow rectangular prism-like crystal, having approximate dimensions of 0.322 × 0.196 × 0.12mm.

[Et₄N]₂[4^{Me}-Hg(Stol)]. Crystals of [Et₄N]₂[4^{Me}-Hg(Stol)] were grown from vapor diffusion of diethyl ether into a concentrated solution of [Et₄N]₂[4^{Me}-Hg(Stol)] in CH₃CN at -30 °C. An arbitrary sphere of data was collected on a yellow rectangular prism-like crystal, having approximate dimensions of 0.2 × 0.146 × 0.058 mm.

Table S3. Crystal and refinement data for [Et₄N]₂[7], [Et₄N]₂[4^{Me}-Cd(Stol)], and [Et₄N]₂[4^{Me}-Cd(Stol)].

Compound	[Et ₄ N] ₂ [7]	[Et ₄ N] ₂ [4 ^{Me} -Cd(Stol)]	[Et ₄ N] ₂ [4 ^{Me} -Hg(Stol)]
Identification	MS_02_116_CdL2_heated	ms03151	ms04102a_c
Empirical formula	C _{35.5} H _{40.67} Cd _{0.67} N _{5.33} O _{3.17} S ₄	C ₄₄ H _{62.5} CdN _{5.5} O ₂ S ₃	C ₄₃ H ₆₁ HgN ₅ O ₂ S ₃
Formula weight	795.96	909.07	976.73
Temperature/K	120	120	120
Crystal system	triclinic	orthorhombic	orthorhombic
Space group	P-1	Pbca	Pbca
a/Å	14.1642(14)	16.8332(15)	16.8803(8)
b/Å	18.917(2)	18.2888(17)	18.3305(8)
c/Å	23.983(2)	30.014(3)	29.6825(14)
α/°	93.388(3)	90	90
β/°	102.363(3)	90	90
γ/°	107.300(4)	90	90
Volume/Å ³	5941.1(10)	9240.2(15)	9184.5(7)
Z	6	8	8
ρ _{calc} /cm ³	1.335	1.307	1.413
μ/mm ⁻¹	0.629	0.649	3.527
F(000)	2474	3816	3984
Crystal size/mm ³	0.262 × 0.132 × 0.122	0.322 × 0.196 × 0.12	0.2 × 0.146 × 0.058
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)

2 θ range for data collection/ $^{\circ}$	3.872 to 56.716	4.264 to 52.768	4.276 to 52.766
Index ranges	$-18 \leq h \leq 18, -25 \leq k \leq 25, -31 \leq l \leq 32$	$-21 \leq h \leq 21, -22 \leq k \leq 22, -37 \leq l \leq 37$	$-21 \leq h \leq 21, -22 \leq k \leq 22, -37 \leq l \leq 37$
Reflections collected	304390	401389	447582
Independent reflections	29528 [$R_{\text{int}} = 0.0640, R_{\text{sigma}} = 0.0328$]	9445 [$R_{\text{int}} = 0.0539, R_{\text{sigma}} = 0.0122$]	9375 [$R_{\text{int}} = 0.0815, R_{\text{sigma}} = 0.0164$]
Data/restraints/parameters	29528/1033/1441	9445/147/562	9375/0/497
Goodness-of-fit on F^2	1.139	1.169	1.182
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0632, wR_2 = 0.1447$	$R_1 = 0.0748, wR_2 = 0.1872$	$R_1 = 0.0514, wR_2 = 0.1027$
Final R indexes [all data]	$R_1 = 0.0716, wR_2 = 0.1489$	$R_1 = 0.0791, wR_2 = 0.1904$	$R_1 = 0.0595, wR_2 = 0.1064$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	1.42/-1.28	1.33/-1.25	2.42/-1.65

Computational Studies

Visualization

All graphics of molecular orbitals were generated using VMD 1.9.4a53 (Visual Molecular Dynamics).¹⁰⁻¹²

Geometry optimizations and single-point energy calculations

All DFT calculations were carried out with ORCA 6.1.0.¹³⁻¹⁷ The choice of functional and basis sets were made according to the recommendations by Grimme et al.¹⁸ Geometry optimizations were performed using the ω B97X-D4³⁴⁻³⁶/def2-TZVPPD¹⁸⁻²⁰ level of theory (LibXC implementation²¹) with SMD²² as an implicit solvation model for dimethyl sulfoxide (DMSO). The RIJCOSX approximation²³⁻²⁷ with the auxiliary basis set def2/J²⁸⁻³⁰ was used throughout, convergence criteria were set to TightSCF for the SCF procedure and TightOpt for geometry optimizations, using the DefGrid3 integration grid. Subsequent high level single-point energy calculations were performed for each optimized geometry at the ω B97X-D4/def2-QZVPPD/SMD(MeCN) level of theory. Harmonic vibrational frequencies were calculated at both the triple-zeta (TZ) and quadruple-zeta (QZ) level of theory and were used to confirm the structures to be minima on the potential energy surface. Frequencies at QZ level were employed to compute thermodynamic properties.

Conformational search and Structural ensemble

For all compounds, relevant conformers were identified using the Conformer-Rotamer Ensemble Sampling Tool (CREST 3.0.2) at the GFN2-xTB/GBSA(DMSO) level of theory.^{10, 11, 31} Each conformer was subsequently subjected to TZ DFT geometry optimization as described above. Only if a conformer lied within an energetic window of 3 kcal·mol⁻¹ relative to the lowest-energy conformer the QZ single-point energy was computed, otherwise the conformer was not further

taken into account.^{10, 32} Gibbs free energies were obtained as implemented in ORCA 6.1.0 at 298.15 K, using the quasi-RRHO treatment.^{10, 33} Conformers within the 3 kcal·mol⁻¹ window were considered for Boltzmann-averaged property calculations of the structural ensemble (SE). The Gibbs free energy of the SE was computed following the approach described by Grimme et al., as detailed in Equations S1–S5.^{10, 14}

$$G_{SE} = \bar{G} + G_{conf} \quad (S1)$$

In equation (1) G_{SE} is the Gibbs free energy of the SE, \bar{G} is the average Gibbs free energy and G_{conf} is the conformational free energy.

$$\bar{G} = \sum_i^N p_i G_i \quad (S2)$$

with

$$p_i = \frac{e^{-\frac{G_i}{kT}}}{\sum_i^N e^{-\frac{G_i}{kT}}} = \frac{e^{-\frac{G_i}{RT}}}{\sum_i^N e^{-\frac{G_i}{RT}}} \quad (S3)$$

and

$$G_{conf} = -TS'_{conf} \quad (S4)$$

with

$$S'_{conf} = -R \sum_i^N p_i \ln p_i \quad (S5)$$

In equation 2-5 p_i is the Boltzmann population, G_i is the molecular free energy of the ensemble member i , k is the Boltzmann constant, R is the gas constant and S'_{conf} conformational entropy.^{11,}

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Table S4. Electronic and thermochemical data at QZ level.

Compound (and Conformer)	Electronic energy (Eh)	thermal energy correction (Eh)	ZPE correction (Eh)	Enthalpy correction (Eh)	Entropy correction (Eh)	Gibbs free energy (Eh)
[1-Cd] ²⁻	-2010.91714993	0.02231842	0.26358187	0.00094421	-0.07254717	-2010.70285260
[2-Cd] ²⁻ Conf. 1	-3205.64660403	0.02710832	0.26921782	0.00094421	-0.08263551	-3205.43196919
[2-Cd] ²⁻ Conf. 2	-3205.64598278	0.02704495	0.26929216	0.00094421	-0.08239489	-3205.43109636
[2-Cd] ²⁻ Conf. 3	-3205.64513412	0.02705170	0.26931845	0.00094421	-0.08233105	-3205.43015081
[6-Cd] ²⁻	-4400.37404170	0.03185170	0.27505742	0.00094421	-0.09217308	-4400.15836144
[2'-Cd] ²⁻ Conf. 1	-3205.64297729	0.02711389	0.26950800	0.00094421	-0.08250679	-3205.42791798
[2'-Cd] ²⁻ Conf. 2	-3205.64443051	0.02721578	0.26941127	0.00094421	-0.08292639	-3205.42978564
[2'-Cd] ²⁻ Conf. 3	-3205.64086403	0.02705846	0.26949349	0.00094421	-0.08234917	-3205.42571704
[2'-Cd] ²⁻ Conf. 4	-3205.64139373	0.02698634	0.26962165	0.00094421	-0.08211432	-3205.42595585
S ₈	-3185.90132107	0.01045157	0.01361361	0.00094421	-0.04805187	-3185.92436355

Table S5. Details on Structural ensemble at QZ level.

Compound and Conformer	G_i (Eh)	G_i (kJ·mol ⁻¹)	p_i (kJ·mol ⁻¹)	\bar{G} (kJ·mol ⁻¹)	G_{conf} (kJ·mol ⁻¹)	G_{SE} (kJ·mol ⁻¹)
[2-Cd] ²⁻ Conf. 1	-3205.43196919	-8415860.417	0.648295199	-8415859.377	-2.114945012	-8415861.491

[2-Cd] ²⁻ Conf. 2	-3205.43109636	-8415858.125	0.257216756			
[2-Cd] ²⁻ Conf. 3	-3205.43015081	-8415855.643	0.094488045			
[2'-Cd] ²⁻ Conf. 1	-3205.42791798	-8415849.781	0.118327645	-8415853.832	-1.239291741	-8415855.071
[2'-Cd] ²⁻ Conf. 2	-3205.42978564	-8415854.684	0.855360857			
[2'-Cd] ²⁻ Conf. 3	-3205.42571704	-8415844.002	0.011500721			
[2'-Cd] ²⁻ Conf. 4	-3205.42595585	-8415844.629	0.014810777			

XYZ-coordinates of the optimized geometries at TZ level

[1-Cd]²⁻

S	1.39480252874982	-1.79821160943416	1.59560496349356
C	5.31825450938646	-1.47433349322142	-0.75024182231727
C	-2.89248305368322	-1.64491229177109	-0.66220651383280
N	-2.14151058653364	0.42143203496409	0.33195265099302
C	-1.15142167131665	2.57959734932519	0.13874026816019
C	-2.40634696308121	1.71601239829487	0.21970793761201
C	-4.35957869691212	-0.47726148097288	0.87749418447763
C	-3.14692781255697	-0.53964574966253	0.18497152138558
N	-0.00001018355099	1.93783253314332	0.00027001873328
C	-1.19451878342838	3.96721631176155	0.14673288595737
C	1.15161372242891	2.57922839981334	-0.13816905011372
H	-2.14080292601654	4.47824683609058	0.26012727698332
C	0.00045593206043	4.66172789213109	0.00043690693455
H	4.53955674290107	0.37103129928147	-1.52395805371959
H	5.81118249133593	-3.34813520689685	0.19295506365967
H	3.67717385789706	-3.48847067288310	1.41847012699648
H	-5.81313787108927	-3.34595798807529	-0.19419882277032
C	3.14595213705043	-0.54074780681107	-0.18522020780236
C	5.07309779470608	-2.56054732160112	0.08238503582032
H	6.25092262464238	-1.40134974584789	-1.29994027759518
Cd	-0.00044039854424	-0.40116408539415	0.00000872085972
C	-5.07478850035682	-2.55865672344517	-0.08336474547564
H	-3.67916704081910	-3.48663574301797	-1.41972259782742
H	-6.25226058486624	-1.39948670354049	1.29928352263720
C	-3.87143962837107	-2.63693357736206	-0.77287198577949
O	-3.50575665652756	2.29028527832452	0.11526324796520
S	-1.39618417634949	-1.79712434699986	-1.59623850307558
C	-5.31959883762104	-1.47261846811728	0.74959351580927
H	-4.54026256729527	0.37220143719892	1.52394793664645
C	2.40622637401368	1.71521978874096	-0.21937459751202
C	1.19519239620904	3.96683161164207	-0.14598781631319
H	0.00063739603857	5.74608940618039	0.00052267340708

N	2.14090709153751	0.42076208603414	-0.33178650076172
O	3.50585680730438	2.28907684963173	-0.11494005331673
H	2.14164766430367	4.47755431103338	-0.25933629500563
C	3.86972862165777	-2.63863498609114	0.77188148818090
C	2.89113624177112	-1.64621490817652	0.66158324722681
C	4.35858503782550	-0.47859127556959	-0.87779326162094

[2-Cd]²⁻ Conf. 1

S	3.91806475505085	-0.38446296452993	0.98044052444057
C	3.27479164060552	3.14121815650749	-1.82093609460155
C	-3.47893969348538	1.57802155121184	-0.20498356162588
N	-2.54738325772562	-0.62024868959070	0.10382811409557
C	-1.37035218435614	-2.61299799088871	-0.42952232450555
C	-2.68294121895351	-1.92879048289492	-0.04698335715377
C	-4.78593757952167	-0.08779203380095	0.98199765824382
C	-3.61528416231949	0.25385593934360	0.29192917792795
N	-0.31823451036770	-1.82906478962872	-0.62185011437935
C	-1.27950711942771	-3.98224186842833	-0.64366484401238
C	0.83984746127004	-2.30108427252606	-1.05940940060061
H	-2.14348431309887	-4.61157023452390	-0.48030871242451
C	-0.06704165314741	-4.50253413644449	-1.07958772048440
H	1.51527214042302	2.10037357545386	-2.48740069213228
H	5.08478365239285	3.94141921135794	-0.96471691309436
H	5.42194477423756	1.99493179016007	0.52902097341790
H	-6.47233477300184	2.85138401802898	0.82940150264686
C	2.56103348854464	0.96966307497954	-1.00429132714677
C	4.38017209305886	3.11783099176053	-0.97541525318760
H	3.10955520192426	3.98976781019731	-2.47624227163889
Cd	-0.47849644507885	0.43589932227133	-0.11945153561429
C	-5.68157375291356	2.12252205932551	0.68573780619025
H	-4.41832954935089	3.49139081064820	-0.37488553570833
H	-6.70349868020491	0.53322917579310	1.71838355078099
C	-4.52317011103108	2.48106276680717	0.00665307477964
O	-3.70132501986340	-2.64277921801619	0.01490695308969
S	-2.05673439737561	2.12997295960040	-1.10873755777282
C	-5.80986676517448	0.83049144204845	1.17914699721573
H	-4.88187671099163	-1.09621446931096	1.35931133441460
C	1.94693950943890	-1.28141332367459	-1.28162694610669
C	1.01166307537613	-3.65551535173044	-1.30590810228817
H	0.03395566782851	-5.56776725897337	-1.25512808513201

N	1.59288534055424	-0.03466168364912	-0.98734844677034
O	3.03796639894186	-1.68265208508716	-1.71793119542270
H	1.96228586569129	-4.02419599178983	-1.66586453180205
C	4.57013944337332	2.02611008093267	-0.14127167354128
C	3.66698423275554	0.96547008068312	-0.13964290135356
C	2.38069384972518	2.08160978421512	-1.83326005028930
S	3.27160797260410	0.37277551384286	2.76858201474441
S	1.31395707584925	-0.15416452245028	2.97701722883843
S	0.16036048354381	1.33455007076957	2.17832044716305

[2-Cd]²⁻ Conf. 2

S	1.90883623881102	2.12900914473886	1.10971800861110
C	4.37180738782075	1.90160084112670	-2.68608959382828
C	-3.21736523420115	1.70831616359947	0.13414205590610
N	-2.50325863852423	-0.57373251933258	-0.12560783036454
C	-1.38226097500771	-2.56091738381909	-0.78736035290614
C	-2.68986353851442	-1.84158761848652	-0.46066949395065
C	-4.83236283732737	-0.05963849935201	0.52147927485735
C	-3.52850348686068	0.31970832708000	0.16343717389597
N	-0.28245604710770	-1.82241036501499	-0.83944498951843
C	-1.33081745865972	-3.92430189461881	-1.04816177480960
C	0.89708989296072	-2.33966316165806	-1.14344056549160
H	-2.23585648281348	-4.51474976317707	-1.00859210207846
C	-0.10004615489146	-4.49177411459814	-1.35439413905965
H	3.34377424783123	0.07837852038728	-3.11381174491868
H	5.25009522150164	3.75824590611566	-2.01477404921389
H	3.90358750757814	3.80442820320200	0.06655460457165
H	-6.25735436879297	2.97827440345688	1.03181550090006
C	2.70611563237994	0.88305550474325	-1.22963280071211
C	4.54670363851247	2.96268583675734	-1.79835941788404
H	4.94017016600831	1.86929906705632	-3.60985767720025
Cd	-0.27892333486702	0.27001483441024	0.15623725348809
C	-5.50571751235904	2.23277211734767	0.79411720629931
H	-3.97389149299099	3.68568332294848	0.42499759500027
H	-6.80581200566996	0.54559133921936	1.10477514664072
C	-4.21850715584995	2.62877600753936	0.45001672889167
O	-3.74065771338902	-2.50302692736160	-0.57720595647961
S	-1.61875430578191	2.33827146469683	-0.29098096020607
C	-5.80913660578433	0.87878085452774	0.83327297415561

H	-5.06715850045130	-1.11345262432844	0.54348125808125
C	2.06826261803571	-1.37230071993697	-1.22891423081191
C	1.03702005553902	-3.69471963567390	-1.40980573324629
H	-0.02770319686641	-5.55481078814688	-1.55576113384646
N	1.74959676567823	-0.09717541635745	-0.98541710375218
O	3.17792606313755	-1.84666374725606	-1.51478677771952
H	2.00797006981513	-4.10091961241031	-1.65719000005869
C	3.79637766176624	2.98670059541945	-0.63723259073906
C	2.88949552377752	1.96392585060084	-0.34916755995511
C	3.47338594640417	0.88818147354845	-2.40870686667426
S	2.83118152344640	1.03098682557296	2.56040104497287
S	2.10010185125718	-0.87745139543151	2.36092260982788
S	0.08163222314950	-0.67560772663471	2.53893965482561

[2-Cd]²⁻ Conf. 3

S	3.28888886206614	0.10650559504106	-1.93630316662591
C	3.85417449340821	2.37310608400786	1.95564234890275
C	-3.28401541946055	1.39538057697364	1.15342903967080
N	-2.55692788584255	-0.78731897548359	0.44523263263677
C	-1.35017053935605	-2.82853179944634	0.31608255096411
C	-2.69397401632149	-2.10453522834168	0.41777543880986
C	-4.93485919619573	-0.15799421252393	0.28464199280342
C	-3.60278660990241	0.11149614807722	0.63029401179890
N	-0.26033613770532	-2.07465732089386	0.34581034860439
C	-1.24662964845699	-4.21202061351992	0.25079498141838
C	0.95849393606303	-2.59125125805281	0.34264754548238
H	-2.14055393514625	-4.82008014354915	0.22823166699883
C	0.02296370720168	-4.77702043407061	0.22376012217987
H	2.25588730367186	1.14539276325062	2.70448906491526
H	5.42986778665164	3.43997125052176	0.94080773384681
H	5.15116458332204	2.16671777778151	-1.16453945596752
H	-6.39667889277985	2.79603942668436	1.08931067492822
C	2.73885789646262	0.63451066035689	0.68438009494083
C	4.67854392826689	2.66173320941294	0.87018054375195
H	3.95869258987959	2.93050657935906	2.88034874019530
Cd	-0.45866480463598	0.22432414652021	0.18695559431549
C	-5.62625108765490	2.04349473455360	0.95804039040461
H	-4.06378569927525	3.30918360542038	1.69981550015922
H	-6.95688903029647	0.54905163757296	0.16398950001514

C	-4.31034460829675	2.33039153098861	1.30172930077789
O	-3.71565310095983	-2.81096137220802	0.50987403962028
S	-1.64883718762833	1.86339704050594	1.65767110009914
C	-5.93674261977036	0.79172065818945	0.44366766208134
H	-5.17175200034361	-1.13515186594154	-0.11118865104284
C	2.11172641820019	-1.60279644550847	0.44089290913852
C	1.14955351920492	-3.96398823382632	0.27807493086161
H	0.13503579784644	-5.85420175828194	0.17038926118572
N	1.73347893178803	-0.33878666846006	0.61456435191776
O	3.27012120548590	-2.04862164038496	0.38377393891759
H	2.15017825516060	-4.37384129596290	0.27591396571083
C	4.52734782799579	1.94464487960701	-0.30589273969735
C	3.56158416344587	0.94665582160826	-0.40628724669301
C	2.90074233436599	1.37201616315737	1.86215725037246
S	2.59613944394335	1.64348346965800	-3.11363638168041
S	0.92352639864088	2.32925371876685	-2.17454216138861
S	-0.51485652524303	0.88312281234057	-2.29185326913079

[6-Cd]²⁻

S	4.18647481737815	0.23751936669907	-1.17931154811644
C	3.85943963918357	-0.22043649947179	3.32448676603225
C	-4.06607617811186	-0.66914705480739	-0.12646195802411
N	-2.07122018461319	0.23139895506232	-1.21823084068620
C	-1.28253004210675	2.45826464537080	-1.52702124250588
C	-2.41498646963773	1.44784399012929	-1.61126870076715
C	-3.04648455543552	-1.85991386455787	-1.94423104275533
C	-3.07058377176356	-0.73619487378663	-1.11294616243483
N	-0.17555840695598	2.06243288917985	-0.91263425131761
C	-1.39975828786184	3.74538761497241	-2.03183592314544
C	0.85702748293780	2.87854452960764	-0.74966909587872
C	-0.32256059156117	4.61004725295752	-1.88574799271164
H	1.93461770758617	0.71097718874972	3.10635822053371
H	5.81919934201898	-1.11679906148469	3.23535474460418
H	6.01210417402320	-0.83031431808465	0.78337276369810
H	-5.71157433330734	-3.57818920942993	-0.72930226019734
C	2.93008357860232	0.54926329743265	1.22068932115477
C	5.01366569670631	-0.65518590513461	2.67568985681533
H	3.76057436149476	-0.34481300101450	4.39762536316694
Cd	0.04823152149039	-0.15400424738068	-0.26364532914756

C	-4.97480414216960	-2.79024495512838	-0.83598184105695
H	-5.77897270760697	-1.60182598280649	0.76122560922127
H	-3.94002514738530	-3.73491729238808	-2.46782797005833
C	-5.01331805397276	-1.68207960971283	-0.00255148730114
O	-3.52167044740577	1.84118844016758	-2.02225940207601
S	-4.11207714781974	0.71427805192549	0.98089234810682
C	-3.98260714953528	-2.87432379167850	-1.80861958173763
H	-2.27022032506543	-1.92613756598440	-2.69829717613420
C	2.05645280410865	2.32661200754570	0.00338345713780
C	0.82585766806888	4.17833873813446	-1.23408516724831
H	-0.37984509321413	5.62065223702930	-2.27419572590074
N	1.86123795074290	1.12040248340273	0.51892945572941
O	3.07044248185901	3.04282786055935	0.08864359344857
H	1.68128645672662	4.82451105647018	-1.09381021005676
C	5.12424062037362	-0.48996374049120	1.30454988589348
C	4.09126495708363	0.09854430835564	0.57924972226193
C	2.83529185671042	0.37441636947110	2.60559682768824
S	4.21623018523117	-1.74269626082314	-1.73467218816869
S	2.49440215110804	-2.53365435159682	-0.99070419301991
S	0.92648145283471	-1.75115980732338	-2.03966213537710
S	-3.48740465331209	-0.11249300035625	2.74633001513476
S	-1.46495596674479	0.10761411710408	2.84442993029843
S	-0.61636986194374	-1.44236651897474	1.80827586034089
H	-2.31438116323872	4.04889920809004	-2.52227060344285

[2⁺-Cd]²⁻ Conf. 1

S	2.19784286188102	2.03313551438003	-1.47595405213077
C	5.10811399237602	1.10987624257654	1.88205703783590
C	-3.48117976332034	1.58965007563120	0.66520467359773
N	-2.34048435602036	-0.48532453050685	0.12475367894034
C	-1.31678411834480	-2.60135199539164	0.53295768713460
C	-2.58027959113507	-1.76230276568030	0.38885301092118
C	-4.39984823561162	0.14456118754353	-1.02665285532310
C	-3.41134423357238	0.38817164212708	-0.06398745844838
N	-0.15655097769322	-1.95953120434994	0.50544525326955
C	-1.36494927576664	-3.98069228693327	0.67998105528721
C	0.99822171512538	-2.60276848592627	0.59506025829402
H	-2.32103506979574	-4.48485694518129	0.70703729876477
C	-0.16584906022371	-4.67440802468095	0.78100457624174

H	3.94692026978967	-0.63282878347649	2.30584316030390
H	6.09283765257801	2.91616363475220	1.22284410313518
H	4.50213917926509	3.27498608599577	-0.63792315060958
H	-6.29673471284807	2.94025508158931	-0.68749508857537
C	3.15072946958182	0.40526543651038	0.60944725735850
C	5.27812994785707	2.22038288251375	1.05869597723240
H	5.79001919175954	0.93403182239201	2.70750339434360
Cd	-0.09819437021705	0.25021957046999	-0.16011605954020
C	-5.49561187484922	2.22992753358490	-0.51661967566810
H	-4.54653698264167	3.41545093718958	1.00147534125291
H	-6.17926046853563	0.82904832074627	-1.99997258156397
C	-4.51643315690878	2.49465363665398	0.42934587081689
O	-3.67260543013164	-2.33591455642536	0.55367084345051
S	-2.29855783294582	1.95295629036081	1.93172199319284
C	-5.42749079472264	1.04720624558231	-1.24846554120425
H	-4.34810234506201	-0.77256855279474	-1.60084859205213
C	2.27046544080809	-1.76755100855130	0.55789236887597
C	1.03804458692711	-3.98336390499904	0.73577868427754
H	-0.16945652908337	-5.75299405641833	0.89159338821496
N	2.06929733245700	-0.45415298650180	0.43985838111245
O	3.34865573596537	-2.37988460564996	0.63187060832760
H	1.99052265458393	-4.48945017026609	0.80812389900522
C	4.38717545478044	2.41990252725822	0.01895062602045
C	3.32535537308186	1.53827484692788	-0.20521170158224
C	4.07095010473731	0.22333585926079	1.65649489407158
S	2.09599887213330	0.49027056909595	-2.81788977177401
S	0.15013008270222	-0.17556839308931	-2.68178795485284
S	-0.59766331356048	2.46605575128044	0.86870000274542

[2'-Cd]²⁻ Conf. 2

S	3.24780109467065	0.45957061662666	-2.17144522136841
C	4.48518281126981	1.72588745152593	2.02162258806104
C	-3.48361103112054	1.46932937986652	0.81892953248417
N	-2.36300545123609	-0.58221848038224	0.18957196775324
C	-1.33316033160104	-2.71207924266990	0.47220884189878
C	-2.60124356868787	-1.88128626276165	0.30366211652387
C	-4.35472495922592	0.16932519766203	-1.01294339005293
C	-3.40979223331896	0.31859173560908	0.01055913870731
N	-0.18101847760707	-2.05522962315484	0.48836404282396

C	-1.36790982177705	-4.09137038282970	0.62322029920297
C	0.97668147961161	-2.67808308361878	0.65926186303294
H	-2.31612502747894	-4.61076365643683	0.60714360103653
C	-0.16499902410751	-4.76522208938547	0.79458666777455
H	3.01717918807060	0.32938495860447	2.73509822501394
H	5.85735888107533	3.05412956048328	1.01952434939826
H	5.12026275935769	2.35736635841938	-1.24009411447116
H	-6.18354420074527	2.99771509919269	-0.57883348195479
C	3.05557959475315	0.37558170466328	0.59763132230157
C	5.08002142679828	2.30729400651847	0.90542125205153
H	4.79740529012969	2.01829036949579	3.01862229230309
Cd	-0.16697198740637	0.21434825696296	-0.00618572336301
C	-5.4132077782201	2.25217155701316	-0.41682084142577
H	-4.51443290340571	3.29980332823933	1.22822893761868
H	-6.06070700820565	0.97590400006749	-2.02322574716889
C	-4.47868927053353	2.42060120905617	0.59441385346730
O	-3.69205039073132	-2.47831950379139	0.33094913953267
S	-2.37621200971339	1.69390234773496	2.18318005874339
C	-5.34243930833813	1.11866884143688	-1.22245916013698
H	-4.29926815682803	-0.70754835472093	-1.64626821046693
C	2.22545673395579	-1.80703669834199	0.69874166029289
C	1.02917673028204	-4.05557165488587	0.81930495958074
H	-0.15866614639452	-5.84291597440745	0.91354078876481
N	1.98980754695830	-0.52332736503129	0.47451924438305
O	3.31582464185486	-2.36048169915162	0.93127027549506
H	1.98258298535169	-4.54563321421114	0.96057295747598
C	4.66476828959811	1.91953980853838	-0.35905433493776
C	3.66229591662904	0.96237438200184	-0.52156005599879
C	3.48819854438911	0.77602899776886	1.86632614699610
S	1.64811805172768	1.63147805268939	-2.67877589977707
S	-0.06100637785926	0.50375263615340	-2.52237950153288
S	-0.59257079403926	2.30008698455074	1.31869722443696

[2⁺-Cd]²⁻ Conf. 3

S	3.33796931850130	0.05269785046552	2.55344812109139
C	4.45006628675537	2.27026079466346	-1.27147961786021
C	-3.48558503148384	1.50688999443165	-1.26040919538273
N	-2.34791115801382	-0.44338775025225	-0.37522033871198
C	-1.28394209898265	-2.57940535537767	-0.42333792564180

C	-2.56385773822916	-1.75102593401287	-0.43084034899561
C	-4.43108353389902	0.34706858259803	0.62622427520139
C	-3.42756048814173	0.43827007234048	-0.34680288633203
N	-0.13700795822603	-1.91550826927232	-0.38123377942186
C	-1.30319859617230	-3.96656580000909	-0.46553583148509
C	1.03265697839487	-2.53982456143392	-0.37484828628251
H	-2.24810200674966	-4.49099890658566	-0.49994887831092
C	-0.08856428524680	-4.64125989701569	-0.46080244643889
H	2.96711765739882	1.11006731085293	-2.30439231737300
H	5.83757165097977	3.26959165835651	0.04471659643383
H	5.10243362011344	2.01957121895925	2.03302749583531
H	-6.31891304809732	3.05155841733921	-0.18157649926193
C	3.06087970977407	0.54452208875006	-0.25200232741656
C	5.06363315148220	2.51612366039565	-0.04766820295703
H	4.73964158960981	2.82994161685642	-2.15423940461357
Cd	-0.16953627909144	0.38921364880433	-0.13750260167692
C	-5.51597010470493	2.32432950453307	-0.22555608200038
H	-4.54512217780222	3.25309592636301	-1.90079258118511
H	-6.22466536956827	1.17550475886898	1.45001033113817
C	-4.52329577380965	2.43626035215993	-1.18783165332898
O	-3.64499056849597	-2.35968295762949	-0.51974650828953
S	-2.28949412562813	1.65477762055317	-2.55718241678179
C	-5.46096255329913	1.27241441762076	0.68525664903212
H	-4.38830779007519	-0.46629308026052	1.34042005255097
C	2.27690113540930	-1.66544456499442	-0.30518986287320
C	1.10109040207650	-3.92529359723405	-0.41410168245381
H	-0.06949108946002	-5.72492465461921	-0.49255752653336
N	2.01929092200562	-0.37195394636958	-0.42189556840869
O	3.37851693769572	-2.22463633725211	-0.16898225881464
H	2.06404423077993	-4.41711887192271	-0.40610338141956
C	4.65426891156925	1.80409410016698	1.06800504262397
C	3.66685817226012	0.81756300041229	0.98446567756687
C	3.45905185905641	1.30670255014498	-1.35769247327130
S	1.44522721886930	-0.69667072694062	2.60646661170312
S	0.15518184210405	0.87098458402720	2.35389814999720
S	-0.59818507615858	2.37686846831833	-1.60398494545134

[2'-Cd]²⁻ Conf. 4

S	2.09644296804835	2.34601787007413	0.48427910279675
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C	5.65988188177650	-0.02357309175448	-1.02592926903098
C	-3.57922741754032	0.96297131357860	0.16906222273587
N	-2.07385793271526	-0.78375059893062	-0.59460616051497
C	-1.19511552182616	-2.72543039233415	0.47026540792707
C	-2.39440319547022	-1.94440134049728	-0.04639174677603
C	-3.63647775983203	0.27061862557603	-2.13779766256491
C	-3.10831959274712	0.12057641553765	-0.85552174127135
N	-0.03284246343163	-2.08530030935472	0.50628979916824
C	-1.30508943791037	-4.03288915946782	0.92198963870127
C	1.06406660067540	-2.66448971737804	0.97482217602548
H	-2.26154323467038	-4.53550264825485	0.88114556020375
C	-0.16924788788701	-4.65494876431673	1.42306500383673
H	4.51990194529315	-1.77780453534273	-0.60817614741934
H	6.58957269733010	1.90168735090828	-1.34667660476710
H	4.61975658572595	3.14732091100299	-0.50183961494462
H	-5.86240386372888	2.77361707604126	-1.58332919507374
C	3.41083278990590	-0.01491773603593	-0.08267774974518
C	5.71015775323467	1.37056382231348	-1.00106494910972
H	6.50430371403219	-0.59006714097333	-1.40496394410893
Cd	0.03250031455026	0.15102211853125	-0.08214893957447
C	-5.09482669648423	2.03435615344280	-1.38323696153117
H	-4.91250329070207	2.55314063757272	0.69483827700794
H	-5.02338616867937	1.30606783427431	-3.40475609316198
C	-4.56381281408352	1.90852844035763	-0.10459438737436
O	-3.52295908580634	-2.44812010980928	0.10089384525318
S	-2.95154160468431	0.79280311720353	1.81697430307942
C	-4.62332737044111	1.21269218340472	-2.40055360072830
H	-3.26348901208382	-0.36925136853051	-2.93062878369268
C	2.35960039457247	-1.86796587623050	0.91311350071013
C	1.03601390638415	-3.96573001557735	1.45725715553540
H	-0.22242870037896	-5.67547884908862	1.78536410960969
N	2.25019628129359	-0.69543601641061	0.28547600662437
O	3.36438495746429	-2.38401271896749	1.42843062759550
H	1.94136640412256	-4.41636780387536	1.83913048853586
C	4.61286864295213	2.06317912112186	-0.52623472489515
C	3.47469990905947	1.38980260358840	-0.07861718859419
C	4.54160416819813	-0.69750967135640	-0.57472590147533
S	1.33145346786367	3.09695521955480	-1.25237085531969
S	0.51153835625394	1.47200138580860	-2.22383693861401
S	-1.04259164113374	1.58782237899377	1.70470602094156

S₈

S	2.21696404033295	0.66176401462208	-0.50316214896716
S	2.03549726129506	-1.09962712270381	0.50315221209515
S	0.66174825705792	-2.21687634955616	-0.50320805084621
S	-1.09958125301212	-2.03539471017668	0.50321519643617
S	-2.21696755046978	-0.66176338635710	-0.50315777861452
S	-2.03549624642685	1.09962925093812	0.50315335001082
S	-0.66174578722771	2.21687590792083	-0.50320957448620
S	1.09958127835053	2.03539239531273	0.50321679447195

References

1. A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen and F. J. Timmers, *Organometallics*, 1996, **15**, 1518–1520.
2. W. L. F. Armarego and C. L. L. Chai, in *Purification of Laboratory Chemicals*, Elsevier, 2009, pp.445–576.
3. Y. Tanabe, K. Nakajima and Y. Nishibayashi, *Chem. Eur. J.*, 2018, **24**, 18618–18622.
4. A. M. Thomas, B. Lin, E. C. Wasinger and T. D. P. Stack, *J. Am. Chem. Soc.*, 2013, **135**, 18912–18919.
5. M. Ballesteros and E. Y. Tsui, *Inorg. Chem.*, 2019, **58**, 10501–10507.
6. *APEX-3*. Bruker AXS. Madison, WI, USA. 2016.
7. L. Krause, R. Herbst-Irmer, G. M. Sheldrick and D. Stalke, *J. Appl. Cryst.*, 2015, **48**, 3–10.
8. G. M. Sheldrick, *Acta Crystallogr. C*, 2015, **71**, 3–8.
9. G. M. Sheldrick, *Acta Crystallogr. A*, 2015, **71**, 3–8.
10. W. Humphrey, A. Dalke and K. Schulten, *J. Mol. Graph.*, 1996, **14**, 33–38.
11. J. E. Stone, 1998, An efficient library for parallel ray tracing and animation.
12. A. Kohlmeyer, J. Vermaas and E. Braun, *Zenodo*, 2017.
13. F. Neese, *Wiley Interdisciplinary Reviews: Comp.*, 2012, **2**, 73–78.
14. F. Neese, *Wiley Interdisciplinary Reviews: Comp. Mol. Sci.*, 2025, **15**, e70019.
15. M. Garcia-Ratés and F. Neese, *J. Comput. Chem.*, 2019, **40**, 1816–1828.
16. M. Garcia-Ratés and F. Neese, *J. Comput. Chem.*, 2020, **41**, 922–939.
17. F. Neese, *J. Comp. Chem.*, 2023, **44**, 381–396.
18. M. Bursch, J. Mewes, A. Hansen and S. Grimme, *Angew. Chem. Int. Ed.*, 2022, **61**, e202205735.
19. D. Rappoport and F. Furche, *J. Chem. Phys.*, 2010, **133**.
20. A. Hellweg and D. Rappoport, *Phys. Chem. Chem. Phys.*, 2015, **17**, 1010–1017.
21. S. Lehtola, C. Steigemann, M. J. Oliveira and M. A. Marques, *SoftwareX*, 2018, **7**, 1–5.
22. A. V. Marenich, C. J. Cramer and D. G. Truhlar, *J. Phys. Chem. B*, 2009, **113**, 6378–6396.
23. K. Eichkorn, O. Treutler, H. Öhm, M. Häser and R. Ahlrichs, *Chem. Phys. Lett.*, 1995, **240**, 283–290.
24. B. Helmich-Paris, B. de Souza, F. Neese and R. Izsák, *J. Chem. Phys.*, 2021, **155**.
25. D. Bykov, T. Petrenko, R. Izsák, S. Kossmann, U. Becker, E. Valeev and F. Neese, *Mol. Phys.*, 2015, **113**, 1961–1977.

26. F. Neese, F. Wennmohs, A. Hansen and U. Becker, *Chem. Phys.*, 2009, **356**, 98–109.
27. F. Neese, *J. Comp. Chem.*, 2003, **24**, 1740–1747.
28. F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297–3305.
29. F. Weigend, *Phys. Chem. Chem. Phys.*, 2006, **8**, 1057–1065.
30. K. Eichkorn, F. Weigend, O. Treutler and R. Ahlrichs, *Theor. Chem. Acc.*, 1997, **97**, 119–124.
31. P. Pracht, F. Bohle and S. Grimme, *Phys. Chem. Chem. Phys.*, 2020, **22**, 7169–7192.
32. M. Garcia-Ratés and F. Neese, *J. Comput. Chem.*, 2019, **40**, 1816–1828.
33. F. Neese, *J. Comput. Chem.*, 2023, **44**, 381–396.
34. J.-D. Chai and M. Head-Gordon, *J. Chem. Phys.*, 2008, **128**, 084106.
35. A. Najibi, L. Goerigk, *J. Comput. Chem.*, 2020, **41**, 2562–2572.
36. A. Najibi, L. Goerigk, *J. Chem. Theory Comput.*, 2018, **14**, 5725–5738.