Supporting Information for:

# Site Specific Redox Properties in Ligand Differentiated Di-Nickel Complexes Inspired by the Acetyl CoA Synthase Active Site

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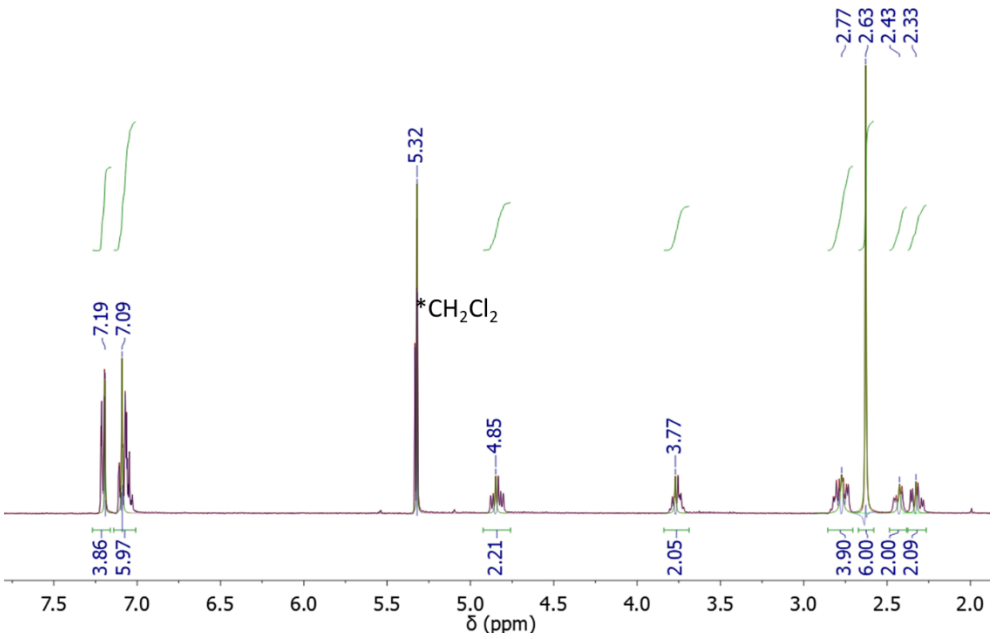



**Figure S1.** $^{1}$H NMR spectrum for Ni(bme-dame)-Ni(dpdt) **(1)**.

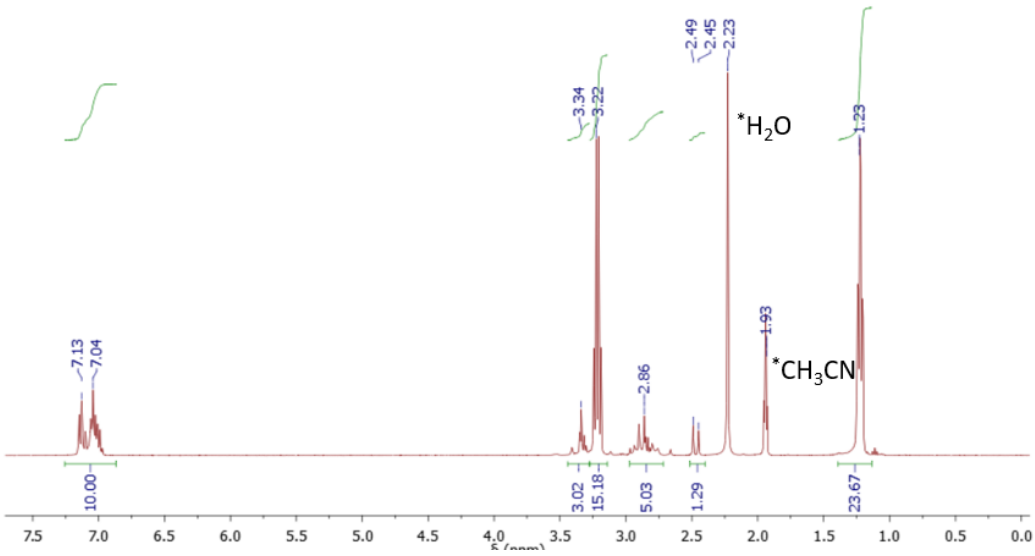



**Figure S2.** $^{1}$H NMR spectrum for $[Ni(ema)-Ni(dpdt)][NEt_4]_2$ **($2^{2-}$)**.

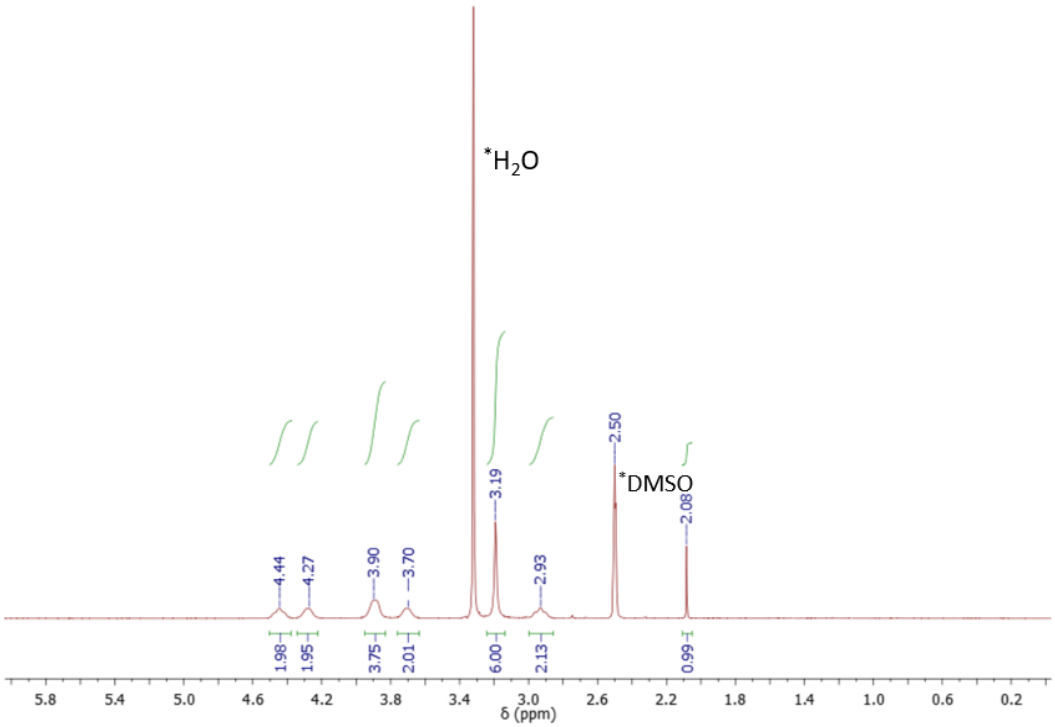



**Figure S3.** $^{1}$H NMR spectrum for Ni(bme-dame)-Ni(mnt) **(3).**

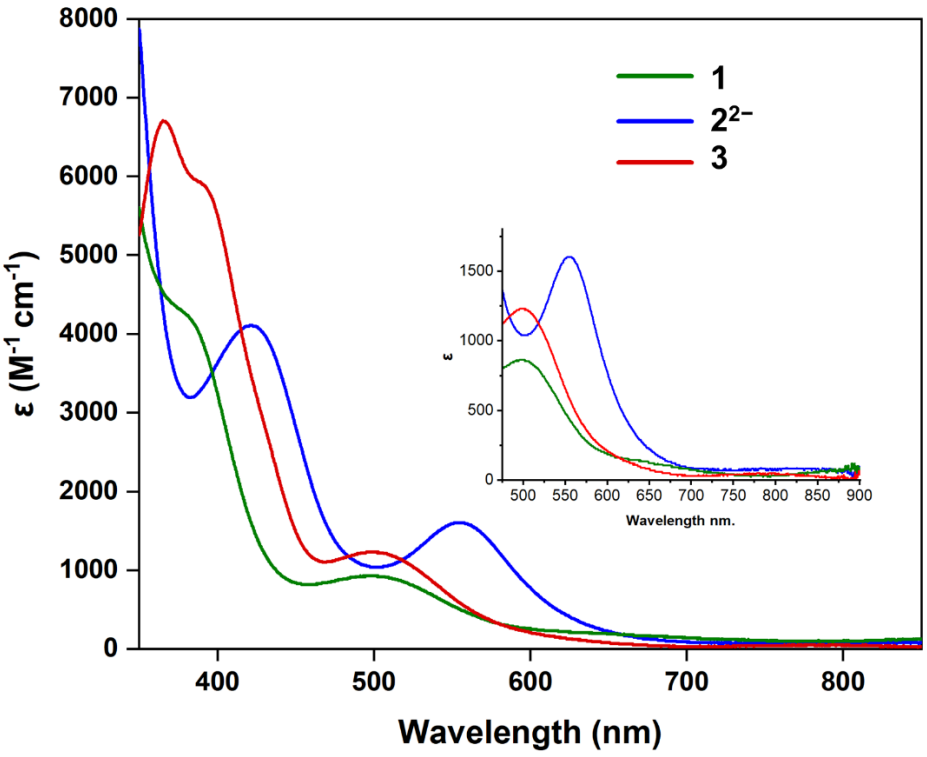



**Figure S4.** UV−vis absorption spectra of **1**, $\mathbf{2}^{2-}$, and **3** in acetonitrile. Inset: expanded spectra in the visible range.

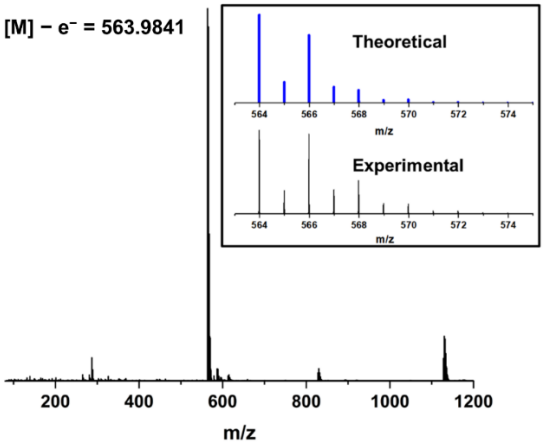



**Figure S5.** Positive-ion ESI mass spectrum of **1** in $CH_2Cl_2$; inset shows theoretical and experimental isotopic distributions for $\mathbf{1}^+$.

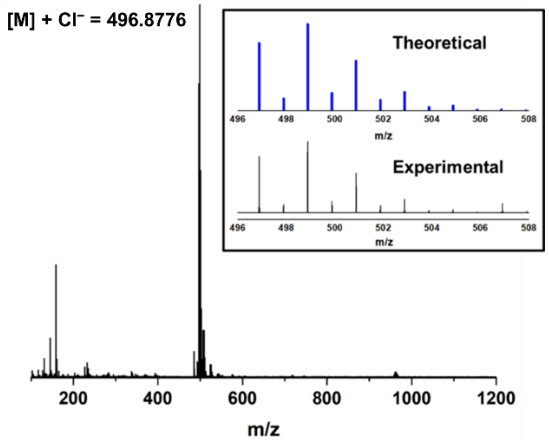



**Figure S6.** Negative-ion ESI mass spectrum of **3** in $CH_3CN$; inset shows theoretical and experimental isotopic distributions for **3**.

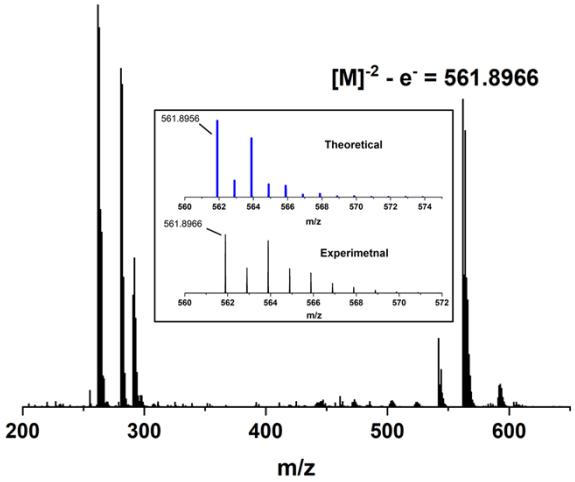



**Figure S7.** Negative-ion ESI mass spectrum of $\mathbf{2}^{2-}$ in $CH_3CN$; inset shows theoretical and experimental isotopic distributions for $\mathbf{2}^{2-}$ + $\mathbf{Cl}^-$.

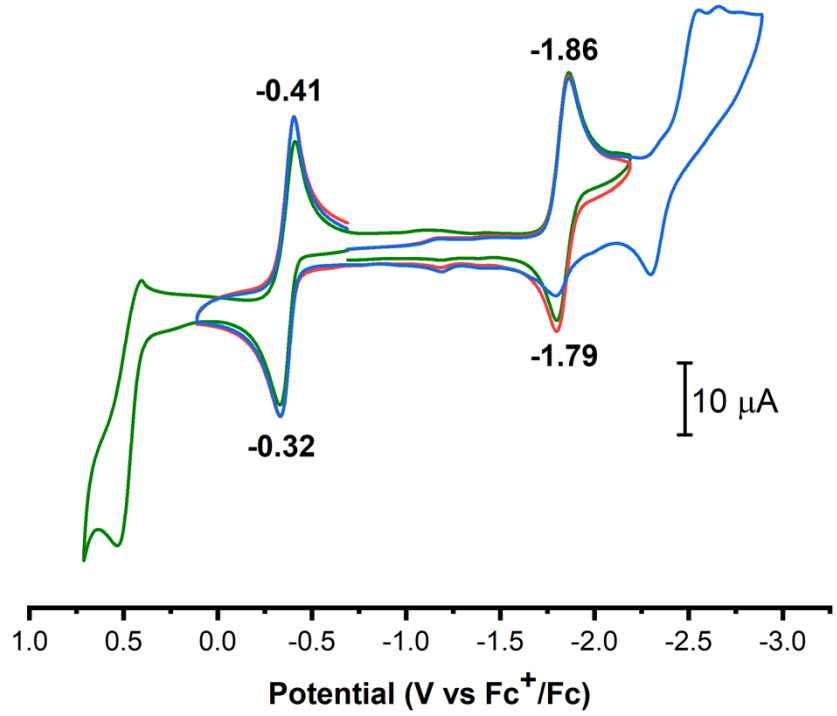



**Figure S8.** Stacked CV plots of **1** with varying potential windows in $CH_3CN$.

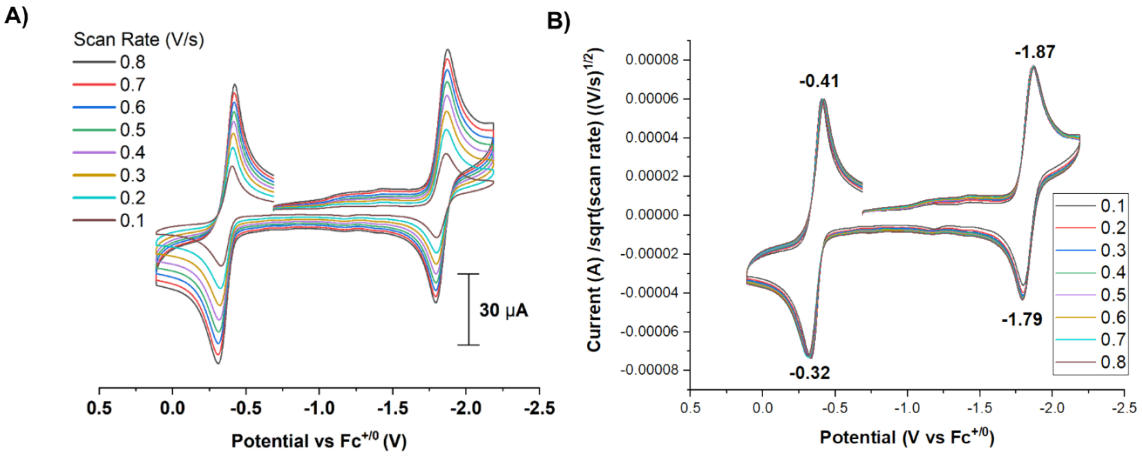
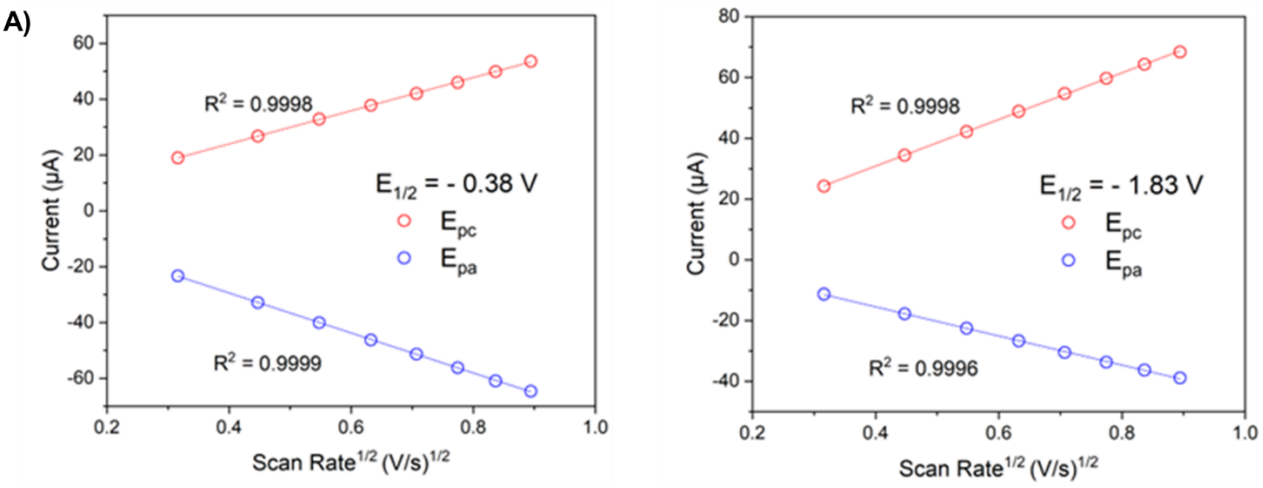



**Figure S9.** A) CV of Complex **1** at different scan rate (V/s). B) CVs of complex **1** are normalized to the square root of scan rate for direct comparison.

A)




B)

**For irreversible system:**

$$i_p = (2.99 \times 10^5)\, n\, (\alpha n_a)^{1/2}\, A\, D_0^{1/2}\, C_0^*\, v^{1/2}$$

Where, $i_p$ = current maximum in amps, $n$ = number of electrons transferred in the redox event (usually 1), $A$ = electrode area in $cm^2$, $D_0$ = diffusion coefficient in $cm^2/s$, $C_0^*$ = concentration in $mol/cm^3$, $v$ = scan rate in V/s, α = electron transfer coefficient.

**For reversible system:** α = 1

$$i_p = (2.69 \times 10^5)\, n^{3/2}\, A\, D_0^{1/2}\, C_0^*\, v^{1/2}$$

**Figure S10.** A) Plot of peak current vs. square root of scan rate of **1** using Randles-Sevčik Equation. B) Equations showing the relationship between peak current and square root of scan rate for reversible and irreversible systems.

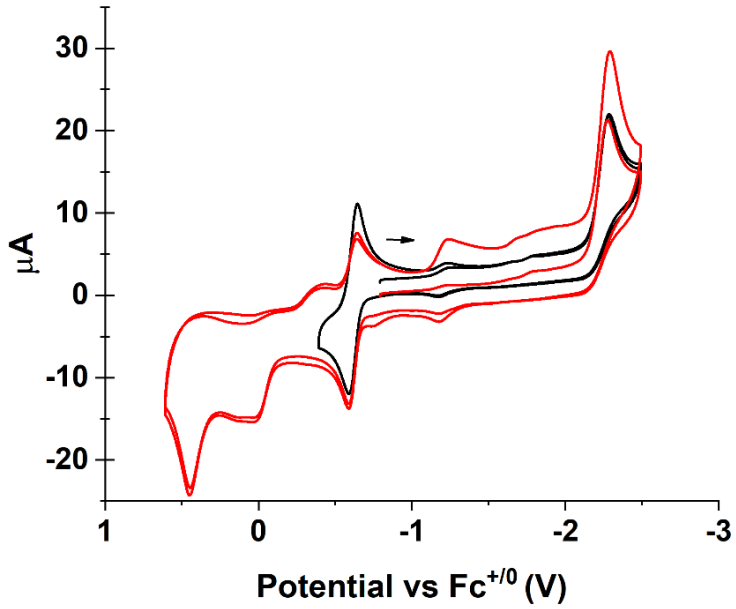



**Figure S11.** Stacked CV plots of $\mathbf{2}^{2-}$ with varying potential windows in $CH_3CN$.

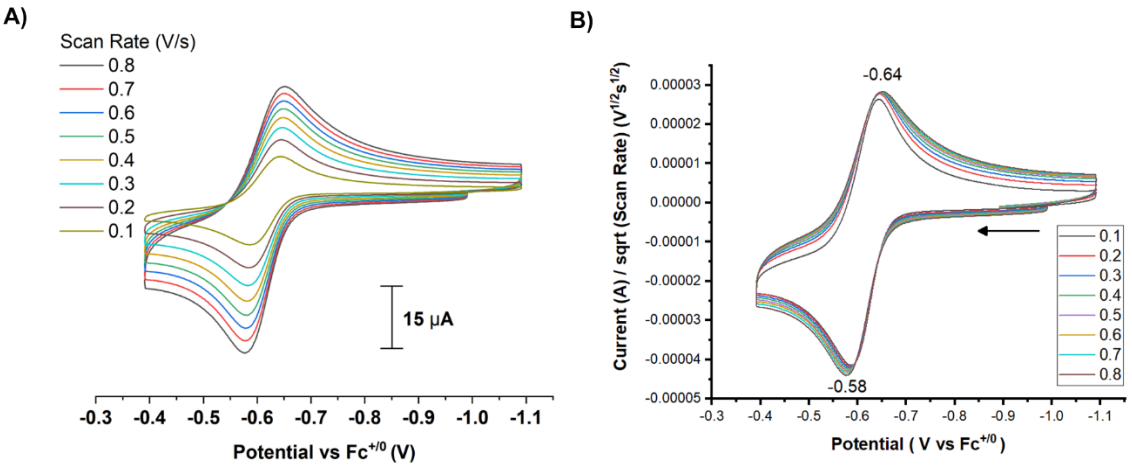



**Figure S12.** A) CV of Complex $\mathbf{2}^{2-}$ at different scan rate (V/s). B) CVs of complex $\mathbf{2}^{2-}$ are normalized to the square root of scan rate for direct comparison.

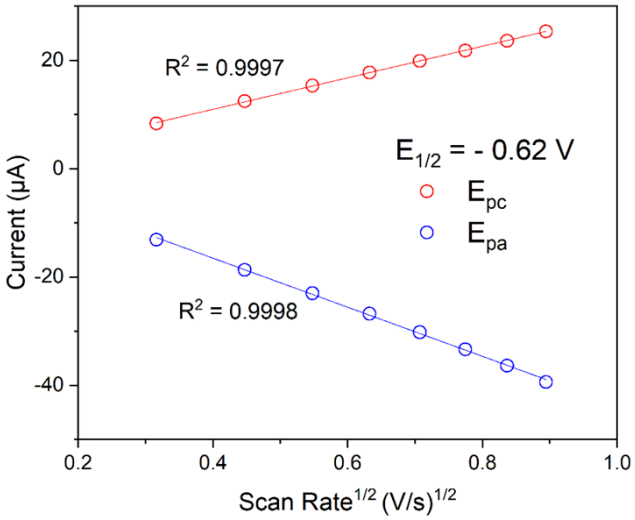



**Figure S13.** Plot of peak current vs. square root of scan rate of $\mathbf{2}^{2-}$.

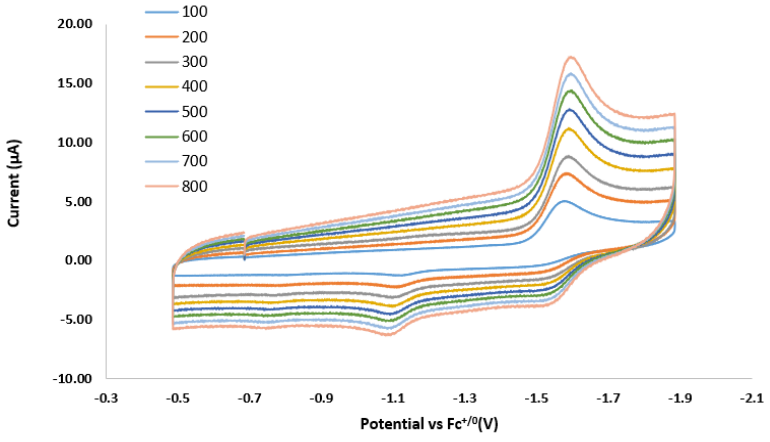



**Figure S14.** Scan rate dependence for the reduction event of **3** in $CH_3CN$.

**Table S1**. Crystal data and structure refinement for **1**, $\mathbf{2^{2-}}$, and **3**.

| | **1** | $\mathbf{2^{2-}}$ | **3** |
|---|---|---|---|
| Identification code | Ni(bme-dame)-Ni(dpdt) | Ni(ema)-Ni(dpdt) | Ni(bme-dame)-Ni(mnt) |
| Empirical formula | $C_{24}H_{32}Cl_4N_2Ni_2S_4$ | $C_{36}H_{58}N_4Ni_2O_2S_4$ | $C_{12}H_{18}N_4Ni_2S_4$ |
| Formula weight | 735.97 | 824.52 | 463.96 |
| Temperature/K | 110.00 | 110.00 | 110.00 |
| Crystal system | monoclinic | triclinic | triclinic |
| Space group | $P2_1/n$ | P-1 | P-1 |
| a/Å | 17.580(2) | 13.2528(5) | 8.2002(3) |
| b/Å | 9.3786(10) | 16.1861(7) | 9.6581(3) |
| c/Å | 18.147(2) | 20.3139(8) | 10.9978(4) |
| α/° | 90 | 83.934(2) | 94.2260(10) |
| β/° | 91.065(4) | 70.9880(10) | 93.7670(10) |
| γ/° | 90 | 68.434(2) | 100.8030(10) |
| Volume/Å$^3$ | 2991.5(6) | 3831.0(3) | 850.43(5) |
| Z | 4 | 4 | 2 |
| $\rho_{calc}$g/cm$^3$ | 1.634 | 1.430 | 1.812 |
| μ/mm$^{-1}$ | 1.914 | 1.239 | 2.703 |
| F(000) | 1512.0 | 1752.0 | 476.0 |
| Crystal size/mm$^3$ | 0.381 × 0.067 × 0.041 | 0.519 × 0.482 × 0.322 | 0.3 × 0.3 × 0.3 |
| Radiation | MoKα (λ = 0.71073) | MoKα (λ = 0.71073) | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 4.89 to 50 | 3.57 to 55.136 | 3.726 to 60.258 |
| Index ranges | -20 ≤ h ≤ 20, -10 ≤ k ≤ 11, -21 ≤ l ≤ 21 | -17 ≤ h ≤ 17, -21 ≤ k ≤ 21, -26 ≤ l ≤ 26 | -11 ≤ h ≤ 11, -13 ≤ k ≤ 13, -15 ≤ l ≤ 15 |
| Reflections collected | 62967 | 149361 | 57235 |
| Independent reflections | 5250 [$R_{int}$ = 0.0450, $R_{sigma}$ = 0.0181] | 17644 [$R_{int}$ = 0.0463, $R_{sigma}$ = 0.0284] | 5008 [$R_{int}$ = 0.0388, $R_{sigma}$ = 0.0193] |
| Data/restraints/parameters | 5250/14/346 | 17644/595/961 | 5008/0/201 |
| Goodness-of-fit on F$^2$ | 1.067 | 1.059 | 1.085 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0246[a], $wR_2$ = 0.0541[b] | $R_1$ = 0.0290[a], $wR_2$ = 0.0682[b] | $R_1$ = 0.0215[a], $wR_2$ = 0.0426[b] |
| Final R indexes [all data] | $R_1$ = 0.0278 [a], $wR_2$ = 0.0567 [b] | $R_1$ = 0.0399[a], $wR_2$ = 0.0718[b] | $R_1$ = 0.0269[a], $wR_2$ = 0.0453[b] |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.97/-0.65 | 0.63/-0.81 | 0.46/-0.35 |

[a]$R_1=\Sigma(||F_o|-|F_c||)/\Sigma|F_o|$. [b]$wR_2=[\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$, $w=1/[\sigma^2(F_o^2)+(ap)^2+bp]$, where $p=[\max(F_o^2, 0)+2F_c^2]/3$.

**Table S2**. Experimental XRD data for **1**, $\mathbf{2^{2-}}$, and **3**.

| **Distances (Å)** | **1** | $\mathbf{2^{2-}}$ | **3** |
|---|---|---|---|
| Ni1–Ni2 | 2.7202(5) | 2.6885(6) | 2.7871(3) |
| Ni1–S1 | 2.1562(7) | 2.1383(5) | 2.1436(4) |
| Ni1–S2 | 2.1651(6) | 2.1446(7) | 2.1544(4) |
| Ni1–N1 | 1.951(2) | 1.8444(2) | 1.938(1) |
| Ni1-N2 | 1.952(2) | 1,838(2) | 1.932(1) |
| Ni2–S1 | 2.2398(6) | 2.2611(6) | 2.2412(4) |
| Ni2–S2 | 2.2398(7) | 2.2809(5) | 2.2302(4) |
| Ni2–S3 | 2.1339(7) | 2.1338(5) | 2.1497(4) |
| Ni2–S4 | 2.1461(6) | 2.1340(6) | 2.1493(4) |
| S3–C1 | 1.766(2) | 1.772(2) | 1.738(2) |
| S4–C2 | 1.764(2) | 1.760(2) | 1.737(1) |
| C1–C2 | 1.348(3) | 1.356(2) | 1.361(2) |
| $Ni1_{disp}$[a] | 0.250 | 0.150 | 0.207 |
| **Angles** | | | |
| S1–Ni1–S2 | 85.32(2) | 90.18(2) | 86.36(3) |
| S1–Ni2–S2 | 81.64(2) | 83.80(2) | 82.26(3) |
| S1–Ni2–S3 | 92.33(2) | 91.24(2) | 92.24(1) |
| S2–Ni2–S4 | 94.94(2) | 94.00(2) | 92.14(1) |
| S3–Ni2–S4 | 91.22(2) | 90.81(2) | 93.39(2) |
| Hinge[b] | 111.82 | 114.08 | 117.98 |
| **Space Group** | $P2_1/n$ | $P\overline{1}$ | $P\overline{1}$ |

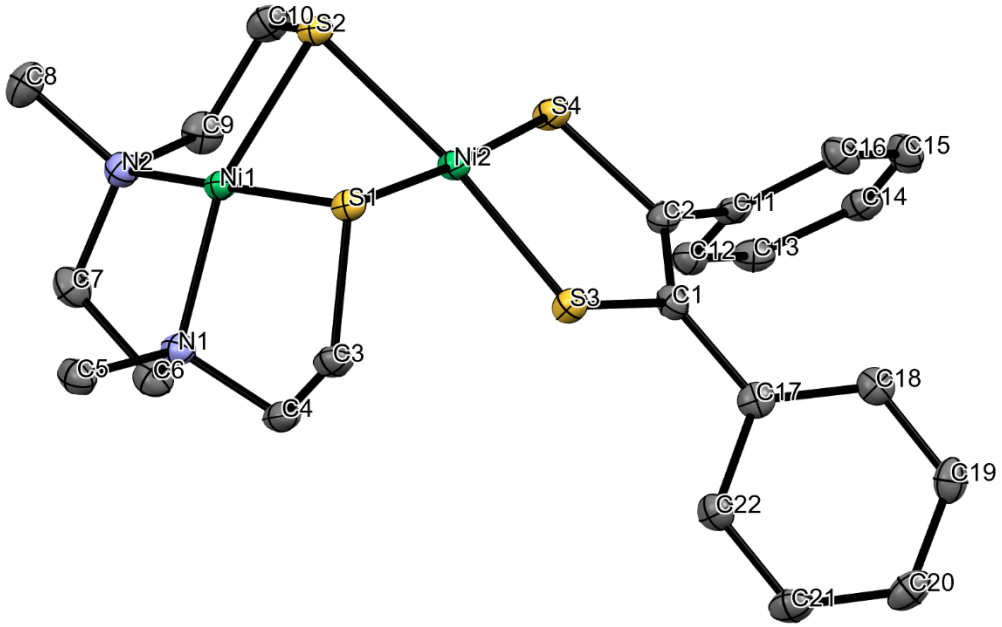



**Figure S15**. Thermal ellipsoid plot of **1** (50%, hydrogens and solvent molecules omitted for clarity).

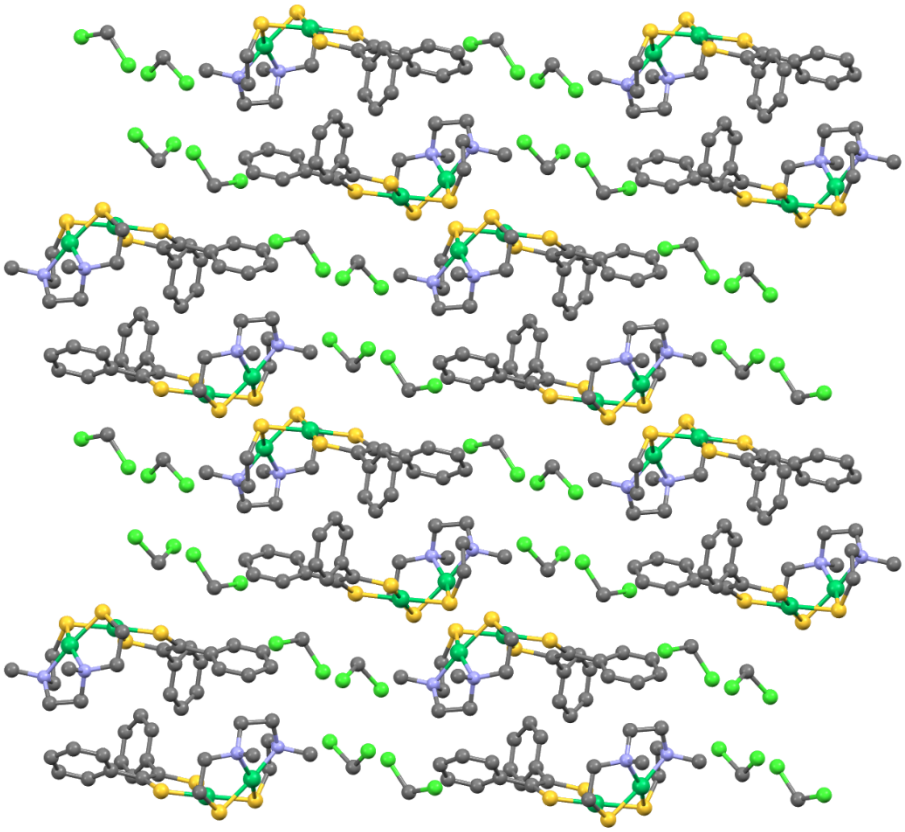


**Figure S16.** X-ray crystal packing of **1** along the *b* axis.

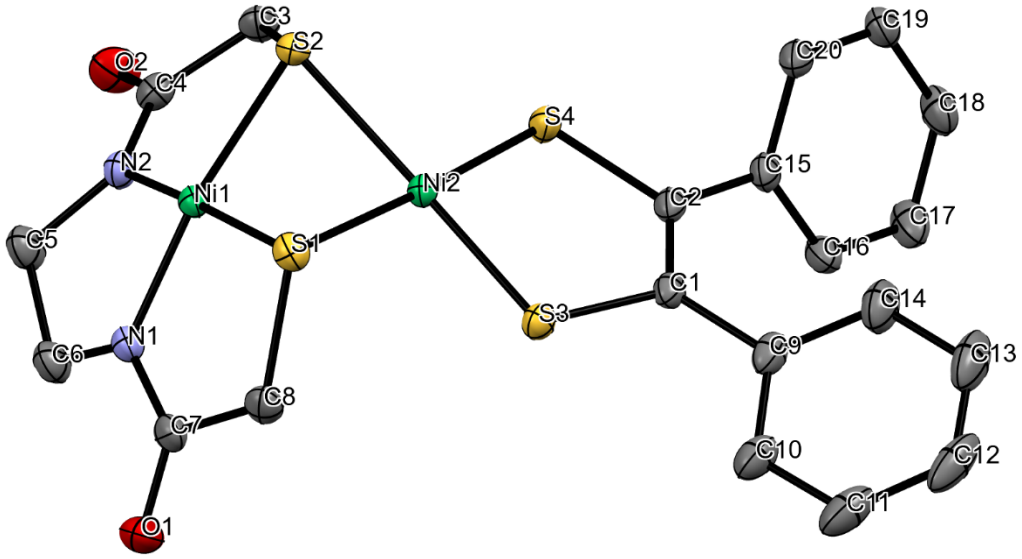



**Figure S17**. Thermal ellipsoid plot of $\mathbf{2}^{2-}$ (50%, hydrogens and $NEt_4^+$ cations omitted for clarity).

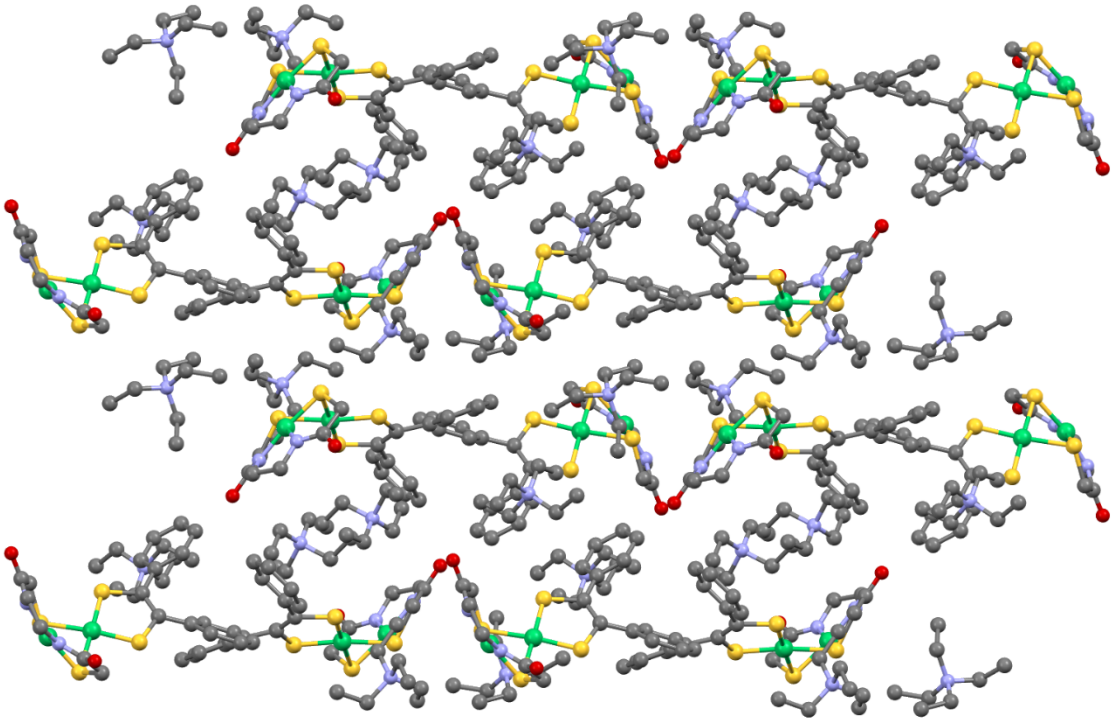


**Figure S18.** X-ray crystal packing of $\mathbf{2}^{2-}$ along the *b* axis.

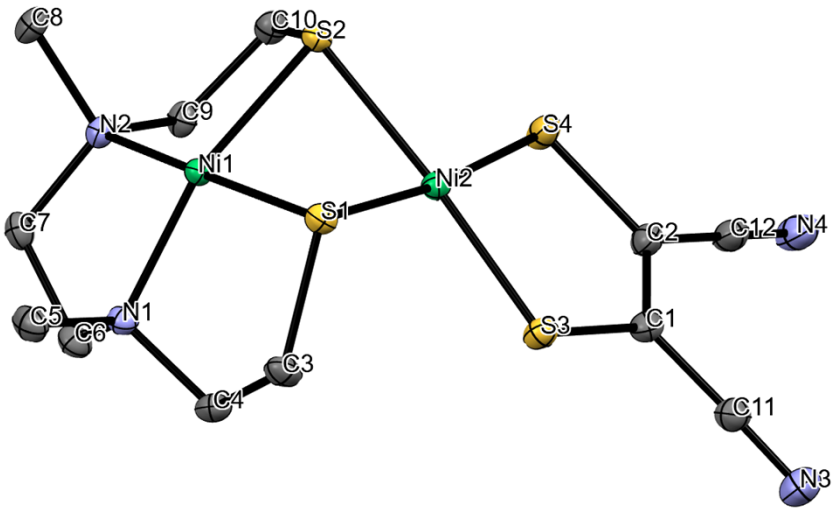



**Figure S19**. Thermal ellipsoid plot of **3** (50%, hydrogens omitted for clarity).

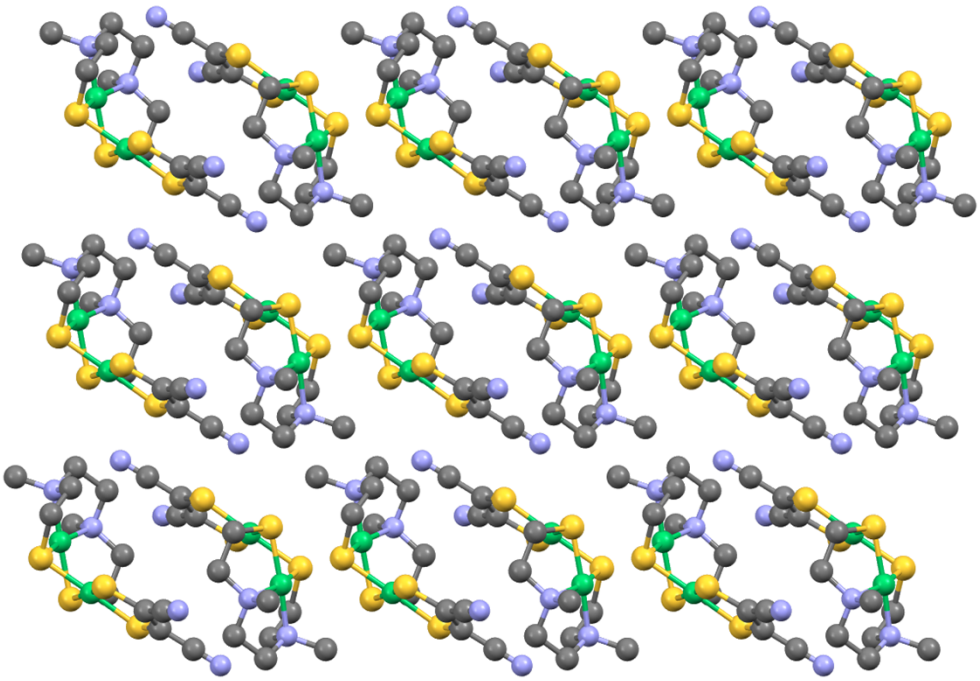


**Figure S20.** X-ray crystal packing of **3** along the *a* axis.

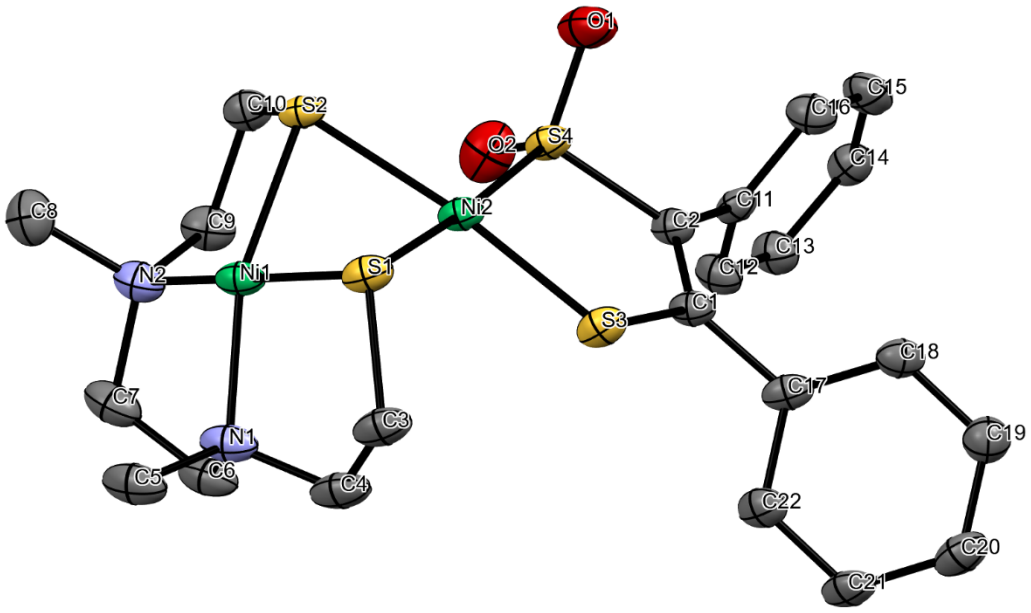



**Figure S21**. Thermal ellipsoid plot of $\mathbf{1_{O2}}$ (50%, hydrogens and solvent molecules omitted for clarity).

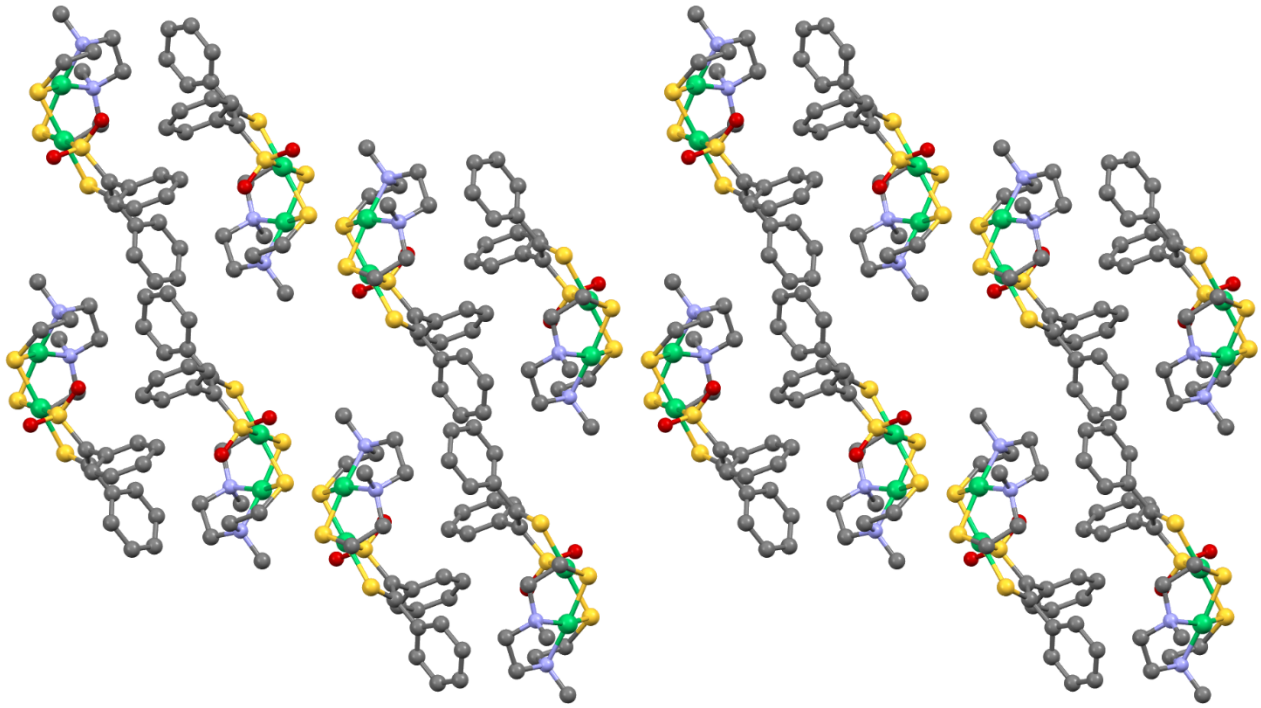


**Figure S22.** X-ray crystal packing of $\mathbf{1_{O2}}$ along the *b* axis.

**Table S3**. Crystal data and structure refinement for $\mathbf{1_{O2}}$.

| Identification code | Nibmedame_Nidpdt_O2_Q_0ma |
|---|---|
| Empirical formula | $C_{22}H_{28}N_2Ni_2O_2S_4$ |
| Formula weight | 598.12 |
| Temperature/K | 110.0 |
| Crystal system | monoclinic |
| Space group | $P2_1/n$ |
| a/Å | 10.8029(6) |
| b/Å | 9.5412(5) |
| c/Å | 25.5522(13) |
| α/° | 90 |
| β/° | 94.968(2) |
| γ/° | 90 |
| Volume/Å$^3$ | 2623.8(2) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.514 |
| μ/mm$^{-1}$ | 1.775 |
| F(000) | 1240.0 |
| Crystal size/mm$^3$ | 0.3 × 0.3 × 0.3 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 4.234 to 51.402 |
| Index ranges | -13 ≤ h ≤ 13, -11 ≤ k ≤ 11, -31 ≤ l ≤ 31 |
| Reflections collected | 57183 |
| Independent reflections | 4980 [$R_{int}$ = 0.0521, $R_{sigma}$ = 0.0212] |
| Data/restraints/parameters | 4980/0/291 |
| Goodness-of-fit on $F^2$ | 1.124 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0371, $wR_2$ = 0.1091 |
| Final R indexes [all data] | $R_1$ = 0.0471, $wR_2$ = 0.1193 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.49/-0.41 |

**Table S4**. Comparison of experimental and calculated XRD data for Ni(bme-dame)-Ni(dpdt) **(1),** [Ni(ema)-Ni(dpdt)]$^{2-}$ **($2^{2-}$),** and Ni(bme-dame)-Ni(dpdt) **(3)**.

| **Distances (Å)** | **1** | | **$2^{2-}$** | | **3** | |
|---|---|---|---|---|---|---|
| | Experimental | Calculated | Experimental | Calculated | Experimental | Calculated |
| Ni1–Ni2 | 2.7202(5) | 2.7142 | 2.6885(6) | 2.6560 | 2.7871(3) | 2.7190 |
| Ni1–S1 | 2.1562(7) | 2.1714 | 2.1383(5) | 2.1761 | 2.1436(4) | 2.1711 |
| Ni1–S2 | 2.1651(6) | 2.1784 | 2.1446(7) | 2.1734 | 2.1544(4) | 2.1750 |
| Ni1–N1 | 1.951(2) | 1.9518 | 1.8444(2) | 1.8634 | 1.938(1) | 1.9493 |
| Ni1-N2 | 1.952(2) | 1.9619 | 1,838(2) | 1.8538 | 1.932(1) | 1.9590 |
| Ni2–S1 | 2.2398(6) | 2.2821 | 2.2611(6) | 2.3181 | 2.2412(4) | 2.2788 |
| Ni2–S2 | 2.2398(7) | 2.2816 | 2.2809(5) | 2.3103 | 2.2302(4) | 2.2770 |
| Ni2–S3 | 2.1339(7) | 2.1653 | 2.1338(5) | 2.1657 | 2.1497(4) | 2.1688 |
| Ni2–S4 | 2.1461(6) | 2.1658 | 2.1340(6) | 2.1657 | 2.1493(4) | 2.1686 |
| S3–C1 | 1.766(2) | 1.7830 | 1.772(2) | 1.7833 | 1.738(2) | 1.7597 |
| S4–C2 | 1.764(2) | 1.7836 | 1.760(2) | 1.7845 | 1.737(1) | 1.7593 |
| C1–C2 | 1.348(3) | 1.3678 | 1.356(2) | 1.3706 | 1.361(2) | 1.3853 |
| $Ni1_{disp}$[a] | 0.250 | 0.183 | 0.150 | 0.153 | 0.207 | 0.190 |
| **Angles** | | | | | | |
| S1–Ni1–S2 | 85.32(2) | 86.16 | 90.18(2) | 90.36 | 86.36(3) | 85.76 |
| S1–Ni2–S2 | 81.64(2) | 81.31 | 83.80(2) | 83.60 | 82.26(3) | 80.96 |
| S1–Ni2–S3 | 92.33(2) | 94.22 | 91.24(2) | 92.89 | 92.24(1) | 93.05 |
| S2–Ni2–S4 | 94.94(2) | 93.92 | 94.00(2) | 92.8 | 92.14(1) | 93.08 |
| S3–Ni2–S4 | 91.22(2) | 90.72 | 90.81(2) | 91.00 | 93.39(2) | 92.90 |
| Hinge[b] | 111.82 | 109.56 | 114.08 | 109.07 | 117.98 | 109.13 |

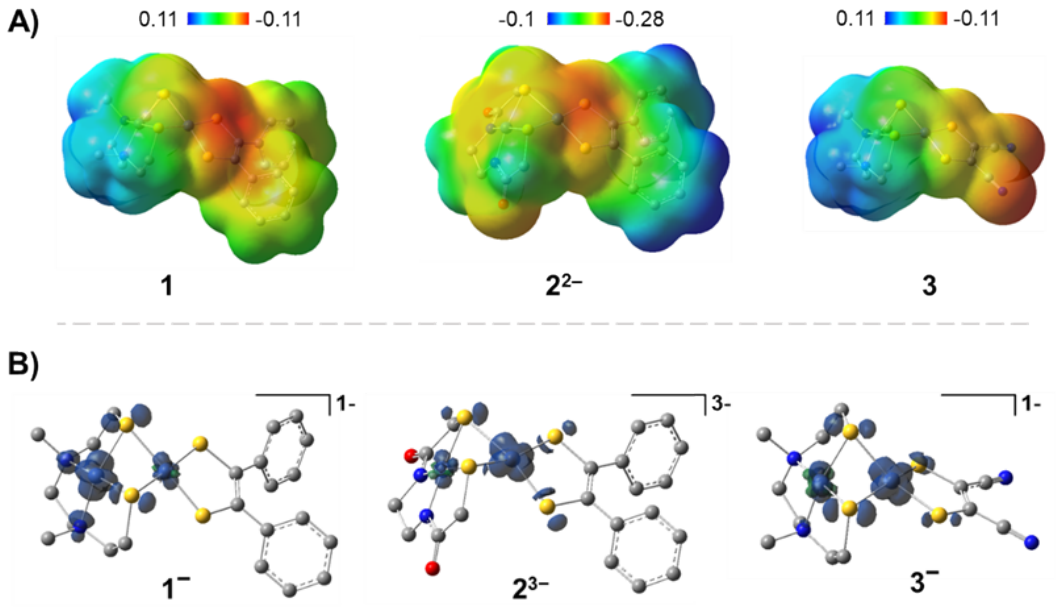



**Figure S23.** A) ESP maps (color scale at a.u.) of **1**, $\mathbf{2}^{2-}$ and **3** (iso surface values = 0.001 au). B) Spin Density plots of reduced complexes $\mathbf{1}^{-}$, $\mathbf{2}^{3-}$ and $\mathbf{3}^{-}$ (iso values = 0.001).

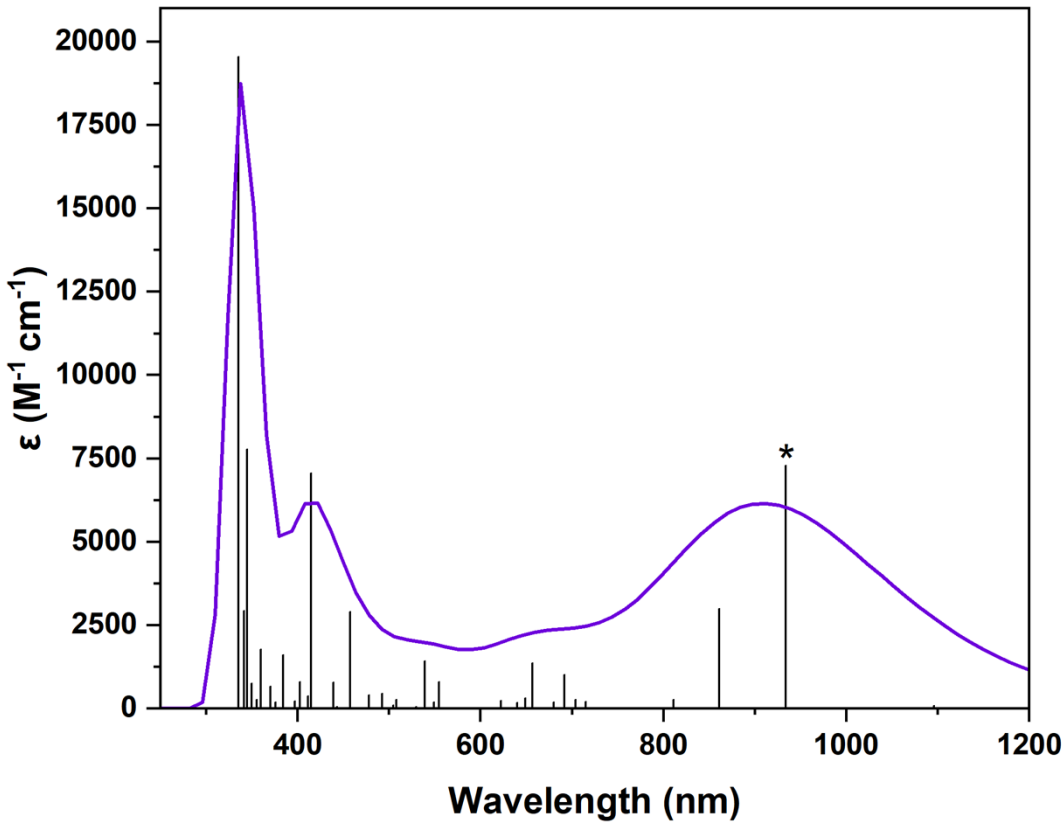
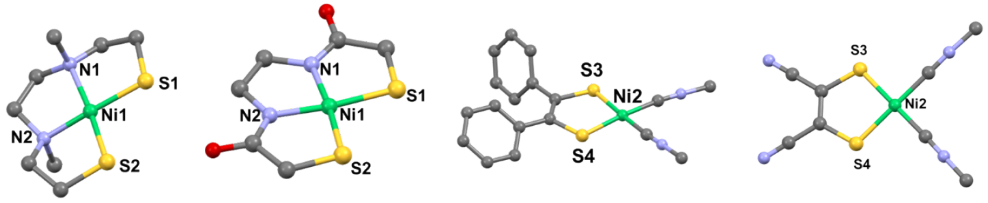



**Figure S24**. TD-DFT calculated electronic absorption spectrum of $\mathbf{1}^{+}$. Asterisk is excited state 9 which is shown in the main paper as the major contributing transition.




| | | | | |
|---|---|---|---|---|
| | | | S-C (Å) | 1.736<br>1.731 | 1.760<br>1.772 |
| | | | C-C (Å) | 1.356 | 1.347 |
| Ni-S (Å) | 2.166<br>2.173 | 2.179 | 2.139<br>2.149 | 2.146<br>2.144 |
| Ni-N (Å) | 1.942<br>1.931 | 1.858 | -- | -- |
| ∠S-Ni-S (°) | 93.99 | 97.47 | 90.03 | 92.80 |
| ∠N-Ni-N (°) | 88.31 | 85.58 | -- | -- |
| $Ni_{disp}$ (Å) | 0.003 | 0.027 | 0.007 | 0.012 |
| $\tau_4$ | 0.13 | 0.09 | 0.07 | 0.01 |

**Figure S25**: Selected bond angles and lengths for the previously reported donor and receiver synthons.[1-4]

## Computational coordinates of optimized structures

**Complex 1** (neutral closed shell singlet)

| | | | |
|---|---|---|---|
| Ni | -3.11810040 | 0.02440529 | -0.27792077 |
| Ni | -0.52407220 | -0.03944885 | -1.07413611 |
| S | -2.17499129 | 1.42969935 | -1.64351421 |
| S | -2.19455165 | -1.53909172 | -1.48127129 |
| S | 0.96560537 | -1.57048331 | -0.717238S33 |
| S | 0.92345948 | 1.50992523 | -0.63523820 |
| N | -3.46589737 | 1.42714973 | 1.03393422 |
| N | -3.80463700 | -1.30904668 | 0.98686435 |
| C | -2.21849701 | 2.92384920 | -0.52878073 |
| H | -3.04491129 | 3.54840090 | -0.88170071 |
| H | -1.28462106 | 3.48098096 | -0.64944057 |
| C | -2.38509818 | 2.47327177 | 0.91186471 |
| H | -2.62552773 | 3.31950124 | 1.57225647 |
| H | -1.45655834 | 2.00351787 | 1.24848056 |

| | | | |
|---|---|---|---|
| C | -3.32011123 | 0.69691804 | 2.34462386 |
| H | -2.25459455 | 0.48195484 | 2.46730670 |
| H | -3.65384552 | 1.33227484 | 3.17653308 |
| C | -4.12164178 | -0.59355066 | 2.28229070 |
| H | -5.19509308 | -0.39024049 | 2.28774339 |
| H | -3.89308941 | -1.24152361 | 3.13661268 |
| C | -2.66244693 | -2.27747517 | 1.16939849 |
| H | -1.83679278 | -1.71442552 | 1.61472188 |
| H | -2.97469360 | -3.07194644 | 1.86409537 |
| C | -2.22961256 | -2.86740184 | -0.16841181 |
| H | -1.22642335 | -3.29515995 | -0.08986582 |
| H | -2.91475755 | -3.64233799 | -0.52476838 |
| C | -4.81865850 | 2.05002340 | 0.90288872 |
| H | -5.58781335 | 1.27603232 | 0.94363680 |
| H | -4.97300510 | 2.77028615 | 1.71832166 |
| H | -4.88695067 | 2.56188337 | -0.05919114 |
| C | -5.03082610 | -2.01631885 | 0.50499853 |
| H | -5.35244848 | -2.75341719 | 1.25406669 |
| H | -5.82147098 | -1.27811001 | 0.35100793 |
| H | -4.82243892 | -2.51943994 | -0.44067139 |
| C | 2.45200838 | -0.70590999 | -0.24354744 |
| C | 2.43999378 | 0.66265542 | -0.23307573 |
| C | 3.58018475 | -1.56982914 | 0.18172983 |
| C | 4.28760771 | -1.31051109 | 1.37679140 |
| H | 4.00285589 | -0.45841685 | 1.98954569 |
| C | 5.33422997 | -2.14112399 | 1.78844707 |
| H | 5.86121362 | -1.92151988 | 2.71520712 |
| C | 5.69610328 | -3.25825859 | 1.02314678 |
| H | 6.50896885 | -3.90543966 | 1.34571875 |
| C | 4.99434426 | -3.53770275 | -0.15689184 |
| H | 5.26426849 | -4.40276859 | -0.75983011 |
| C | 3.94795527 | -2.70695368 | -0.57082408 |
| H | 3.41440657 | -2.92868558 | -1.49261278 |
| C | 3.61104859 | 1.54149025 | 0.00724038 |
| C | 4.84116241 | 1.31074363 | -0.64738312 |
| H | 4.92942107 | 0.47131275 | -1.33319301 |

| | | | |
|---|---|---|---|
| C | 5.93629673 | 2.15468034 | -0.43862096 |
| H | 6.87231095 | 1.95833388 | -0.95831536 |
| C | 5.82942065 | 3.25494723 | 0.42305944 |
| H | 6.68139650 | 3.91239991 | 0.58283957 |
| C | 4.61156766 | 3.50515764 | 1.06910903 |
| H | 4.51547143 | 4.35684544 | 1.74002974 |
| C | 3.51515757 | 2.66177833 | 0.86139141 |
| H | 2.57581264 | 2.86053589 | 1.37299272 |

**Complex [1]**$^{+}$ (cation doublet)

| | | | |
|---|---|---|---|
| Ni | -3.07218756 | 0.06167977 | -0.26385003 |
| Ni | -0.58130245 | 0.03891308 | -1.06503043 |
| S | -2.19394567 | 1.55502506 | -1.57992842 |
| S | -2.22917902 | -1.42751668 | -1.61728719 |
| S | 0.86515877 | -1.51721464 | -0.66851261 |
| S | 0.93636340 | 1.53790291 | -0.70851514 |
| N | -3.32938151 | 1.37225536 | 1.15428739 |
| N | -3.69564226 | -1.34818566 | 0.94779332 |
| C | -2.17434021 | 2.97737625 | -0.37607805 |
| H | -3.02205210 | 3.60997772 | -0.65560033 |
| H | -1.25312911 | 3.55076876 | -0.51548284 |
| C | -2.26964124 | 2.44220170 | 1.04203017 |
| H | -2.49720324 | 3.24773686 | 1.75384906 |
| H | -1.32239155 | 1.97347110 | 1.32124554 |
| C | -3.09667126 | 0.55476080 | 2.40229683 |
| H | -2.02744108 | 0.32554911 | 2.43171255 |
| H | -3.36325727 | 1.13919009 | 3.29257722 |
| C | -3.91517370 | -0.72137235 | 2.31176084 |
| H | -4.98331448 | -0.51392000 | 2.40761576 |
| H | -3.63181649 | -1.42981081 | 3.09780963 |
| C | -2.57272258 | -2.35446634 | 0.98781973 |
| H | -1.70821578 | -1.84812014 | 1.42654520 |
| H | -2.86836365 | -3.19288660 | 1.63465431 |
| C | -2.23921507 | -2.85156975 | -0.41357496 |

| | | | |
|---|---|---|---|
| H | -1.25706826 | -3.33256806 | -0.43074501 |
| H | -2.97779003 | -3.56071824 | -0.79758709 |
| C | -4.69898154 | 1.97590801 | 1.13457824 |
| H | -5.45012778 | 1.18351305 | 1.13264083 |
| H | -4.82879278 | 2.61221863 | 2.01978112 |
| H | -4.81501296 | 2.57366390 | 0.22825835 |
| C | -4.97081642 | -1.98105591 | 0.48303754 |
| H | -5.27182729 | -2.76081077 | 1.19506757 |
| H | -5.74264230 | -1.20950493 | 0.43095975 |
| H | -4.83153148 | -2.41914027 | -0.50661011 |
| C | 2.35318028 | -0.71241970 | -0.23089001 |
| C | 2.38982040 | 0.67577422 | -0.26393103 |
| C | 3.46631714 | -1.59223458 | 0.19670299 |
| C | 4.16174849 | -1.34047857 | 1.39859811 |
| H | 3.88339011 | -0.48685457 | 2.01140261 |
| C | 5.18732753 | -2.19290370 | 1.81527350 |
| H | 5.70851709 | -1.98965240 | 2.74830750 |
| C | 5.53918799 | -3.30745091 | 1.04212864 |
| H | 6.34042177 | -3.96721796 | 1.36742281 |
| C | 4.85187692 | -3.56921769 | -0.14991122 |
| H | 5.12095444 | -4.43024394 | -0.75785617 |
| C | 3.82052850 | -2.72369910 | -0.56799505 |
| H | 3.29854036 | -2.92534185 | -1.50065532 |
| C | 3.59204392 | 1.50944587 | -0.02721379 |
| C | 4.80957292 | 1.21809378 | -0.67862615 |
| H | 4.86586026 | 0.36987232 | -1.35610261 |
| C | 5.93139136 | 2.02586046 | -0.47673119 |
| H | 6.86022152 | 1.79358907 | -0.99324176 |
| C | 5.86101020 | 3.13363202 | 0.37881689 |
| H | 6.73730174 | 3.75828406 | 0.53697382 |
| C | 4.65588246 | 3.43487956 | 1.02581174 |
| H | 4.59396165 | 4.29133921 | 1.69366819 |
| C | 3.52822571 | 2.63472833 | 0.82116328 |
| H | 2.59802488 | 2.86662803 | 1.33496873 |

**Complex [1]$^{-}$** (anion doublet)

| | | | |
|---|---|---|---|
| Ni | -3.12913849 | 0.04678318 | -0.37134394 |
| Ni | -0.55931310 | -0.01931907 | -1.06969698 |
| S | -2.14804236 | 1.56365812 | -1.67442701 |
| S | -2.17145169 | -1.61068899 | -1.54567817 |
| S | 0.94725287 | -1.57305752 | -0.72203048 |
| S | 0.92660577 | 1.52787620 | -0.61433017 |
| N | -3.44149119 | 1.46470514 | 1.11052550 |
| N | -3.87217295 | -1.34703453 | 0.98642619 |
| C | -2.14824813 | 2.96045640 | -0.43816312 |
| H | -2.95479174 | 3.64039513 | -0.73558506 |
| H | -1.20057101 | 3.50406740 | -0.50761935 |
| C | -2.32120609 | 2.44359204 | 0.99042218 |
| H | -2.48015540 | 3.28802560 | 1.68382980 |
| H | -1.40569166 | 1.91564919 | 1.27581612 |
| C | -3.31658023 | 0.65710031 | 2.35934176 |
| H | -2.25840636 | 0.39688235 | 2.46684920 |
| H | -3.62126010 | 1.23869281 | 3.24514216 |
| C | -4.16676886 | -0.61173655 | 2.25705582 |
| H | -5.23002160 | -0.35416634 | 2.24309063 |
| H | -3.99222907 | -1.25295802 | 3.13391483 |
| C | -2.71129445 | -2.27437361 | 1.15360320 |
| H | -1.89481553 | -1.69290795 | 1.59443751 |
| H | -2.98391605 | -3.08557437 | 1.85252295 |
| C | -2.24295120 | -2.87502787 | -0.17638547 |
| H | -1.24585402 | -3.30565086 | -0.04306798 |
| H | -2.91583149 | -3.66843276 | -0.52091718 |
| C | -4.75086466 | 2.16091506 | 1.04268917 |
| H | -5.56382744 | 1.43205252 | 1.09398278 |
| H | -4.85473720 | 2.87942190 | 1.87297288 |
| H | -4.82678395 | 2.69482613 | 0.09167187 |
| C | -5.07359231 | -2.09771427 | 0.54144297 |

| | | | |
|---|---|---|---|
| H | -5.34905826 | -2.87658740 | 1.27196139 |
| H | -5.90714335 | -1.39925875 | 0.42519102 |
| H | -4.87170541 | -2.56602930 | -0.42565069 |
| C | 2.43427705 | -0.71531206 | -0.23927196 |
| C | 2.43202783 | 0.65867805 | -0.22135796 |
| C | 3.56171728 | -1.57594401 | 0.19457523 |
| C | 4.27102505 | -1.30818068 | 1.38822261 |
| H | 3.98807428 | -0.44910116 | 1.99223047 |
| C | 5.31478286 | -2.13691843 | 1.81169022 |
| H | 5.83942533 | -1.90838761 | 2.73790514 |
| C | 5.67671063 | -3.26338001 | 1.06005615 |
| H | 6.48702916 | -3.90952962 | 1.39130166 |
| C | 4.97459122 | -3.55268530 | -0.11828204 |
| H | 5.24277726 | -4.42516755 | -0.71168434 |
| C | 3.93016952 | -2.72467339 | -0.54199645 |
| H | 3.39410983 | -2.95750411 | -1.45959841 |
| C | 3.62323445 | 1.51433610 | 0.00577601 |
| C | 4.84407090 | 1.25930014 | -0.65949683 |
| H | 4.91021187 | 0.41436510 | -1.34127582 |
| C | 5.95718753 | 2.08442390 | -0.46971226 |
| H | 6.88286158 | 1.86775963 | -1.00021495 |
| C | 5.88178581 | 3.19216570 | 0.38589846 |
| H | 6.74719027 | 3.83548211 | 0.53108052 |
| C | 4.67502353 | 3.46745455 | 1.04373198 |
| H | 4.60151387 | 4.32520930 | 1.71014489 |
| C | 3.56093576 | 2.64361118 | 0.85270761 |
| H | 2.62986567 | 2.86460875 | 1.37022128 |

**Complex $2^{2-}$** (dianion closed shell singlet)

| | | | |
|---|---|---|---|
| Ni | 3.16659209 | -0.00114830 | -0.35434799 |
| Ni | 0.61843884 | 0.05675406 | -1.10112248 |
| S | 2.26633180 | -1.46298925 | -1.69126787 |
| S | 2.27564648 | 1.61621195 | -1.50062270 |

| | | | |
|---|---|---|---|
| S | -0.88223384 | 1.58130664 | -0.76275793 |
| S | -0.80898697 | -1.50456115 | -0.63738660 |
| O | 3.22494719 | -3.45919208 | 1.67378889 |
| O | 3.69668478 | 3.32998528 | 1.85226808 |
| N | 3.65469955 | -1.34080740 | 0.84525490 |
| N | 3.75886110 | 1.20106703 | 0.92651691 |
| C | 2.39987080 | -2.90909244 | -0.52566577 |
| H | 1.38995006 | -3.25253320 | -0.27723492 |
| H | 2.91106979 | -3.71730545 | -1.06190829 |
| C | 3.14644612 | -2.58453456 | 0.77212331 |
| C | 4.17672094 | -0.85534902 | 2.14287533 |
| H | 5.00246059 | -1.48406689 | 2.50231991 |
| H | 3.37356002 | -0.90114929 | 2.89430839 |
| C | 4.63806464 | 0.59870993 | 1.94338050 |
| H | 4.59768586 | 1.16460063 | 2.88227779 |
| H | 5.67705882 | 0.61698754 | 1.58023192 |
| C | 3.36671510 | 2.48383234 | 0.97999043 |
| C | 2.40704404 | 2.89375315 | -0.14432910 |
| H | 2.74883469 | 3.82994456 | -0.59851927 |
| H | 1.40490383 | 3.05602329 | 0.26844056 |
| C | -2.35223534 | 0.70626022 | -0.25483172 |
| C | -2.32693991 | -0.66375114 | -0.22588141 |
| C | -3.48423815 | 1.56064576 | 0.17862568 |
| C | -3.87776613 | 2.68660258 | -0.57843002 |
| H | -3.35964303 | 2.90656241 | -1.50939879 |
| C | -4.92860770 | 3.50823665 | -0.15764127 |
| H | -5.21739207 | 4.36434380 | -0.76481194 |
| C | -5.61059877 | 3.23180510 | 1.03484167 |
| H | -6.42658712 | 3.87227593 | 1.36310093 |
| C | -5.22302023 | 2.12686913 | 1.80541964 |
| H | -5.73296148 | 1.91012129 | 2.74243357 |
| C | -4.17195039 | 1.30552006 | 1.38649154 |
| H | -3.86699360 | 0.46390068 | 2.00400864 |
| C | -3.48944079 | -1.54635633 | 0.04001072 |

| | | | |
|---|---|---|---|
| C | -4.73210160 | -1.32983245 | -0.59653243 |
| H | -4.83696347 | -0.49696773 | -1.28812189 |
| C | -5.81862115 | -2.17880563 | -0.36392184 |
| H | -6.76369642 | -1.99262327 | -0.87104499 |
| C | -5.69171338 | -3.27146080 | 0.50484958 |
| H | -6.53687634 | -3.93302380 | 0.68327338 |
| C | -4.46185587 | -3.50817338 | 1.13340961 |
| H | -4.34916939 | -4.35369153 | 1.80966108 |
| C | -3.37421233 | -2.65981378 | 0.90130654 |
| H | -2.42556591 | -2.84840661 | 1.39931408 |

**Complex 2**$^{-}$ (anion doublet)

| | | | |
|---|---|---|---|
| Ni | 3.06820301 | -0.00931754 | -0.29143899 |
| Ni | 0.72987639 | 0.06047210 | -1.11707005 |
| S | 2.34134698 | -1.46854605 | -1.74371911 |
| S | 2.36161617 | 1.62256271 | -1.55628710 |
| S | -0.77553122 | 1.56675739 | -0.77982895 |
| S | -0.71453626 | -1.48843690 | -0.68263571 |
| O | 2.92884789 | -3.48684694 | 1.67632838 |
| O | 3.45334908 | 3.33751142 | 1.89810680 |
| N | 3.39970976 | -1.34771910 | 0.94744963 |
| N | 3.51349757 | 1.18767162 | 1.04349631 |
| C | 2.36347517 | -2.92777048 | -0.59698310 |
| H | 1.34488339 | -3.31354482 | -0.48627452 |
| H | 2.96883992 | -3.70209103 | -1.08171936 |
| C | 2.93108580 | -2.60496666 | 0.78913580 |
| C | 3.73741974 | -0.86730410 | 2.30882991 |
| H | 4.49705638 | -1.50784812 | 2.77351933 |
| H | 2.83465982 | -0.90450229 | 2.93572770 |
| C | 4.23987610 | 0.57797465 | 2.17486201 |
| H | 4.07267393 | 1.14817244 | 3.09576257 |
| H | 5.31751426 | 0.58734130 | 1.95626697 |
| C | 3.18201146 | 2.49304088 | 1.01488903 |

| | | | |
|---|---|---|---|
| C | 2.38994719 | 2.92370987 | -0.22654524 |
| H | 2.84257782 | 3.82031477 | -0.66179566 |
| H | 1.35885559 | 3.16032696 | 0.05828590 |
| C | -2.23137609 | 0.71426117 | -0.27649900 |
| C | -2.21101844 | -0.66458805 | -0.26029020 |
| C | -3.36556184 | 1.56862647 | 0.15191743 |
| C | -3.78173794 | 2.66402692 | -0.63385324 |
| H | -3.28803420 | 2.85987357 | -1.58318467 |
| C | -4.83356729 | 3.48444507 | -0.21464259 |
| H | -5.14633554 | 4.31869227 | -0.83920764 |
| C | -5.48521001 | 3.23243084 | 0.99937665 |
| H | -6.30239144 | 3.87215052 | 1.32546591 |
| C | -5.07335171 | 2.15405124 | 1.79394467 |
| H | -5.56475699 | 1.95810199 | 2.74479249 |
| C | -4.02357986 | 1.33069212 | 1.37749939 |
| H | -3.69790467 | 0.50721878 | 2.00830451 |
| C | -3.37473711 | -1.54373806 | 0.01143599 |
| C | -4.60906329 | -1.32742690 | -0.63756578 |
| H | -4.70749803 | -0.50224252 | -1.33865118 |
| C | -5.69512467 | -2.17504783 | -0.40228104 |
| H | -6.63708880 | -1.99650041 | -0.91685176 |
| C | -5.57147833 | -3.25485905 | 0.48247140 |
| H | -6.41834947 | -3.91287054 | 0.66464879 |
| C | -4.34884337 | -3.48470996 | 1.12597633 |
| H | -4.24336646 | -4.31956147 | 1.81569464 |
| C | -3.25888071 | -2.64093794 | 0.89047394 |
| H | -2.31562515 | -2.81919812 | 1.40198602 |

**Complex $2^{3-}$** (trianion doublet)

| | | | |
|---|---|---|---|
| Ni | -3.14542540 | -0.11220680 | -0.33340795 |
| Ni | -0.62704041 | -0.24119774 | -1.02952476 |
| S | -2.40967746 | 1.12750187 | -1.98822842 |
| S | -2.39166659 | -1.97315455 | -1.21313507 |

| | | | |
|---|---|---|---|
| S | 1.06166616 | -1.70444811 | -0.78688019 |
| S | 0.73827311 | 1.44787440 | -0.40200662 |
| O | -3.45666757 | 3.70908504 | 0.93914362 |
| O | -3.89555934 | -3.04773269 | 2.36157575 |
| N | -3.67423859 | 1.42611946 | 0.59716422 |
| N | -3.75417070 | -1.06687679 | 1.15327806 |
| C | -2.61867991 | 2.76615040 | -1.12511869 |
| H | -1.62848971 | 3.21232681 | -0.97746732 |
| H | -3.19356936 | 3.43521644 | -1.77761567 |
| C | -3.30476256 | 2.66649235 | 0.24043614 |
| C | -4.15596136 | 1.18223445 | 1.97203238 |
| H | -4.97239124 | 1.86727293 | 2.23984382 |
| H | -3.33242905 | 1.35883127 | 2.68270549 |
| C | -4.61606640 | -0.28338574 | 2.05326802 |
| H | -4.56336618 | -0.66237987 | 3.08244219 |
| H | -5.66364423 | -0.36509435 | 1.72016037 |
| C | -3.48143074 | -2.35906312 | 1.38498971 |
| C | -2.54853804 | -2.98867094 | 0.34463731 |
| H | -2.91767747 | -3.98594489 | 0.07978656 |
| H | -1.54969477 | -3.10225836 | 0.78555206 |
| C | 2.44811472 | -0.70992372 | -0.27031228 |
| C | 2.31011020 | 0.65872723 | -0.12066040 |
| C | 3.68583329 | -1.45648664 | 0.06700306 |
| C | 4.20469795 | -2.44954377 | -0.79744209 |
| H | 3.69196894 | -2.64499737 | -1.73696431 |
| C | 5.35869457 | -3.16859911 | -0.47228201 |
| H | 5.73878222 | -3.91677266 | -1.16645912 |
| C | 6.02834383 | -2.93132856 | 0.73815892 |
| H | 6.92292797 | -3.49550736 | 0.99427232 |
| C | 5.52064975 | -1.96422947 | 1.61680964 |
| H | 6.01697779 | -1.77888084 | 2.56834652 |
| C | 4.36928315 | -1.24043365 | 1.28787044 |
| H | 3.97969857 | -0.50479588 | 1.98825806 |
| C | 3.43882725 | 1.57876172 | 0.17095953 |

| | | | |
|---|---|---|---|
| C | 4.65450987 | 1.50833482 | -0.55002761 |
| H | 4.76701123 | 0.75194675 | -1.32388762 |
| C | 5.70210298 | 2.40215449 | -0.30072256 |
| H | 6.62082645 | 2.32708832 | -0.88070739 |
| C | 5.56990075 | 3.39802624 | 0.67691749 |
| H | 6.38327576 | 4.09494739 | 0.86910151 |
| C | 4.36860932 | 3.48964590 | 1.39668408 |
| H | 4.24888441 | 4.25712984 | 2.16001819 |
| C | 3.32031839 | 2.60016188 | 1.14282136 |
| H | 2.39176645 | 2.68315505 | 1.70374928 |

**Complex 3** (neutral closed shell singlet)

| | | | |
|---|---|---|---|
| Ni | -1.89202411 | 0.05651473 | -0.39238346 |
| Ni | 0.78579950 | -0.02541363 | -0.85502301 |
| S | -0.83778935 | -1.47825713 | -1.51657054 |
| S | -0.76390453 | 1.47748231 | -1.58481414 |
| S | 2.22228432 | 1.52194580 | -0.35900906 |
| S | 2.11767998 | -1.61730457 | -0.22678134 |
| N | -2.74793170 | -1.29884390 | 0.73370503 |
| N | -2.36868302 | 1.42048661 | 0.91606236 |
| N | 5.62197375 | 2.00576343 | 1.08661367 |
| C | 4.70999650 | 1.36521694 | 0.72630636 |
| C | -2.38639325 | 0.64624113 | 2.21070312 |
| H | -2.80201528 | 1.26416050 | 3.01797100 |
| H | -1.34613206 | 0.40404515 | 2.44698152 |
| C | 3.59119828 | 0.62268112 | 0.28455525 |
| C | -0.92483734 | 2.94115395 | -0.43966396 |
| H | -1.69951452 | 3.57682944 | -0.87920854 |
| H | 0.01654532 | 3.49787764 | -0.43397564 |
| C | -3.19880947 | -0.62284974 | 2.01234931 |
| H | -3.07753227 | -1.30641297 | 2.86025487 |
| H | -4.26253890 | -0.39800248 | 1.90588495 |
| C | -3.92758083 | -1.94252439 | 0.07512107 |

| | | | |
|---|---|---|---|
| H | -3.62137709 | -2.41451100 | -0.86000386 |
| H | -4.66957206 | -1.16995672 | -0.13968458 |
| H | -4.35982368 | -2.69655507 | 0.74715513 |
| C | -1.08305636 | -2.85859104 | -0.28422354 |
| H | -0.11964107 | -3.34242409 | -0.10171256 |
| H | -1.74485017 | -3.58213212 | -0.76935176 |
| N | 5.48677028 | -2.20473569 | 1.25057089 |
| C | -3.69162834 | 2.06347274 | 0.64509762 |
| H | -4.45959166 | 1.29465684 | 0.53839433 |
| H | -3.63189548 | 2.63131711 | -0.28538801 |
| H | -3.94931289 | 2.73583661 | 1.47462537 |
| C | -1.27115795 | 2.45600802 | 0.95663471 |
| H | -0.39710261 | 1.96930224 | 1.39819960 |
| H | -1.58528870 | 3.28915378 | 1.60181017 |
| C | -1.66424039 | -2.31060275 | 1.01361423 |
| H | -2.08304912 | -3.12331467 | 1.62530659 |
| H | -0.88713301 | -1.79480892 | 1.58519944 |
| C | 3.54622051 | -0.76080973 | 0.33974340 |
| C | 4.61643570 | -1.53713753 | 0.83993922 |

**Complex [3]**$^{+}$ (cation doublet)

| | | | |
|---|---|---|---|
| Ni | -1.86147288 | 0.06552751 | -0.39835066 |
| Ni | 0.70181106 | 0.00194833 | -0.79350632 |
| S | -0.84199636 | -1.45936504 | -1.58856262 |
| S | -0.76915207 | 1.52614796 | -1.59271826 |
| S | 2.19216773 | 1.51325079 | -0.35636078 |
| S | 2.03362877 | -1.59665047 | -0.18411047 |
| N | -2.67005850 | -1.31331290 | 0.73605537 |
| N | -2.29824552 | 1.40199019 | 0.95209679 |
| N | 5.62407596 | 1.96601727 | 0.99755114 |
| C | 4.69139256 | 1.34262255 | 0.67174990 |
| C | -2.25573111 | 0.60267470 | 2.23495639 |
| H | -2.63884568 | 1.20975148 | 3.06483595 |
| H | -1.20531411 | 0.36252062 | 2.42150004 |
| C | 3.54554528 | 0.61075311 | 0.27181612 |

| | | | |
|---|---|---|---|
| C | -0.91462814 | 2.96838151 | -0.42088323 |
| H | -1.70675136 | 3.59376232 | -0.84336763 |
| H | 0.01863778 | 3.53880888 | -0.43665424 |
| C | -3.07048383 | -0.66389726 | 2.04958352 |
| H | -2.90316688 | -1.36624301 | 2.87263746 |
| H | -4.13911876 | -0.44692657 | 1.99398135 |
| C | -3.88271942 | -1.91130916 | 0.08989572 |
| H | -3.61587271 | -2.36446144 | -0.86613947 |
| H | -4.61165315 | -1.11500406 | -0.07693628 |
| H | -4.30790173 | -2.67211271 | 0.75678838 |
| C | -1.06378338 | -2.86409507 | -0.38197001 |
| H | -0.10475633 | -3.37399529 | -0.25236717 |
| H | -1.75264180 | -3.55733556 | -0.87326703 |
| N | 5.41844874 | -2.25187260 | 1.19497605 |
| C | -3.64795220 | 2.01200502 | 0.72174588 |
| H | -4.39166783 | 1.22292693 | 0.59144539 |
| H | -3.61871050 | 2.62317150 | -0.18198027 |
| H | -3.90982188 | 2.63560739 | 1.58558304 |
| C | -1.22265637 | 2.46294029 | 0.97672255 |
| H | -0.33283767 | 1.99652478 | 1.40701300 |
| H | -1.54843497 | 3.28494471 | 1.62806006 |
| C | -1.59052854 | -2.34491668 | 0.94954070 |
| H | -2.00196170 | -3.17051854 | 1.54619462 |
| H | -0.79221703 | -1.85625796 | 1.51517923 |
| C | 3.47643074 | -0.77344801 | 0.34211342 |
| C | 4.54839002 | -1.57310642 | 0.81185696 |

**Complex [3]**$^{-}$ (anion doublet)

| | | | |
|---|---|---|---|
| Ni | -1.85389031 | 0.20834083 | -0.38627390 |
| Ni | 0.74669114 | 0.13041197 | -0.82028583 |
| S | -0.95145014 | -1.10402514 | -1.88993919 |
| S | -0.77560535 | 1.91029845 | -1.25083217 |
| S | 2.57436934 | 1.41949186 | -0.73774247 |
| S | 1.77681651 | -1.54166580 | 0.27860900 |

| | | | |
|---|---|---|---|
| N | -2.81709888 | -1.33606059 | 0.40606672 |
| N | -2.25903798 | 1.24286119 | 1.24681636 |
| N | 6.10986004 | 1.36209159 | 0.43340085 |
| C | 5.03752935 | 0.90660600 | 0.27807640 |
| C | -2.31316343 | 0.17429540 | 2.30151290 |
| H | -2.68110326 | 0.58362032 | 3.25374311 |
| H | -1.28752478 | -0.18079276 | 2.44243843 |
| C | 3.73843659 | 0.39202126 | 0.08085276 |
| C | -0.78544126 | 3.00145026 | 0.26389046 |
| H | -1.51922199 | 3.79625310 | 0.09464963 |
| H | 0.20314462 | 3.45834246 | 0.37116870 |
| C | -3.20764697 | -0.95926306 | 1.81548767 |
| H | -3.13037757 | -1.83009496 | 2.47832717 |
| H | -4.25460028 | -0.64605779 | 1.79284287 |
| C | -4.03604334 | -1.73350054 | -0.35868435 |
| H | -3.76027207 | -1.97025289 | -1.38827253 |
| H | -4.73836720 | -0.89613903 | -0.36115529 |
| H | -4.50776315 | -2.60987186 | 0.11015445 |
| C | -1.28189256 | -2.71461625 | -1.00232985 |
| H | -0.34702361 | -3.28094303 | -0.94964464 |
| H | -1.99617886 | -3.28239740 | -1.60683135 |
| N | 5.08805324 | -2.42963597 | 1.72437152 |
| C | -3.53468566 | 2.01233677 | 1.18293080 |
| H | -4.36419293 | 1.33739213 | 0.96197913 |
| H | -3.46604619 | 2.75277112 | 0.38296380 |
| H | -3.71667597 | 2.51900738 | 2.14239035 |
| C | -1.10027553 | 2.16817868 | 1.49759309 |
| H | -0.24022698 | 1.53183552 | 1.72993326 |
| H | -1.32373119 | 2.80644956 | 2.36715265 |
| C | -1.80867162 | -2.45299919 | 0.40591882 |
| H | -2.27453008 | -3.35950844 | 0.82487749 |
| H | -0.98885939 | -2.13810729 | 1.05852793 |
| C | 3.39050573 | -0.89205666 | 0.52284114 |
| C | 4.32744983 | -1.71861398 | 1.17896289 |

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