Scrutinizing Formally Ni^{IV} Centers through the Lenses of Core Spectroscopy, Molecular Orbital Theory, and Valence Bond Theory

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Materials and Methods

General Considerations

$(NEt_4)_2[NiCl_4]$ (**1**) (NEt_4 = tetra-N-ethylammonium),[1] $\{Na(benzo\text{-}15\text{-}crown\text{-}5)\}_2[Ni(mnt)_2]$ (**2**) (mnt = maleonitriledithiolate),[2] $(PPh_4)_2[Ni(CF_3)_4]$ (**3**) (PPh_4 = tetraphenylphosphonium),[3] $(PPh_4)[Ni(CF_3)_3MeCN]$ (**4**),[3] (dtbpy)$Ni(CF_3)_2$ (**5**) (dtbpy = 4,4′-di-tert-butyl-2,2′-bipyridine),[4] (dtbpy)$Ni(C_4F_8)$ (**6**),[5] $(py)_2Ni(C_4F_8)$ (**7**) (py = pyridine),[6] $[Ni(cyclam)(NO_3)_2](NO_3)$ (**8**),[7] $[(tBuMe_2tacn)Ni(cycloneophyl)](PF_6)$ (**9**, cycloneophyl = $-CH_2CMe_2$-*o*-C_6H_4-),[8] $[(tpy)Ni(C_4F_8)(MeCN)](BF_4)$ (**10**, tpy = terpyridine),[9] $TpNi(CF_3)_2MeCN$ (**11**),[10] $(py)_2Ni(C_4F_8)F_2$ (**12**),[6] $(py)_2NiF_2(CF_3)_2$ (**13**),[11] $TpNi(CF_3)_2Ph$ (**14**) (Ph = phenyl),[12] $TpNi(CF_3)_3$ (**15**),[13] and $Ni(iPr_2NBC_4Ph_2)_2$ ($iPr_2NBC_4Ph_2$ = 1-diisopropylamino-2,5-diphenyl-3-borolide) (**16**)[14] were prepared according to literature procedures.

XAS Data Collection

All data were measured at the Stanford Synchrotron Radiation Lightsource (SSRL) under ring conditions of 3.0 GeV and 500 mA. All air-sensitive samples were prepared in an inert-atmosphere glovebox and were measured as solids. For Ni K-edge measurements, samples were ground with BN to a final concentration of 5 weight % Ni, pressed into 1 mm aluminum spacers and sealed with 37μm Kapton tape. For Ni $L_{2,3}$-edge measurements, samples were ground to a fine powder and spread in a thin layer on carbon tape affixed to an aluminum sample rod.

All Ni K-edge measurements were carried out at SSRL beamline 9-3. Beamline 9-3 is equipped with a 16-pole, 2-Tesla wiggler source. Incident X-ray radiation was monochromated using a double Si(220) crystal monochromator. Samples were maintained at 10 K in a liquid He cryostat during data collection. Spectra were collected in fluorescence mode, with X-rays detected by a PIPs detector placed at a 90° angle to the sample. A Ni foil and a third ionization chamber upstream of the sample were used for internal energy calibration, setting the first inflection point of the Ni foil scan to

8331.6 eV. Data were collected from 8010 eV to 8730 eV. Four scans were measured and averaged for each compound. Spectra were processed using Sixpack[15] and Igor Pro. The region below 8300 eV was used to fit a linear background, while the region above 8400 eV was flattened with a piecewise spline and set to an average intensity of 1.0.

Ni $L_{2,3}$-edge XAS measurements were collected on beamline 10-1, equipped with a 31-pole wiggler source, a 1000 lines/mm spherical grating monochromator and 29 μm entrance and exit slits. Data were measured by monitoring fluorescence using a transition edge sensor (TES) operated under typical conditions as described previously.[16] Raw TES data were processed into pulse heights via a matched filter,[17] and these pulse heights were calibrated by measuring the non-resonant emission from a blended powder of copper oxide. To create the Ni partial fluorescence yield X-ray absorption spectrum (PFY-XAS), the measured emission was windowed between 800 eV and 880 eV. The signal was normalized to incident photon flux with a gold-grid reference monitor. Incident beam energy was calibrated to the L_3-edge position at 853.7 eV of $\{Na(benzo\text{-}15\text{-}crown\text{-}5)\}_2[Ni(mnt)_2]$. Samples were maintained at room temperature under an ultra-high vacuum (10^{-9} Torr) during collection. Data were collected from 830.0 to 910.0 eV for **1** and **3**-**16** and 840.0 to 890.0 eV for **2**. Processing was carried out using PyMCA.[18] Data were desaturated as described in the IPFY Desaturation Standard Procedure section (vide infra). Background subtraction was achieved with E_0 set at 875 eV, by fitting a line to the pre-edge region below 845.0 eV and subtracting from the entire spectrum. The post edge region above 885.0 eV was set to a flattened polynomial and normalized to 1.0. The edge jumps at L_3 and L_2 were subtracted using a statistics-sensitive non-linear iterative peak-clipping (SNIP) algorithm[19] as implemented in PyMCA. Integrated peak areas under the L_2 and L_3 main-lines were quantified by pseudo-Voigt peak fitting in Igor Pro.

Electronic Structure Calculations

Density functional theory (DFT) calculations were performed with version 4.20 of the ORCA software package.[20] Spectra were calculated from crystallographic coordinates when available or

geometry optimized coordinates using the BP86[21,22] functional. Single-point energies were calculated by using the B3LYP[23,24] functional. Ni K-edge XAS spectra were calculated using time-dependent DFT (TDDFT)[25,26] with 50 root excitations and a line-width broadening of 1 eV. Calculations with hybrid functionals used the RIJCOSX algorithm[27] to speed the calculation of Hartree−Fock exchange. The CP(PPP)[28] basis set was used for Ni with a special integration accuracy (ORCA Grid7). The scalar relativistically recontracted ZORA-def2-TZVP(-f) basis set[29] with ORCA Grid4 was used for all other atoms. Calculations included the zeroth-order regular approximation (ZORA) for relativistic effects as implemented by van Wüllen.[30,31] Solvation was modeled with the conductor-like polarizable continuum model (CPCM)[32] in an infinite dielectric.

Electronic structure calculations of the [NiFe]H_2ase^{Hex} active-site were performed using ORCA version 5.0.3,[20] the def2-tzvp basis set, and the previously reported Cartesian coordinates.[33] Initial hybrid DFT calculations performed at the PBE0[34,35] level indicated an apparent triplet, not singlet ground state, while broken symmetry solutions indicated the structure is multiconfigurational in nature. The singlet and triplet states were therefore examined using a multiconfigurational method. Fully internally contracted N electron valence state perturbation theory (FIC-NEVPT2)[36–38] calculations were therefore performed using a CAS-SCF(14,13) active space and employed the resolution of identity approximation necessitating the def2/jk (Coulomb + exchange) auxiliary basis set.[39] Guess orbitals, as quasi-restricted orbitals, were obtained from the broken symmetry solution. Charges and *d*-populations from the Löwdin analysis are reported following the generation of the unrelaxed density of the FIC-NEVPT2 results.

Ab initio valence bond (VB) calculations of NiF_6^{2-} were performed at the L-BOVB level of theory[40,41] using the XMVB *v* 3.0 package[42,43] employing the Sapporo all electron gaussian basis set of double-ξ quality (Sapporo-DZVP-2012).[44] Valence bond orbitals were constructed as atomic-centered hybrid atomic orbitals. The molecular geometry of NiF_6^{2-} was obtained from DFT calculations at the BP86/def2-tzvp level of theory. To make the L-BOVB calculations tractable, all

core orbitals were frozen from the corresponding VBSCF[45] results (F(1s) and Ni(1s) through Ni(2p)) while the valence orbitals were allowed to breathe. For comparisons between the L-BOVB results of NiF_6^{2-} and more commonly used density functional and molecular orbital results, additional hybrid-DFT (PBE0) and CCSD(T) calculations of NiF_6^{2-} were performed using ORCA version 4.1.2 with Ahlrichs' def2-QZVPP basis set. All atomic charges and populations are reported as Mulliken populations while bond orders are reported as Mayer bond orders.

Example Orca Input Files

Single Point Calculation

```
!B3LYP RIJCOSX ZORA-def2-TZVP(-f) Autoaux ZORA CPCM UKS
!NormalPrint VeryTightSCF SlowConv Grid4 NoFinalGrid UNO UCO
!PrintBasis

%pal nprocs #Processors end

%output print[p_mos] 1 end

%basis newgto Ni "CP(PPP)" end
          end

%method SpecialGridAtoms 28
       SpecialGridIntAcc 7
       end

%tddft   NRoots 50
        MaxDim 500
        OrbWin[0] = 0, 0, -1, -1
        OrbWin[1] = 0, 0, -1, -1
        DoQuad true
        end

%MaxCore 4000

%SCF
    MaxIter 500
    end

* xyz Charge SpinMultiplicity
Coordinates
*
```

Note 1: For the calculation of **17**, the SARC-ZORA-def2-TZVPP basis set[46] must be explicitly added for iodine. The following %basis block is used:

```
%basis newgto Ni "CP(PPP)" end
NewGTO I
 S    8
   1    1800697.570348     0.002887579368
   2     800310.031266    -0.001374357993
   3     355693.347229     0.005735294262
   4     158085.932102     0.002649217523
   5      70260.414267     0.012134056749
   6      31226.850786     0.017700366612
   7      13878.600349     0.040940121830
   8       6168.266822     0.079877906223
 S    1
   1       2741.451921     1.0
 S    1
   1       1218.423076     1.0
 S    1
   1        541.521367     1.0
 S    1
   1        240.676163     1.0
 S    1
   1        106.967184     1.0
 S    1
   1         47.540970     1.0
 S    1
   1         21.129320     1.0
 S    1
   1          9.390809     1.0
 S    1
   1          4.173693     1.0
 S    1
   1          1.854975     1.0
 S    1
   1          0.824433     1.0
 S    1
   1          0.366415     1.0
 S    1
   1          0.162851     1.0
 S    1
   1          0.072378     1.0
 P    6
   1      27078.048041     0.001140859432
   2      10831.219216     0.001278436284
   3       4332.487687     0.006716369770
   4       1732.995075     0.021526440632
   5        693.198030     0.079489673354
   6        277.279212     0.240711281689
 P    1
   1        110.911685     1.0
 P    1
   1         44.364674     1.0
 P    1
   1         17.745870     1.0
```

```
P     1
   1          7.098348     1.0
P     1
   1          2.839339     1.0
P     1
   1          1.135736     1.0
P     1
   1          0.454294     1.0
P     1
   1          0.181718     1.0
P     1
   1          0.072687     1.0
P     1
   1          0.029075     1.0
D     5
   1        984.734293     0.002199249101
   2        351.690819     0.014062179404
   3        125.603864     0.087318454593
   4         44.858523     0.343269336240
   5         16.020901     0.566974302765
D     1
   1          5.721750     1.0
D     1
   1          2.043482     1.0
D     1
   1          0.729815     1.0
D     1
   1          0.260648     1.0
F  1
  1    0.372727     1.0
end
end
```

Note 2: For TDDFT calculations of the Ni K-edge, the following block is included within the above input:

```
%tddft   NRoots 50
        MaxDim 500
        OrbWin[0] = 0, 0, -1, -1
        OrbWin[1] = 0, 0, -1, -1
        DoQuad true
        end
```

Geometry Optimization

```
!BP86 ZORA-def2-TZVP(-f) def2/J ZORA CPCM RKS
!NormalPrint VeryTightSCF SlowConv Grid4 NoFinalGrid
!D3 Opt

#%basis newgto Ni "CP(PPP)" end
#           end

%pal nprocs #Processors end

%method SpecialGridAtoms 28
```

```
      SpecialGridIntAcc 7
      end

%MaxCore 4000

%SCF
   MaxIter 500
   end

* xyz ***Charge SpinMultiplicity***
*
```

Input Coordinates for Calculations

1
Charge = -2 Spin Multiplicity = 3

Ni	0.00000	0.00000	0.00000
Cl	1.63984	1.43727	-0.65760
Cl	0.75680	-2.07224	-0.58532
Cl	0.00000	0.00000	2.27723
Cl	-1.95249	1.02104	-0.59555

2
Charge = -2 Spin Multiplicity = 1

Ni	-0.00000	0.00000	0.00000
S	2.14815	0.00000	0.00000
S	-0.09794	1.85333	-1.07338
S	0.09006	-1.75092	1.23458
S	-2.14719	-0.04775	-0.07052
C	2.53409	1.43567	-0.84779
C	1.55625	2.25163	-1.32152
C	3.91963	1.74759	-1.04676
C	1.85778	3.47003	-2.00089
C	-1.53747	-2.19665	1.40839
C	-2.53265	-1.44394	0.82426
C	-1.86359	-3.36311	2.16738
C	-3.90737	-1.82816	0.97251
N	5.01959	1.99549	-1.19868
N	2.09096	4.44323	-2.52125
N	-2.13020	-4.30379	2.75654
N	-4.98647	-2.16745	1.08848

3
Charge = -2 Spin Multiplicity = 1

Ni	0.000000	0.000000	0.000000
F	2.575850	-1.211670	-0.031680
C	1.929580	0.000000	0.000000
F	2.512230	0.672490	-1.078240
C	-0.023060	-0.100330	1.935960
C	-1.886070	0.396320	0.002440
F	2.570900	0.643570	1.055460
F	0.909420	-0.993330	2.465160
C	-0.059740	-0.343320	-1.891530
F	0.212150	1.025590	2.680820
F	-1.185170	-0.594280	2.499900
F	-2.437310	0.911030	-1.159090
F	-2.771110	-0.607330	0.318420
F	-2.234820	1.399090	0.898380
F	-1.135540	-1.110090	-2.317610
F	1.000460	-1.094210	-2.436390
F	-0.109120	0.733130	-2.766130

4
Charge = -1 Spin Multiplicity = 1

Ni	0.000000	0.000000	0.000000
F	-2.356530	1.043630	1.063850
F	-2.641150	-0.886490	0.218160
F	-2.526910	0.842820	-1.015140
F	-1.116540	-1.123260	-2.274930
F	1.007510	-1.051900	-2.377250
F	-0.133250	0.749700	-2.666780
F	2.554690	-1.230880	-0.039320
F	2.540130	0.709940	-0.999720
F	2.506500	0.567220	1.130280
N	-0.002820	0.034730	1.892890
C	-0.041390	0.011410	3.027420
C	-0.091750	0.005290	4.473520
C	-1.911790	0.259800	0.028820
C	-0.047180	-0.341740	-1.864170
C	1.935720	-0.000000	0.000000
H	0.501240	-0.694820	4.818600
H	-1.010360	-0.171310	4.767470
H	0.197940	0.877120	4.814200

5
Charge = 0 Spin Multiplicity = 1

Ni	0.000000	0.000000	0.000000
F	1.054410	-2.407530	-1.056860
F	-0.441500	-2.746740	0.498160
F	-1.032030	-2.031460	-1.484980
F	2.172990	-1.351620	1.149920
F	2.774400	-0.094150	-0.490810
F	2.210550	0.781170	1.415810
N	-1.955260	0.276920	0.180460
N	-0.000000	1.954870	-0.000000
C	-0.066640	-1.808340	-0.476020
C	1.810530	-0.186260	0.484620
C	1.026250	2.776750	-0.367770
C	0.878170	4.143720	-0.487170
C	-0.351710	4.770200	-0.207800
C	-1.396880	3.922390	0.175810
C	-1.202090	2.543470	0.226710
C	-2.297380	1.558270	0.502340
C	-3.532440	1.890440	1.033200
C	-4.509510	0.905790	1.254420
C	-4.164660	-0.405090	0.876230
C	-2.908620	-0.671170	0.354780
C	-0.524840	6.277780	-0.352270
C	-0.630870	6.609390	-1.820480
C	-1.705700	6.780530	0.318040
C	0.658920	7.008640	0.150150
C	-5.845930	1.262850	1.916720
C	-6.778720	0.033010	2.062070
C	-6.569770	2.320220	1.085210
C	-5.556760	1.825170	3.304830

H	1.875630	2.393380	-0.548900
H	1.618390	4.670150	-0.761950
H	-2.242970	4.289600	0.402740
H	-3.721910	2.795240	1.248770
H	-4.794880	-1.109160	0.978900
H	-2.705480	-1.564490	0.107090
H	-0.539740	7.577850	-1.945510
H	-1.502790	6.317550	-2.160130
H	0.080760	6.148950	-2.311630
H	-1.772610	7.749450	0.181410
H	-1.643520	6.587690	1.276330
H	-2.501410	6.343030	-0.052590
H	1.096650	6.480500	0.850500
H	0.377600	7.872250	0.520960
H	1.286800	7.160160	-0.586880
H	-7.551530	0.273450	2.614840
H	-6.288130	-0.700920	2.487740
H	-7.086140	-0.249830	1.174820
H	-6.032560	3.138190	1.058280
H	-7.440130	2.512310	1.490130
H	-6.700500	1.984530	0.173440
H	-6.401450	2.054530	3.745570
H	-5.003400	2.630460	3.220620
H	-5.081570	1.155250	3.836460

6

Charge = 0 Spin Multiplicity = 1

Ni	0.00000	0.00000	0.00000
N	-0.20252	1.90918	0.39446
N	-1.94663	0.00035	0.24239
C	1.91268	-0.00000	0.00000
C	0.12119	-1.81314	-0.59765
C	-2.79829	-1.04912	0.21144
C	-4.15299	-0.93715	0.48983
C	-4.71435	0.30560	0.82417
C	-3.82696	1.38621	0.86311
C	-2.47037	1.21407	0.57631
C	-1.48834	2.30509	0.61516
C	-1.82696	3.64099	0.84549
C	-0.84891	4.64124	0.85244
C	0.46565	4.21504	0.60482
C	0.74485	2.87345	0.38663
C	-6.20927	0.43685	1.12076
C	-6.57225	-0.49973	2.29717
C	-6.60400	1.87508	1.49395
C	-7.00195	0.01421	-0.13956
C	-1.16169	6.11787	1.10095
C	-0.34706	6.60390	2.32320
C	-2.65542	6.35708	1.37651
C	-0.74708	6.92949	-0.14984
H	-4.18571	2.37813	1.12568
H	-2.87003	3.89682	1.01445
H	-7.64806	-0.41912	2.51105
H	-6.01860	-0.22245	3.20609

H	-6.35186	-1.55095	2.06609
H	-7.68153	1.91071	1.70798
H	-6.40301	2.58031	0.67411
H	-6.07458	2.22561	2.39238
H	-6.76734	0.67141	-0.98961
H	-8.08051	0.08591	0.06347
H	-6.78098	-1.02144	-0.43325
H	-0.55398	7.66950	2.50013
H	0.73460	6.49194	2.16546
H	-0.62367	6.04461	3.22894
H	-3.28396	6.05994	0.52396
H	-2.82292	7.42836	1.55602
H	-2.99793	5.81152	2.26811
H	-0.96340	7.99514	0.01585
H	-1.30647	6.59872	-1.03707
H	0.32675	6.83056	-0.36237
C	2.50421	-1.42515	-0.12189
C	1.55108	-2.19526	-1.05212
F	1.75670	-1.76014	-2.34072
F	1.80654	-3.54440	-1.03952
F	2.49323	-2.03424	1.11205
F	2.46490	0.74315	-1.06248
F	-0.73148	-2.11090	-1.67329
F	2.47858	0.56847	1.15325
F	-0.23357	-2.74682	0.39740
F	3.79970	-1.46293	-0.57527
H	-4.76054	-1.84022	0.44003
H	-2.37448	-2.01360	-0.04776
H	1.29654	4.91912	0.58091
H	1.76471	2.55335	0.20020

7

Charge = 0 Spin Multiplicity = 1

Ni	-0.00000	0.00000	0.00000
F	-2.51582	0.79429	-0.89015
F	-2.41608	0.24511	1.22273
F	-2.38250	-1.62421	-1.71496
F	-3.67591	-1.71534	0.03272
N	-0.03134	1.93034	0.06653
C	-0.13663	2.63736	-1.05343
H	-0.24808	2.16886	-1.87260
C	-0.09392	3.99809	-1.08988
H	-0.15208	4.45718	-1.92024
C	0.03221	4.69071	0.06516
H	0.04595	5.64186	0.06818
C	0.13672	3.98921	1.21962
H	0.21827	4.44511	2.04895
C	0.12696	2.60732	1.18801
H	0.23714	2.12842	2.00021
C	-1.88244	-0.06364	-0.02247
C	-2.40264	-1.44680	-0.35460
F	0.80387	-2.53320	0.83022
F	0.32624	-2.36787	-1.29589
F	-1.64344	-2.46516	1.57402

F	-1.65333	-3.69786	-0.21928
C	-0.03382	-1.88282	-0.04461
C	-1.41898	-2.43503	0.22081
N	1.93174	-0.00000	0.00000
C	2.60139	-0.13377	1.13972
H	2.10682	-0.28083	1.93767
C	3.95919	-0.07193	1.22519
H	4.39028	-0.15220	2.06861
C	4.68903	0.10491	0.10011
H	5.63937	0.13303	0.13085
C	4.02610	0.23920	-1.07389
H	4.50891	0.35655	-1.88347
C	2.64429	0.20759	-1.09099
H	2.19191	0.33891	-1.91518

8

Charge = 1 Spin Multiplicity = 2

Ni	6.407850	0.000000	0.000000
O	4.487450	0.168510	0.898761
O	4.329878	2.356231	0.951983
O	2.757082	1.115641	1.795909
N	7.257109	1.019349	1.465875
N	6.653317	-1.585370	1.148449
N	3.843761	1.245264	1.228062
C	7.938999	0.038711	2.358918
H	8.133012	0.448831	3.238765
H	8.791635	-0.262773	1.954402
C	6.995216	-1.115905	2.515065
H	7.424436	-1.843823	3.030569
H	6.178295	-0.829764	2.993915
C	5.576116	-2.606395	1.191408
H	4.759602	-2.205357	1.581995
H	5.857523	-3.355211	1.774063
C	7.555778	3.140142	0.193681
H	8.171422	3.909857	0.105564
H	6.719066	3.469844	0.606994
C	8.184393	2.114709	1.114581
H	8.983719	1.731836	0.674437
H	8.482034	2.565127	1.944139
H	6.589299	1.363247	1.930943
H	7.339309	-1.969037	0.806392
N	5.558591	-1.019349	-1.465875
N	6.162383	1.585370	-1.148449
C	4.876701	-0.038711	-2.358918
H	4.682688	-0.448831	-3.238765
H	4.024065	0.262773	-1.954402
C	5.820484	1.115905	-2.515065
H	5.391264	1.843823	-3.030569
H	6.637405	0.829764	-2.993915
C	7.239584	2.606395	-1.191408
H	8.056098	2.205357	-1.581995
H	6.958177	3.355211	-1.774063
C	5.259922	-3.140142	-0.193681
H	4.644278	-3.909857	-0.105564
H	6.096634	-3.469844	-0.606994

C	4.631307	-2.114709	-1.114581
H	3.831981	-1.731836	-0.674437
H	4.333666	-2.565127	-1.944139
H	6.226401	-1.363247	-1.930943
H	5.476391	1.969037	-0.806392
O	8.328250	-0.168510	-0.898761
O	8.485822	-2.356231	-0.951983
O	10.058618	-1.115641	-1.795909
N	8.971939	-1.245264	-1.228062

9

Charge = 1 Spin Multiplicity = 2

Ni	4.985108	11.822483	7.848359
N	5.596533	13.792054	7.556481
N	3.684598	12.666632	9.279512
N	6.427990	11.790179	9.505890
C	5.733800	10.990408	6.229406
C	4.095810	10.063379	7.810930
H	4.730534	9.356767	8.089840
H	3.327894	10.058321	8.434577
C	6.997436	11.214742	5.665514
H	7.608963	11.800784	6.096929
C	7.364730	10.583507	4.473379
H	8.225906	10.738665	4.104018
C	6.479377	9.730385	3.825109
H	6.726347	9.324137	3.002499
C	5.228552	9.470484	4.383747
H	4.622653	8.883626	3.948065
C	4.871818	10.079694	5.589015
C	3.611630	9.799235	6.378628
C	2.491643	10.761016	5.963302
H	1.714855	10.627721	6.545087
H	2.237209	10.583670	5.033167
H	2.807201	11.684946	6.046039
C	3.095114	8.361377	6.250911
H	3.798936	7.736668	6.523746
H	2.844830	8.185336	5.320448
H	2.311737	8.244071	6.827444
C	4.377524	14.579263	7.900234
H	3.689529	14.443847	7.201730
H	4.603349	15.543491	7.924037
C	3.822781	14.161104	9.236995
H	4.428980	14.461793	9.959630
H	2.938291	14.582526	9.378501
C	4.182392	12.125457	10.570308
H	3.971491	11.159597	10.626122
H	3.723394	12.583914	11.318881
C	5.684163	12.323849	10.700487
H	5.877663	13.290362	10.800133
H	6.004243	11.862782	11.515873
C	7.394843	12.823910	9.009139
H	7.935464	12.430551	8.278624
H	8.012518	13.063581	9.744579
C	6.722549	14.091438	8.497122
H	6.375039	14.608630	9.266872

H	7.393927	14.651050	8.032383
C	5.958770	14.189166	6.172771
H	6.797353	13.750451	5.916352
H	6.072083	15.161715	6.131402
H	5.246267	13.916866	5.558481
C	2.235862	12.358601	9.145721
H	1.908681	12.694857	8.285191
H	1.741478	12.789485	9.874266
H	2.102933	11.388010	9.189716
C	7.191734	10.508457	9.894458
C	8.343672	10.826440	10.869244
H	9.072161	11.265646	10.381523
H	8.673370	9.994692	11.267991
H	8.018176	11.422272	11.576613
C	7.783239	9.842144	8.650777
H	7.065940	9.650441	8.011042
H	8.224921	9.005990	8.907360
H	8.437524	10.443360	8.237584
C	6.242261	9.506867	10.570472
H	5.968882	9.854381	11.445284
H	6.702376	8.650319	10.690145
H	5.450011	9.376345	10.008878

10

Charge = 1 Spin Multiplicity = 2

Ni	11.017661	5.113813	10.503046
F	10.395615	6.391651	12.884489
F	10.270680	7.710308	11.179734
F	8.037495	6.746195	10.291488
F	7.816442	6.801917	12.465157
F	7.002155	4.430511	11.065579
F	8.552651	4.245205	12.643481
F	8.790347	4.246500	9.128191
F	9.401704	2.871604	10.660296
N	10.853114	6.015336	8.543367
N	11.819146	3.735936	9.355284
N	11.732300	3.678918	11.968009
N	12.670827	6.133258	10.808900
C	10.025635	6.431304	11.573534
C	8.506331	6.213601	11.501934
C	8.283110	4.747994	11.392507
C	9.290769	4.195962	10.369843
C	10.340090	7.210109	8.201579
H	10.101487	7.820455	8.889209
C	10.150517	7.582018	6.884409
H	9.776323	8.429504	6.672310
C	10.509420	6.709911	5.887412
H	10.374973	6.944460	4.976876
C	11.066466	5.493108	6.214341
H	11.335907	4.885355	5.536167
C	11.223852	5.169146	7.559880
C	11.808906	3.895325	8.023254
C	12.318083	2.918254	7.185669
H	12.330195	3.046543	6.244061
C	12.810595	1.750693	7.746311

H	13.150883	1.062597	7.188371
C	12.807116	1.587416	9.120220
H	13.135333	0.787877	9.516047
C	12.315169	2.618913	9.907820
C	12.279025	2.592996	11.389805
C	12.778622	1.525215	12.134175
H	13.161042	0.769735	11.704575
C	12.705160	1.595191	13.517542
H	13.042956	0.882474	14.048462
C	12.142596	2.699256	14.120062
H	12.074339	2.757569	15.065723
C	11.676537	3.722977	13.309496
H	11.301282	4.491416	13.721534
C	13.630834	6.693065	11.038560
C	14.869475	7.386345	11.330364
H	15.313721	7.606640	10.604907
H	15.426275	6.777296	11.672153
H	14.704208	8.228648	11.726190

11

Charge = 0 Spin Multiplicity = 2

Ni	0.000000	0.000000	0.000000
F	2.609000	-0.590780	0.951680
F	2.535260	0.958070	-0.524750
F	2.332570	-1.089850	-1.123970
F	-1.146000	-2.353100	0.874030
F	-0.365790	-2.493940	-1.129570
F	0.950870	-2.638830	0.575450
N	-1.982010	0.090690	-0.059570
N	-2.638320	0.888240	0.825780
N	-0.941950	0.965450	2.658440
N	-0.027460	0.106790	2.104530
N	-0.889710	2.643860	0.843150
N	0.000000	2.017970	-0.000000
N	-0.049330	0.133810	-2.188260
C	-2.907440	-0.478670	-0.846200
H	-2.725090	-1.075090	-1.562080
C	-4.178100	-0.059380	-0.450740
H	-5.012090	-0.317330	-0.826890
C	-3.969100	0.805930	0.599110
H	-4.645390	1.267110	1.082690
C	-0.823210	0.937960	4.007360
H	-1.340420	1.444490	4.621530
C	0.173330	0.053160	4.334600
H	0.481810	-0.171490	5.203860
C	0.639010	-0.448110	3.111010
H	1.330600	-1.092270	3.015020
C	-0.823720	3.973310	0.654900
H	-1.333700	4.624820	1.123550
C	0.109520	4.237320	-0.333190
H	0.362850	5.084910	-0.681040
C	0.594800	2.984970	-0.705480
H	1.257900	2.838640	-1.370300
C	1.940030	-0.202100	-0.171210

C	-0.110440	-1.955950	0.085030
C	-0.010150	0.367210	-3.300740
C	0.046710	0.648280	-4.723170
H	0.981310	0.742410	-5.001420
H	-0.435770	1.480330	-4.910800
H	-0.368140	-0.089180	-5.218820
B	-1.818570	1.815370	1.745570
H	-2.495470	2.492290	2.302840

12

Charge = 0 Spin Multiplicity = 1

Ni	0.000000	0.000000	0.000000
F	-0.363340	-0.047540	-1.743050
F	0.284950	-0.058660	1.764550
F	-2.633180	0.462500	-0.615980
F	-2.184480	0.836790	1.457200
F	-3.677700	-1.586660	0.589790
F	-2.086650	-1.667270	2.068880
F	-1.735770	-3.649130	0.322660
F	-2.029960	-2.292710	-1.348260
F	0.514220	-2.510480	1.002780
F	0.533490	-2.448140	-1.150320
N	0.000000	2.031130	-0.000000
N	1.998860	-0.024700	-0.356210
C	-1.924630	0.023190	0.429990
C	-2.353880	-1.411100	0.776560
C	-1.562330	-2.374610	-0.087540
C	-0.085030	-1.968880	-0.063420
C	-0.337790	2.708800	-1.099490
H	-0.601250	2.224460	-1.873250
C	-0.317270	4.083650	-1.152020
H	-0.575810	4.539250	-1.945050
C	0.083130	4.788230	-0.043850
H	0.118950	5.737850	-0.062470
C	0.431760	4.094340	1.096340
H	0.708700	4.558800	1.877630
C	0.373740	2.720180	1.085780
H	0.605400	2.243900	1.874180
C	2.499650	-0.193690	-1.591200
H	1.900980	-0.371650	-2.307840
C	3.848410	-0.115680	-1.855930
H	4.172140	-0.243780	-2.740280
C	4.722050	0.147780	-0.822370
H	5.655430	0.217370	-0.983780
C	4.213940	0.309190	0.454090
H	4.795010	0.482130	1.186450
C	2.856000	0.218690	0.649110
H	2.511500	0.332560	1.526950

13

Charge = 0 Spin Multiplicity = 1

Ni	0.00000	0.00000	0.00000
F	-0.06742	0.10114	-1.77807

F	-0.00000	0.00000	1.78777
F	1.12733	2.34619	0.76237
F	-0.07091	2.56892	-0.98503
F	-0.98467	2.39886	0.93527
F	-2.46173	1.05952	-0.72212
F	-2.37197	-1.04601	-0.83695
F	-2.51331	-0.10302	1.06491
N	2.05548	-0.08422	-0.05422
N	-0.01117	-2.03514	-0.04795
C	0.00731	1.95226	0.17250
C	-1.96572	-0.00753	-0.11429
C	2.67372	-0.28377	-1.21468
H	2.15300	-0.36643	-2.00421
C	4.04611	-0.37554	-1.30775
H	4.45993	-0.52818	-2.14936
C	4.81351	-0.24612	-0.16945
H	5.76122	-0.28980	-0.21604
C	4.17830	-0.05219	1.03142
H	4.68131	0.03257	1.83305
C	2.79905	0.01919	1.06091
H	2.36258	0.14493	1.89541
C	0.05391	-2.69889	-1.20384
H	0.14650	-2.20842	-2.01175
C	-0.00890	-4.07787	-1.25966
H	0.02809	-4.52532	-2.09711
C	-0.12512	-4.78928	-0.10244
H	-0.17339	-5.73808	-0.12464
C	-0.17037	-4.11505	1.10291
H	-0.23782	-4.58985	1.92212
C	-0.11622	-2.74826	1.09057
H	-0.15404	-2.28257	1.91780

14

Charge = 0 Spin Multiplicity = 1

Ni	0.000000	0.000000	0.000000
N	0.189560	-1.993100	-0.007490
N	-0.228290	-2.700640	1.078880
N	-2.136890	-1.211400	1.602220
N	-1.919220	-0.232380	0.678570
N	0.548440	0.046710	1.930580
N	0.033510	-0.908950	2.756050
C	0.731050	-2.872590	-0.854050
H	1.109430	-2.651520	-1.696620
C	0.661260	-4.152250	-0.328930
H	0.964400	-4.958770	-0.730110
C	0.058280	-4.003140	0.901240
H	-0.124100	-4.702060	1.519130
C	-3.451980	-1.312070	1.855030
H	-3.856550	-1.922050	2.460390
C	-4.115270	-0.380030	1.085100
H	-5.051380	-0.220050	1.050560
C	-3.117120	0.275630	0.369820
H	-3.266030	0.981250	-0.247890
C	0.532070	-0.749430	3.997290

H	0.330830	-1.292050	4.750270
C	1.380250	0.329760	3.990780
H	1.875570	0.681520	4.721630
C	1.358870	0.794090	2.684710
H	1.852600	1.542310	2.369600
C	1.904730	0.129350	-0.596020
C	2.357480	0.919960	-1.642900
H	1.757560	1.498470	-2.098450
C	3.696000	0.860770	-2.022170
H	4.003520	1.397710	-2.743360
C	4.585620	0.030440	-1.361740
H	5.493880	-0.018830	-1.635990
C	4.131260	-0.730100	-0.293390
H	4.739700	-1.289020	0.174980
C	2.800030	-0.685950	0.101530
H	2.500630	-1.205420	0.838450
C	0.000000	1.997990	-0.000000
F	-1.063460	2.437460	0.694880
F	-0.060270	2.618980	-1.191990
F	1.075100	2.544790	0.603120
F	0.146210	-0.216090	-2.808040
F	-1.546010	0.919150	-2.128010
F	-1.506740	-1.198130	-1.878320
C	-0.684930	-0.117090	-1.847140
B	-0.942340	-1.954980	2.216620
H	-1.236100	-2.584140	2.936330

15

Charge = 0 Spin Multiplicity = 1

Ni	0.000000	0.000000	0.000000
F	1.190200	-0.318540	2.510600
F	0.880640	-2.442010	-0.948610
F	-0.887870	-0.870060	2.506880
F	-0.997090	-2.672680	0.001230
F	0.775440	-2.466220	1.165420
N	0.584880	0.573150	-2.766390
N	-0.192350	-0.188500	-1.954150
N	2.514170	0.744850	-1.223150
N	2.003210	0.010500	-0.188400
C	0.297430	0.291460	-4.051180
H	0.705000	0.690850	-4.810320
C	3.852560	0.640820	-1.234290
H	4.436880	1.061100	-1.853320
C	-0.685670	-0.671920	-4.080670
H	-1.086880	-1.065080	-4.846560
C	-0.963640	-0.944300	-2.752110
H	-1.606810	-1.574580	-2.449790
C	-0.000000	0.000000	1.980510
C	3.056790	-0.553490	0.429470
H	3.000490	-1.125900	1.185410
C	0.151230	-2.009230	0.077960
C	4.234830	-0.179070	-0.194250
H	5.118960	-0.434130	0.043000
B	1.584270	1.552490	-2.136280

H	2.152840	2.109650	-2.924230
F	-0.294360	1.196410	2.510600
N	0.795640	2.498560	-1.223150
N	0.051090	2.002590	-0.188400
C	0.718760	3.838780	-1.234290
H	1.150790	4.414460	-1.853320
C	-0.491430	3.067380	0.429470
H	-1.064870	3.022690	1.185410
C	-0.093220	4.237590	-0.194250
H	-0.330310	5.126700	0.043000
F	-2.423660	0.929940	-0.948610
F	-2.692330	-0.942720	0.001230
F	-2.450000	0.825250	1.165420
C	-2.005750	0.191920	0.077960

16

Charge = 0 Spin Multiplicity = 1

Ni	0.00000	0.00000	0.00000
N	2.58876	2.35705	1.03603
N	-2.19949	1.59334	-2.49548
C	2.95139	2.58341	2.45580
H	2.68071	1.74733	2.93113
C	2.17982	3.70905	3.15312
H	2.57054	4.57390	2.90958
H	2.23380	3.58914	4.12388
H	1.24104	3.68409	2.87256
C	3.09218	3.25826	-0.02790
H	2.48373	3.12500	-0.81095
C	4.48893	2.87631	-0.51510
H	5.15644	3.18227	0.13318
H	4.65837	3.29728	-1.38340
H	4.54750	1.90275	-0.60885
C	1.88706	0.51380	-0.82357
C	2.19636	1.01653	-2.18840
C	1.41820	1.96701	-2.85513
H	0.64197	2.31456	-2.43322
C	1.76122	2.41133	-4.12436
H	1.22009	3.05943	-4.55942
C	2.88445	1.91451	-4.75643
H	3.11802	2.21850	-5.62578
C	3.66070	0.97694	-4.11573
H	4.43600	0.63468	-4.54776
C	3.32603	0.52687	-2.85034
H	3.87210	-0.12426	-2.42533
C	1.68985	-0.87967	-0.63786
H	1.70337	-1.51376	-1.34553
C	1.46887	-1.22121	0.73570
H	1.32732	-2.10315	1.05937
C	1.49065	-0.06587	1.53930
C	1.14836	-0.13099	2.97673
C	0.33277	0.83585	3.57301
H	-0.01322	1.54597	3.04512
C	0.02276	0.77646	4.91964
H	-0.53705	1.43751	5.30865
C	1.33132	-1.20913	5.13379

H	1.67641	-1.91153	5.67331
C	1.63779	-1.16090	3.78594
H	2.18835	-1.83518	3.40483
C	-1.74752	0.18326	0.95463
H	-1.80927	0.20038	1.90295
C	-1.64163	1.34752	0.14791
C	-1.68281	2.68202	0.79846
C	-0.86383	4.93386	1.15376
H	-0.21728	5.60403	0.96964
C	-1.91213	5.21257	1.99679
H	-1.99658	6.07240	2.39233
C	-2.84047	4.22839	2.26328
H	-3.56003	4.40560	2.85736
C	-2.73131	2.98277	1.66772
H	-3.38440	2.31873	1.85633
C	-2.36942	3.06370	-2.36571
H	-1.71439	3.35086	-1.66576
C	-3.74273	3.46248	-1.83114
H	-3.71792	4.39508	-1.53176
H	-3.98069	2.88342	-1.07710
H	-4.40993	3.36532	-2.54127
C	-2.01773	3.86532	-3.61394
H	-1.10400	3.64885	-3.89459
H	-2.07890	4.82352	-3.41651
H	-2.64236	3.63960	-4.33449
C	-2.66742	0.89137	-3.71574
H	-2.66400	-0.07940	-3.47618
C	-1.73665	1.00758	-4.92081
H	-1.86008	1.88178	-5.34625
H	-1.94436	0.29808	-5.56436
H	-0.80610	0.91769	-4.62519
C	-4.10690	1.19901	-4.11009
H	-4.68726	1.10367	-3.32741
H	-4.39445	0.57394	-4.80844
H	-4.16351	2.11627	-4.44895
C	-1.63585	-0.71739	-1.19138
C	-1.75268	-1.02551	0.17341
H	-1.82450	-1.90290	0.52977
C	-1.52149	-1.79638	-2.20458
C	-0.58221	-1.73956	-3.23017
H	0.01754	-1.00472	-3.27639
C	-0.50946	-2.73963	-4.18397
H	0.13991	-2.69108	-4.87511
C	-1.38392	-3.81054	-4.12867
H	-1.34151	-4.49247	-4.78989
C	-2.31078	-3.88955	-3.12288
H	-2.90459	-4.62970	-3.08359
C	-2.38535	-2.89265	-2.16320
H	-3.03167	-2.95580	-1.46885
C	-0.74064	3.68135	0.56786
H	-0.00000	3.50314	0.00000
C	0.52829	-0.24503	5.69841
H	0.32155	-0.28266	6.62497
C	4.45279	2.71290	2.69910
H	4.91894	1.96900	2.26346

H	4.63112	2.69045	3.66263
H	4.77223	3.56161	2.32666
C	3.03251	4.74536	0.29755
H	2.13218	4.97680	0.60623
H	3.24680	5.26393	-0.50546
H	3.68253	4.95218	1.00156
B	-1.82224	0.85918	-1.34836
B	2.01984	1.12514	0.63328

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Charge = 0 Spin Multiplicity = 1

I	-0.65801603642675	2.51643336654027	4.49624248981579
Ni	1.26278047730485	1.16616349531000	3.09010885369282
P	1.09749128585535	2.63355958679598	1.39041526635874
P	1.32434605915146	-0.47171946413010	4.61932787542725
O	2.68677594293028	-0.52137711870692	1.30386378975506
O	2.60013664865331	2.24000462379200	4.03778536065127
C	2.77497118215806	0.34642986694518	2.14061775754599
C	3.99576012789169	0.98601068741656	2.64992094801503
C	5.25965417104027	0.60894319662772	2.14298465178935
C	6.37976546635499	1.21819101245834	2.64843695552293
C	6.21684812497164	2.18378026366357	3.66478772021087
C	4.98098876693594	2.60858412879742	4.17576705571029
C	3.81262475634974	1.95638602635166	3.65042496675626
C	7.77092595663579	0.82685025352478	2.19021799344996
C	4.88043534993963	3.68216578552050	5.28104566855006
C	4.09940278913185	4.88022481706117	4.72018039542159
C	6.26208592447652	4.18053979393656	5.74195568048506
C	4.13680284551512	3.13866746843737	6.52364902939298
C	1.72652273735545	4.27096068388124	1.84465682599024
C	2.04066496621416	2.24258573465653	-0.12867376649845
C	-0.58888924562604	2.93802593573139	0.77794285388590
C	-0.31730018908624	-1.13727823563930	5.27840164332670
C	2.09798134114406	0.03399617453869	6.18682834322210
C	2.23386317585801	-1.98007278205582	4.12779196861073
C	0.00716194206745	0.00418973604880	2.07235050587545
H	5.31880815778631	-0.15671134319934	1.36800473473898
H	7.12207357941321	2.64231857343452	4.06537421784419
H	7.72352856429301	0.08031608772560	1.38660723172359
H	8.35503668460451	0.39891983727109	3.01980467647781
H	8.33096343579169	1.69797568527071	1.81676867284770
H	4.60473300179856	5.30019470207752	3.83752037991168
H	4.02479278569910	5.67370165950014	5.48023073168892
H	3.08484641760575	4.57805366483339	4.43218958276771
H	6.82909614065859	4.63942869412623	4.91838269793544
H	6.86859341514841	3.36735245589322	6.16779212076275
H	6.12368607448045	4.94363503120217	6.52124593280201
H	3.12482103388894	2.81110336365336	6.25803341957916
H	4.06741151374517	3.92902516796679	7.28603653266789
H	4.67882760971546	2.28691854244133	6.96134163365389
H	1.60077205266733	4.96219065586655	1.00026692883839
H	2.78806290450011	4.19021123750317	2.10479914568914
H	1.17355849187576	4.63565285095920	2.71846460369708
H	1.84158611445098	3.01823385095872	-0.88001739585428

H	1.73876317154212	1.26470946067461	-0.52183394858292
H	3.11267608123412	2.22120889063052	0.10199409780855
H	-0.54788573612955	3.70751055314786	-0.00474161606575
H	-1.21534645978702	3.27811507876659	1.61088085662617
H	-1.01028043964723	2.01620970154075	0.36045920588033
H	-0.91969169064392	-1.54913278510273	4.46070865516160
H	-0.84952504187704	-0.30440496832797	5.74973426155692
H	-0.08133445473394	-1.92125037259573	6.00870204824903
H	3.12720865196946	0.36795710775164	6.01100392980318
H	2.09292432606763	-0.81096457691136	6.88795108235986
H	1.52270402519869	0.87208067253642	6.59858935719692
H	1.81299340270952	-2.38855390416914	3.20136852724868
H	2.15742998262808	-2.72768926745628	4.92790748539859
H	3.28796128482724	-1.72703705613439	3.95916008855361
H	0.17252254249939	0.13833728212106	0.99782858446314
H	-1.01185925748421	0.29224684242087	2.35344597967167
H	0.18874706670661	-1.05151841388075	2.30441472393428

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Charge = 0 Spin Multiplicity = 1

Ni	5.418145	0.302945	11.823975
P	4.476425	-1.260969	13.047047
Si	7.108247	0.603618	13.339809
Si	4.342240	1.970873	12.888448
C	6.552237	1.856586	14.617587
C	7.286679	2.189354	15.770030
C	6.848411	3.188564	16.616627
C	5.698880	3.889558	16.342311
C	4.944332	3.553154	15.230857
C	5.351199	2.538486	14.359036
C	5.283069	-2.834886	12.564945
C	2.710640	-1.569279	12.796694
C	4.583717	-1.260151	14.850913
H	8.340587	1.143774	12.733633
H	7.626615	-0.576433	14.061072
H	3.962007	3.163107	12.117210
H	3.044815	1.427444	13.498250
H	8.105211	1.702932	15.974979
H	7.373981	3.409500	17.403315
H	5.411118	4.594188	16.931933
H	4.113691	4.042303	15.047979
H	4.802987	-3.581339	12.966960
H	6.175920	-2.864889	12.899169
H	2.442263	-2.389378	13.220781
H	2.480244	-1.592918	11.888613
H	2.185766	-0.859194	13.223934
H	5.472874	-1.095586	15.161490
H	4.280684	-2.086614	15.234010
H	4.019425	-0.557340	15.237163
C	5.553221	-2.834886	11.083006
P	6.359865	-1.260969	10.600903
Si	3.728043	0.603618	10.308142
C	4.284053	1.856586	9.030364
C	3.549611	2.189354	7.877921
C	3.987879	3.188564	7.031324

C	5.137410	3.889558	7.305640
C	5.891958	3.553154	8.417094
C	5.485091	2.538486	9.288915
Si	6.494050	1.970873	10.759502
H	6.874283	3.163107	11.530741
H	7.791475	1.427444	10.149700
H	6.722599	4.042303	8.599971
H	5.425172	4.594188	6.716018
H	3.462309	3.409500	6.244636
H	2.731079	1.702932	7.672972
H	2.495703	1.143774	10.914318
H	3.209675	-0.576433	9.586879
C	8.125650	-1.569279	10.851256
H	8.394027	-2.389378	10.427170
H	8.356045	-1.592918	11.759338
H	8.650524	-0.859194	10.424017
C	6.252573	-1.260151	8.797038
H	5.363416	-1.095586	8.486461
H	6.555606	-2.086614	8.413941
H	6.816865	-0.557340	8.410788
H	6.033303	-3.581339	10.680991
H	4.660370	-2.864889	10.748782

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Charge = 0 Spin Multiplicity = 1

Br	15.191275	-1.659109	3.868367
Ni	15.073673	0.695600	3.502934
C	16.451986	1.716070	2.616035
C	16.652904	3.229397	2.642535
H	17.042055	3.525063	3.502378
H	15.799173	3.707290	2.488727
C	17.648924	3.452655	1.462104
H	17.259774	4.047607	0.774600
H	18.499227	3.843658	1.784545
C	17.868357	2.041906	0.906171
H	18.200935	2.017770	-0.037062
C	18.718660	1.253865	1.888319
H	19.529533	1.761928	2.144048
H	18.989523	0.383762	1.502872
C	17.772527	1.052330	3.118784
H	17.640353	0.091717	3.320773
H	18.123791	1.509707	3.924887
C	16.492787	1.395061	1.108160
H	16.490044	0.423587	0.919143
H	15.775173	1.847611	0.596701
C	14.894012	1.792098	5.082154
C	14.458575	3.240258	5.144233
H	13.705988	3.417658	4.525295
H	15.209447	3.849692	4.929273
C	14.017995	3.388694	6.632281
H	14.554577	4.080191	7.095558
H	13.059690	3.630054	6.697140
C	14.276857	2.004495	7.225276
H	13.769418	1.817441	8.066588
C	15.771744	1.781237	7.340169

H	15.972319	0.969060	7.868305
H	16.219182	2.559623	7.758972
C	16.217467	1.609871	5.849712
H	16.879195	2.298954	5.590833
H	16.604904	0.712012	5.690901
C	13.896278	1.093361	6.044845
H	12.951688	1.193525	5.765025
H	14.112282	0.141196	6.204212
C	13.529242	1.235763	2.466675
C	13.303295	2.615136	1.856075
H	14.115711	2.939765	1.391686
H	13.039118	3.274048	2.546173
C	12.161386	2.360501	0.869109
H	12.408248	2.654960	-0.044475
H	11.335084	2.828739	1.148928
C	11.976240	0.763904	0.935821
H	11.551088	0.349972	0.129718
C	11.235653	0.608227	2.181110
H	10.867074	-0.306527	2.260794
H	10.489924	1.258692	2.231144
C	12.255331	0.874930	3.268886
H	12.399677	0.071201	3.826672
H	11.972811	1.626766	3.847056
C	13.424668	0.270323	1.254555
H	13.467698	-0.685462	1.506578
H	14.074567	0.470652	0.535549

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Charge = 0 Spin Multiplicity = 1

Br	7.60114	5.14594	3.39321
Br	8.07464	4.35807	6.68416
Br	5.58068	7.76196	4.58958
Ni	6.88157	6.01745	5.52198
N	4.43944	4.11797	5.08505
N	4.59274	5.21349	6.96000
N	8.22646	7.96631	7.05288
N	9.34120	7.93698	5.18433
C	5.23111	4.96998	5.76847
C	3.27922	3.84096	5.82825
C	2.19217	3.02887	5.52729
H	2.14490	2.53352	4.71899
C	1.18022	2.98327	6.47436
H	0.41902	2.43892	6.31280
C	1.25424	3.72025	7.66043
H	0.53239	3.67446	8.27501
C	2.34413	4.51323	7.96733
H	2.39493	5.00271	8.77922
C	3.36502	4.55372	7.01869
C	5.25375	6.09521	7.84026
C	4.93393	6.43446	9.15090
H	4.18367	6.05093	9.58939
C	5.75357	7.35932	9.79842
H	5.54849	7.60246	10.69304
C	6.86368	7.94171	9.18368
H	7.39821	8.58067	9.63935

C	7.15938	7.55383	7.88272
C	6.37156	6.63332	7.24473
C	9.19182	8.96155	7.18916
C	9.51000	9.85330	8.21241
H	9.02557	9.86730	9.02899
C	10.56435	10.71572	7.97982
H	10.80790	11.33746	8.65590
C	11.28325	10.70210	6.78298
H	12.00293	11.31097	6.66403
C	10.96253	9.81035	5.76050
H	11.44381	9.79729	4.94065
C	9.90558	8.94150	5.99794
C	8.31454	7.34646	5.83091
C	4.68122	3.42546	3.83685
C	5.19494	2.12804	3.91740
C	5.36120	1.44348	2.71400
H	5.72018	0.56385	2.72087
C	5.01096	2.02814	1.50795
H	5.14820	1.55152	0.69778
C	4.46316	3.30096	1.47111
H	4.21276	3.68013	0.63690
C	4.27617	4.03017	2.64454
C	5.54993	1.45616	5.24271
H	5.41886	2.13050	5.96937
C	7.01105	1.00338	5.28798
H	7.12913	0.22138	4.70962
H	7.25205	0.76819	6.20821
H	7.58870	1.73127	4.97500
C	4.61981	0.27473	5.53181
H	3.69214	0.58844	5.55726
H	4.85443	-0.12299	6.39709
H	4.71793	-0.39734	4.82670
C	3.62733	5.40251	2.62190
H	3.87225	5.86362	3.47485
C	4.12753	6.27572	1.46955
H	5.10726	6.30258	1.48142
H	3.77531	7.18430	1.57195
H	3.82012	5.89957	0.61817
C	2.09463	5.27858	2.58896
H	1.82472	4.77188	1.79518
H	1.69486	6.17203	2.55696
H	1.78765	4.81161	3.39367
C	9.99715	7.57143	3.94003
C	11.08996	6.70125	4.02277
C	11.78660	6.43957	2.84560
H	12.52557	5.84280	2.86292
C	11.42131	7.03369	1.64923
H	11.91071	6.84373	0.85700
C	10.34420	7.90406	1.60318
H	10.10182	8.30254	0.77583
C	9.61069	8.20358	2.75147
C	11.53256	6.06077	5.32357
H	10.87223	6.31772	6.02869
C	11.52413	4.54047	5.20915
H	10.64813	4.24209	4.88602

H	11.69981	4.14559	6.08801
H	12.21905	4.25722	4.57849
C	12.91070	6.57637	5.76347
H	13.58067	6.33475	5.09051
H	13.15166	6.17203	6.62344
H	12.87932	7.55137	5.85854
C	8.47354	9.20677	2.69418
H	8.01826	9.20507	3.58412
C	7.43477	8.83554	1.63596
H	7.83268	8.91747	0.74461
H	6.66627	9.43969	1.70620
H	7.13937	7.91276	1.77801
C	9.02086	10.61449	2.45050
H	9.64674	10.84930	3.16733
H	8.28033	11.25610	2.43989
H	9.48638	10.63928	1.58913

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Charge = 2 Spin Multiplicity = 1

Ni	2.306687	4.625098	46.022246
N	3.928502	4.744354	44.703849
N	1.468412	6.047684	44.935725
N	1.539840	3.268397	44.617688
N	3.117885	3.279905	47.013736
C	2.784004	5.915337	47.436307
C	3.841294	6.754015	47.414767
H	4.409390	6.768400	46.653886
C	4.109561	7.586938	48.472145
H	4.836293	8.195447	48.427798
C	3.290639	7.535150	49.637859
H	3.449274	8.112011	50.372765
C	2.294810	6.650439	49.654965
H	1.779038	6.571318	50.448790
C	1.970895	5.847725	48.589350
C	0.813108	4.866631	48.624829
C	0.690187	4.354505	47.224072
H	-0.088038	4.796142	46.799600
H	0.494177	3.384919	47.268419
C	1.184364	3.722980	49.620120
H	2.041492	3.328816	49.359101
H	0.487533	3.033912	49.599847
H	1.256622	4.089811	50.524815
C	-0.509958	5.581593	49.006853
H	-0.489194	5.824708	49.954629
H	-1.265758	4.980277	48.839599
H	-0.612115	6.391499	48.465810
C	3.650267	5.913899	43.797254
H	4.486631	6.430340	43.669912
H	3.371202	5.574400	42.909664
C	2.593808	6.823065	44.323725
H	2.244146	7.382663	43.587552
H	2.986658	7.425820	45.006682
C	0.612115	5.404650	43.853005
H	-0.243351	5.896636	43.777614
H	1.079715	5.475140	42.985689

C	0.326406	3.971850	44.136831
H	-0.384545	3.908553	44.822955
H	-0.004983	3.533091	43.315130
C	2.504108	3.125980	43.472881
H	2.239993	3.733050	42.738608
H	2.480853	2.196673	43.131403
C	3.899432	3.462601	43.932831
H	4.242449	2.730377	44.506185
H	4.494106	3.540283	43.144074
C	0.613776	7.122285	45.649725
H	-0.159466	6.695034	46.071029
H	0.303981	7.782581	44.994011
H	1.154465	7.569675	46.330780
C	5.324656	4.834983	45.294309
H	5.438441	5.705308	45.728917
H	5.989096	4.740038	44.582210
H	5.448408	4.120021	45.950656
C	1.170245	1.931979	45.053564
H	1.963420	1.464449	45.386806
H	0.788192	1.437116	44.297117
H	0.505805	1.995276	45.773265
C	3.622859	2.422526	47.530071
C	4.254077	1.317716	48.256742
H	4.493276	0.607070	47.623202
H	3.629504	0.963832	48.921959
H	5.063033	1.639952	48.700220

22

Charge = –2 Spin Multiplicity = 1

Ni	0.000000	0.000000	0.000000
F	1.775830	0.000000	0.000000
F	-0.000000	-0.000000	-1.775830
F	0.000000	1.775830	0.000000
F	0.000000	0.000000	1.775830
F	-0.000000	-1.775830	0.000000
F	-1.775830	0.000000	0.000000

23 (Optimized Geometry)

Charge = 0 Spin Multiplicity = 1

Ni	0.220645	0.316839	0.065083
N	0.242780	-1.632489	-0.339900
N	-0.302277	-2.498996	0.558188
N	-1.974035	-0.929458	1.524751
N	-1.666185	0.137225	0.735092
N	0.886773	-0.166657	1.944928
N	0.263007	-1.190356	2.591599
C	0.724833	-2.362773	-1.360351
H	1.225276	-1.879407	-2.191518
C	0.484056	-3.724554	-1.122809
H	0.750359	-4.561553	-1.758149
C	-0.167069	-3.768138	0.107674
C	-3.285624	-0.892886	1.856537
C	-3.850525	0.233984	1.265441
H	-4.880819	0.565358	1.328113
C	-2.795355	0.847676	0.571591

H	-2.796253	1.755973	-0.020561
C	0.769383	-1.326876	3.839810
C	1.755192	-0.358850	4.013593
H	2.364825	-0.188389	4.893791
C	1.788167	0.346028	2.799501
H	2.405023	1.188785	2.506965
C	1.938289	0.399844	-0.802816
C	0.257127	2.206517	0.545839
F	-0.178889	2.378971	1.844668
F	-0.559606	3.048166	-0.180094
F	1.495560	2.806031	0.514120
C	-0.477929	0.714556	-1.750682
B	-0.874985	-1.951829	1.881873
H	-1.307870	-2.835655	2.571270
C	1.929760	0.747330	-2.160858
C	3.124660	-0.003234	-0.187337
C	4.318017	-0.023845	-0.920481
C	4.324171	0.344205	-2.269257
C	3.130274	0.721683	-2.885725
H	3.140011	-0.325576	0.851194
H	5.241582	-0.339833	-0.431345
H	5.253670	0.325507	-2.840553
H	3.125593	0.993831	-3.943607
C	0.599111	1.139005	-2.761956
C	0.326341	0.406087	-4.093944
H	0.384618	-0.684463	-3.971015
H	1.050128	0.708060	-4.864642
H	-0.679802	0.657671	-4.460286
C	0.581111	2.656324	-3.035470
H	-1.270840	1.456899	-1.630353
H	-0.913292	-0.258434	-1.999530
H	1.326733	2.904515	-3.804954
H	0.815562	3.233531	-2.134362
H	-0.409419	2.966874	-3.401049
H	-3.716441	-1.666939	2.482794
H	0.395043	-2.097684	4.505258
H	-0.539865	-4.601811	0.693310

24 (Optimized Geometry)

Charge = 0 Spin Multiplicity = 1

Ni	-0.020441	-0.085728	0.029077
N	0.155360	-2.071496	0.152674
N	-0.414779	-2.722169	1.203066
N	-2.255448	-1.107626	1.647028
N	-1.975907	-0.220693	0.649458
N	0.535719	-0.032054	1.966579
N	-0.076598	-0.895220	2.828994
C	0.736107	-3.000848	-0.626518
H	1.247455	-2.722350	-1.540666
C	0.540391	-4.273191	-0.070824
H	0.887215	-5.222723	-0.462028
C	-0.193303	-4.051569	1.092045
H	-0.567636	-4.734907	1.846867
C	-3.582639	-1.115085	1.904913
H	-3.988122	-1.759441	2.677806

C	-4.193533	-0.206290	1.046072
H	-5.247836	0.038278	0.983884
C	-3.148447	0.328401	0.278998
H	-3.187374	1.071128	-0.506183
C	0.505830	-0.817729	4.046497
H	0.149889	-1.436180	4.863686
C	1.531071	0.120885	3.979143
H	2.193663	0.435073	4.777471
C	1.518474	0.580250	2.655091
H	2.159248	1.309827	2.178275
C	1.889566	-0.055983	-0.512183
C	0.012721	1.872796	-0.145393
F	-1.206171	2.439811	0.108608
F	0.389248	2.346424	-1.378409
F	0.873722	2.483808	0.729948
F	0.295979	-0.218161	-2.799733
F	-1.547281	0.759720	-2.178411
F	-1.358697	-1.396365	-2.011970
C	-0.665326	-0.230142	-1.826890
B	-1.117967	-1.901507	2.303321
H	-1.525907	-2.609494	3.183585
H	2.196821	0.950681	-0.799884
H	1.991263	-0.747373	-1.348687
H	2.418778	-0.410901	0.374359

$[Ni(mft)_2]^{2-}$

Charge = –2 Spin Multiplicity = 1

S	-1.592461	4.665128	0.182557
S	-0.957400	1.951422	-1.180956
C	-0.353690	4.588866	-1.058276
C	-0.077055	3.391312	-1.672399
C	0.931946	3.213579	-2.758134
C	0.291834	5.887520	-1.419476
F	1.632932	5.802285	-1.697462
F	0.193921	6.835568	-0.436467
F	-0.271317	6.485990	-2.536749
F	2.240169	3.182352	-2.307828
F	0.768590	2.050629	-3.455417
F	0.896951	4.219845	-3.704330
F	-6.953510	1.417066	3.051566
F	-6.182025	-0.877377	1.474244
C	-5.821551	2.175230	3.222720
C	-4.992161	-0.589421	2.121389
F	-6.252736	3.473723	3.258490
F	-4.179717	-1.656291	1.845264
C	-4.781621	1.946557	2.169578
C	-4.387430	0.715301	1.706361
S	-4.005893	3.388454	1.546553
S	-3.093855	0.611828	0.533108
F	-5.388767	1.908423	4.508327
F	-5.265584	-0.672417	3.465856
Ni	-2.405099	2.654307	0.274409

$[Ni(mft)_2]^{1-}$

Charge = –1 Spin Multiplicity = 2

S	-1.705929	4.693460	0.064825
S	-0.983251	1.969658	-1.171828
C	-0.438223	4.605620	-1.117404
C	-0.122435	3.389201	-1.678642
C	0.970874	3.153708	-2.691683
C	0.200137	5.924374	-1.478444
F	1.557051	5.846846	-1.605873
F	-0.039571	6.882012	-0.538380
F	-0.276051	6.428797	-2.661042
F	2.216679	3.130775	-2.119552
F	0.828087	1.956646	-3.328015
F	1.008970	4.103653	-3.671084
F	-6.892467	1.471847	3.062442
F	-6.224278	-0.719410	1.381019
C	-5.749088	2.183122	3.286456
C	-5.022359	-0.578076	2.025468
F	-6.123339	3.491830	3.360003
F	-4.266133	-1.647460	1.647784
C	-4.692822	1.955683	2.233032
C	-4.347974	0.732890	1.703563
S	-3.834245	3.375577	1.723953
S	-3.079336	0.645049	0.522182
F	-5.316184	1.843216	4.542139
F	-5.272883	-0.739762	3.357504
Ni	-2.400761	2.670624	0.284505

$[Ni(mft)_2]^0$

Charge = 0 Spin Multiplicity = 1

S	-1.731294	4.680330	0.055385
S	-0.998155	1.967693	-1.157712
C	-0.476506	4.595125	-1.101127
C	-0.146035	3.362426	-1.655817
C	0.969655	3.126347	-2.666160
C	0.168486	5.924790	-1.471632
F	1.518612	5.833779	-1.548905
F	-0.116951	6.880531	-0.551703
F	-0.288515	6.375282	-2.669985
F	2.188832	3.148844	-2.065319
F	0.841706	1.914218	-3.262420
F	0.973598	4.058399	-3.650203
F	-6.858642	1.518895	3.041671
F	-6.223373	-0.661882	1.378987
C	-5.716852	2.204152	3.294198
C	-5.014181	-0.573556	1.993765
F	-6.049311	3.516286	3.388940
F	-4.273636	-1.628423	1.569488
C	-4.662351	1.980731	2.217468
C	-4.326765	0.746730	1.668837
S	-3.816790	3.376653	1.711661
S	-3.084793	0.663851	0.498346
F	-5.260557	1.818915	4.515385
F	-5.211882	-0.732654	3.325194
Ni	-2.409829	2.672417	0.274586

[NiFe]H2ase^{hex}

Charge = 1 Spin Multiplicity = 3

Fe	-41.705448	-23.79927	11.210161
C	-42.718929	-24.17084	12.775891
N	-43.292421	-24.39357	13.791316
C	-42.550119	-25.27520	10.357733
N	-43.075847	-26.18219	9.8049802
C	-42.956234	-22.71389	10.655458
O	-43.820046	-21.99941	10.301130
Ni	-38.682112	-23.43540	11.442176
C	-36.556650	-24.44864	12.199076
O	-37.272985	-23.78493	13.027037
O	-36.981804	-24.62633	11.000766
S	-39.970363	-25.26557	11.888420
S	-40.379379	-22.12174	12.288151
S	-37.357992	-21.84135	10.504926
S	-40.127049	-23.52631	9.6042934
C	-33.524571	-26.95158	12.856513
H	-33.367456	-28.01853	12.616858
H	-32.697327	-26.37586	12.400697
H	-33.448448	-26.83503	13.953636
C	-36.816193	-19.22332	11.206569
H	-37.156891	-18.17438	11.320706
H	-36.414764	-19.56784	12.175156
H	-35.986087	-19.23193	10.477181
C	-39.868895	-21.39882	15.044976
H	-39.675851	-20.35410	14.741559
H	-40.297810	-21.38813	16.064651
H	-38.899128	-21.92507	15.081183
C	-38.845196	-26.51226	14.065546
H	-37.870383	-26.03001	13.899248
H	-38.908904	-26.79210	15.135976
H	-38.889273	-27.44217	13.471019
C	-39.733090	-21.80188	7.4042710
H	-40.009718	-20.85633	6.8995829
H	-38.641909	-21.80580	7.5719884
H	-39.984151	-22.63741	6.7277527
C	-35.184082	-24.97554	12.640140
H	-35.093874	-24.77606	13.723429
H	-34.424357	-24.34719	12.132740
C	-34.901174	-26.46603	12.335784
H	-34.972592	-26.62496	11.244346
H	-35.699354	-27.08510	2.7878903
C	-37.968195	-20.12489	10.748238
H	-38.398008	-19.74359	9.8013294
H	-38.780903	-20.13849	11.497016
C	-40.844362	-22.09589	14.091618
H	-41.813636	-21.56344	14.057166
H	-41.099531	-23.11506	14.418279
C	-39.980897	-25.56354	13.702891
H	-39.865827	-24.60700	14.232687
H	-40.979832	-25.96562	13.944461

C	-40.481815	-21.92433	8.7326252
H	-41.573847	-21.92067	8.5764717
H	-40.244312	-21.09860	9.4241114

Experimental and TDDFT-Calculated Ni K-edge XAS

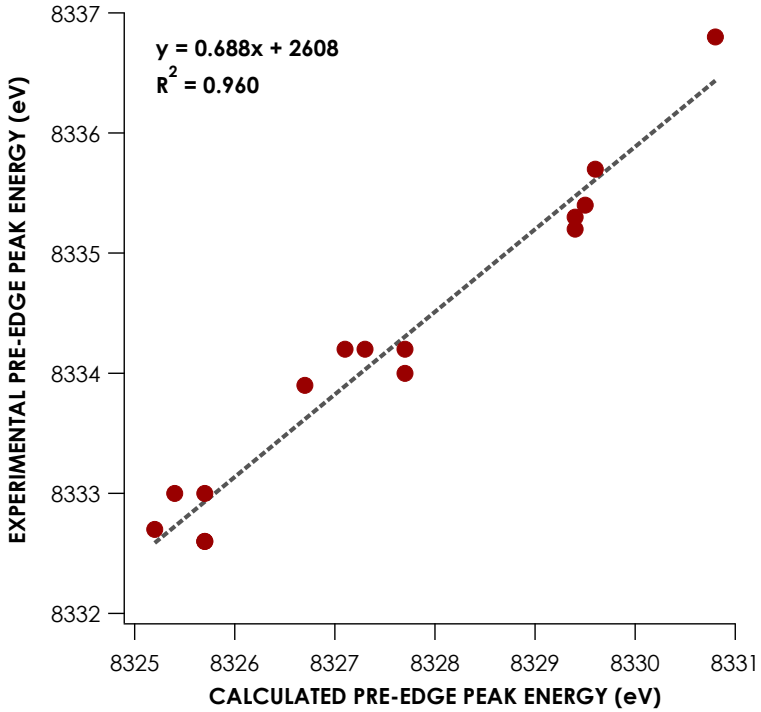

Fig. S1. Correlation of experimental and calculated Ni K-edge pre-edge energy used to apply a scalar shift to calculated data.

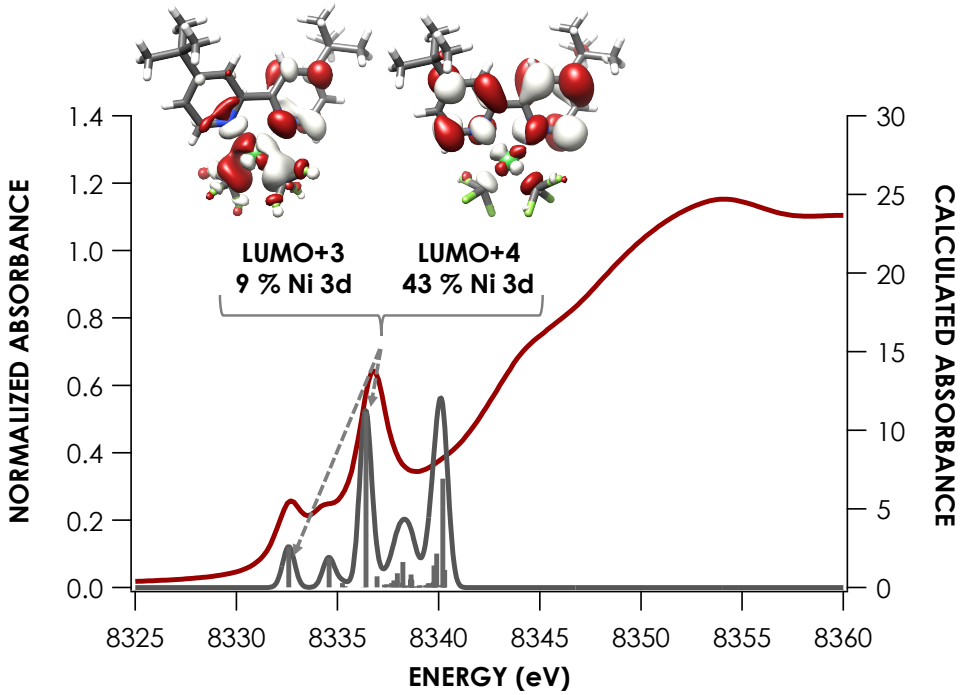

Fig. S2. Comparative experimental and calculated Ni K-edge spectrum of **5** with orbital plots for pertinent pre-edge transitions shown. Orbitals are plotted at an iso value of 0.03.

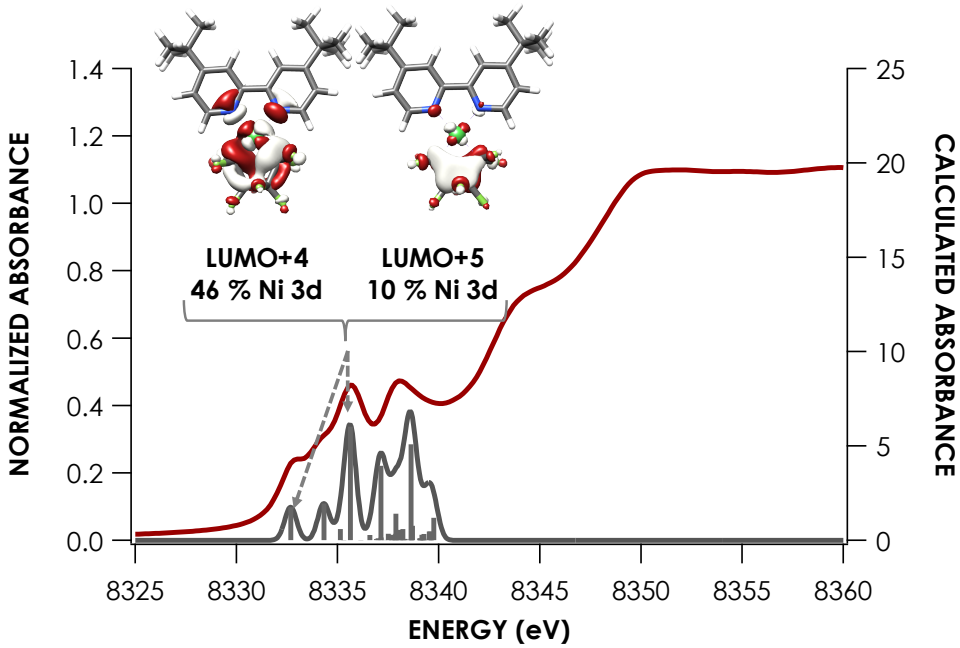

Fig. S3. Comparative experimental and calculated Ni K-edge spectrum of **6** with orbital plots for pertinent pre-edge transitions shown. Orbitals are plotted at an iso value of 0.03.

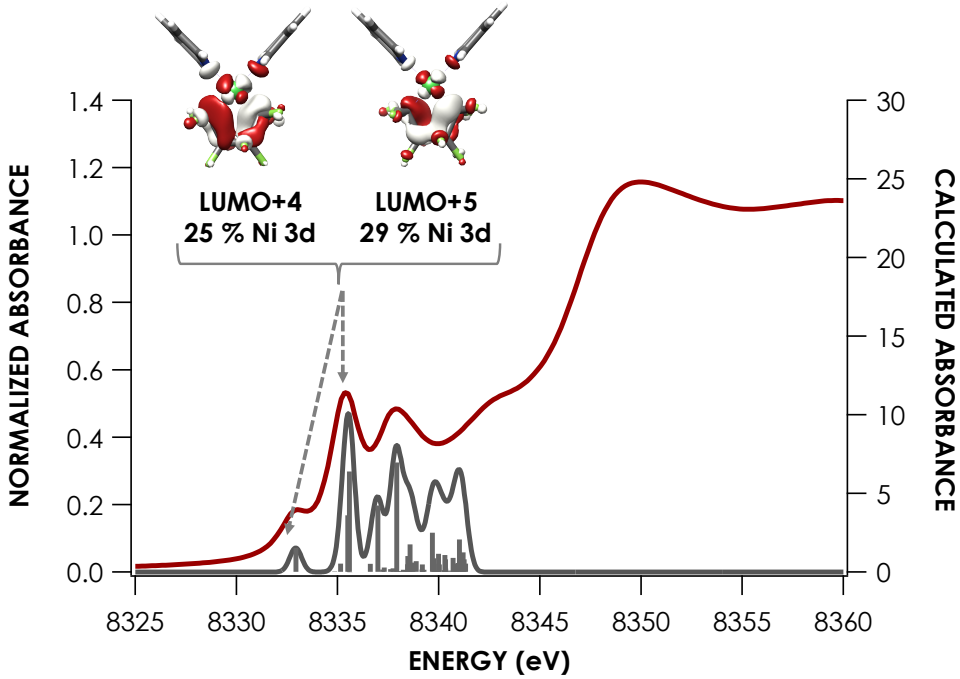

Fig. S4. Comparative experimental and calculated Ni K-edge spectrum of **7** with orbital plots for pertinent pre-edge transitions shown. Orbitals are plotted at an iso value of 0.03.

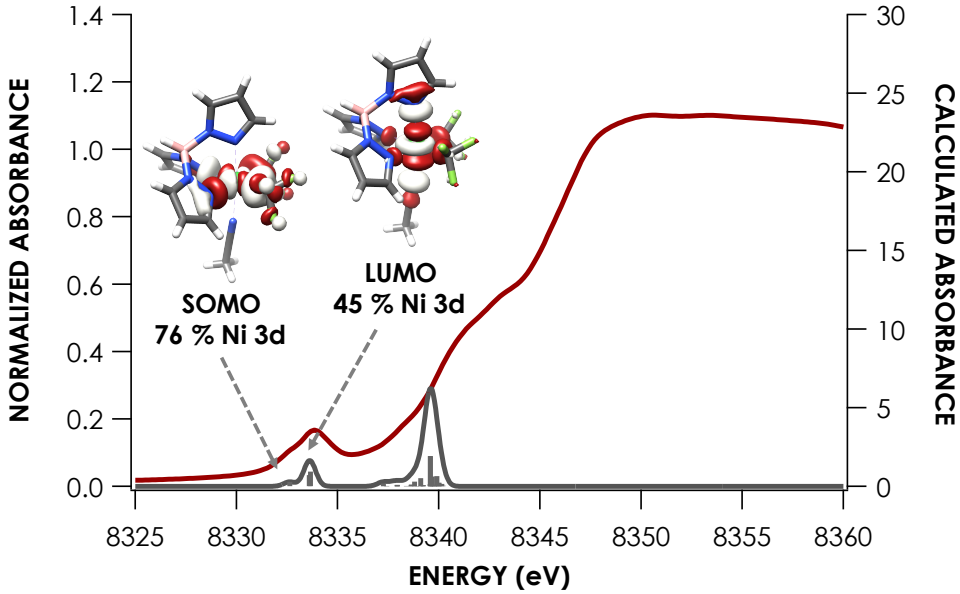

Fig. S5. Comparative experimental and calculated Ni K-edge spectrum of **11** with orbital plots for pertinent pre-edge transitions shown. Orbitals are plotted at an iso value of 0.03.

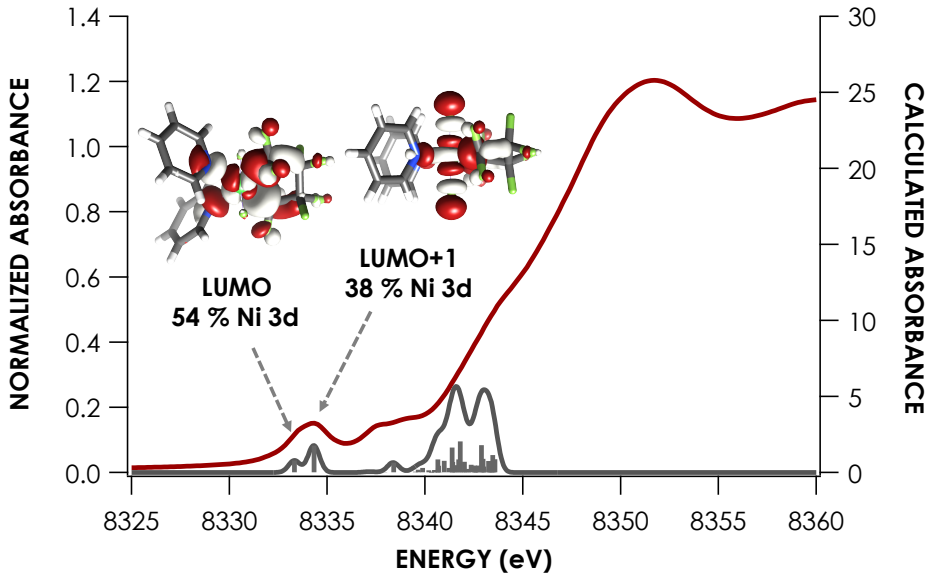

Fig. S6. Comparative experimental and calculated Ni K-edge spectrum of **12** with orbital plots for pertinent pre-edge transitions shown. Orbitals are plotted at an iso value of 0.03.

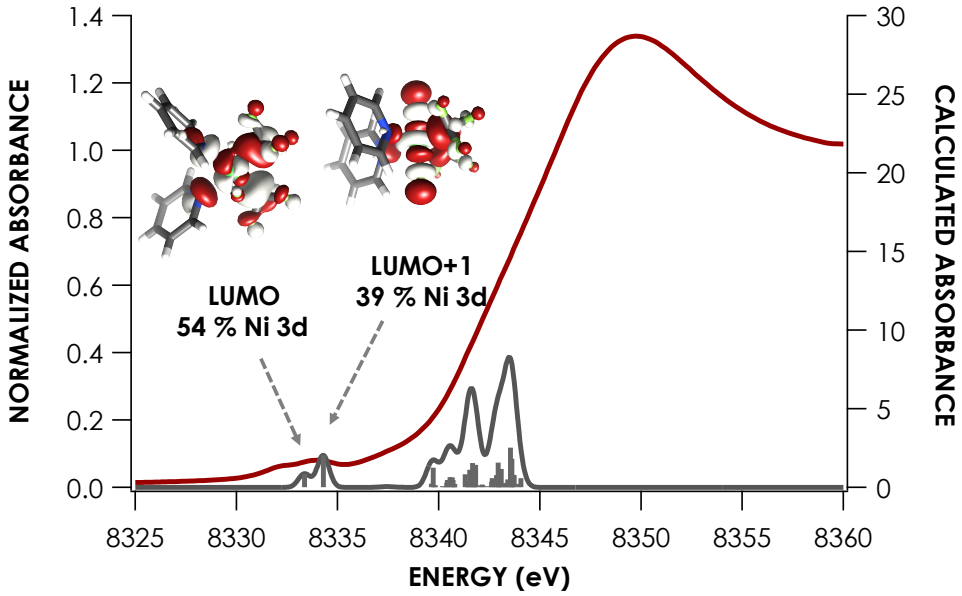

Fig. S7. Comparative experimental and calculated Ni K-edge spectrum of **13** with orbital plots for pertinent pre-edge transitions shown. Orbitals are plotted at an iso value of 0.03.

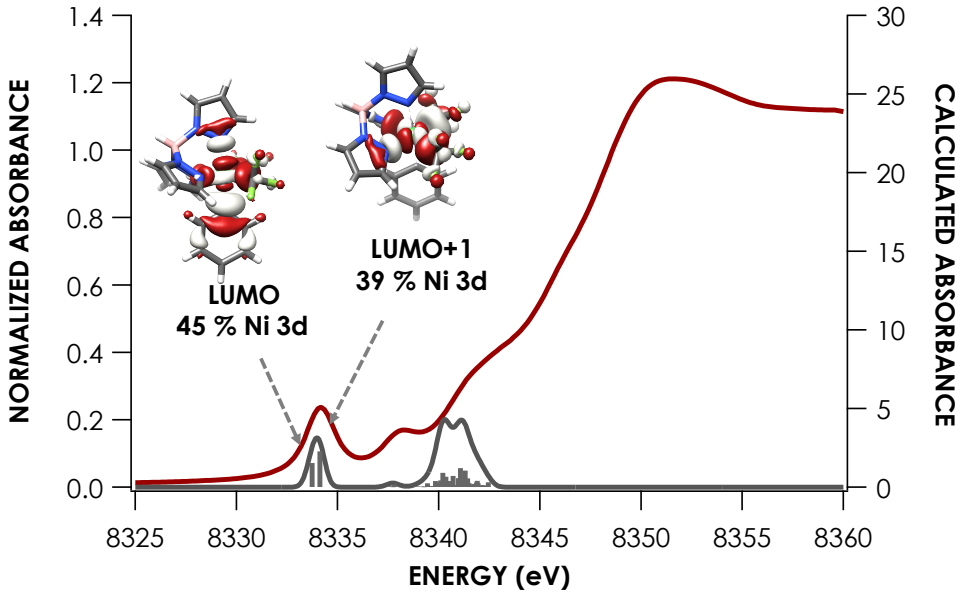

Fig. S8. Comparative experimental and calculated Ni K-edge spectrum of **14** with orbital plots for pertinent pre-edge transitions shown. Orbitals are plotted at an iso value of 0.03.

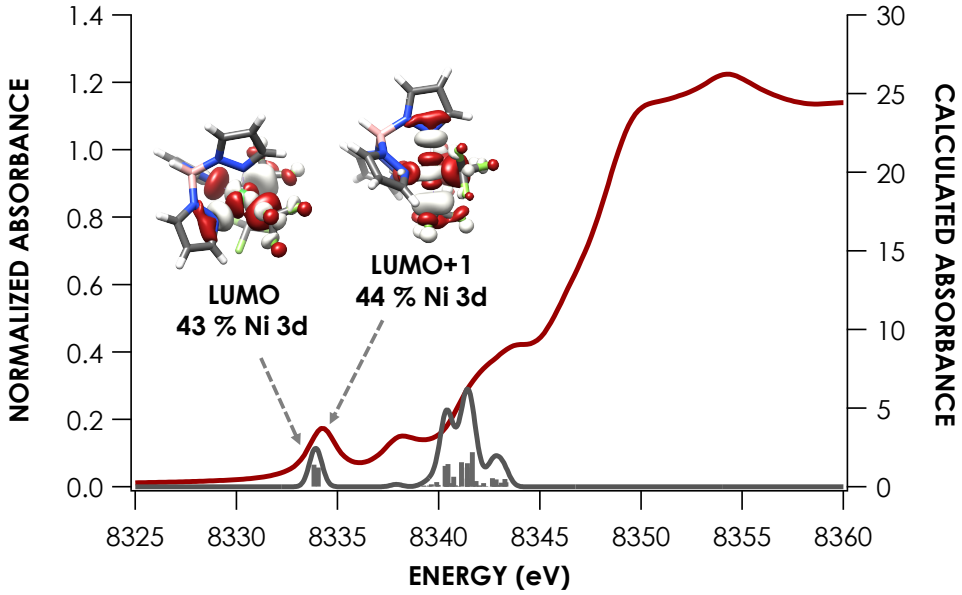

Fig. S9. Comparative experimental and calculated Ni K-edge spectrum of **15** with orbital plots for pertinent pre-edge transitions shown. Orbitals are plotted at an iso value of 0.03.

IPFY Desaturation Standard Procedure

The Ni species studied herein present a technical complication – sample saturation. XAS saturation manifests itself as diminished intensity in the most intense peaks in the spectrum and, for the purposes of bulk solid collection at a 90º angle between incident and emitted beam, is largely dependent on total metal concentration in the bulk material. The theory of saturation can be discussed starting with the integrated Beer-Lambert law yielding the measured intensity for a FY experiment given by equation **1**.[47]

$$PFY(E) = I_0(E) \int_0^t e^{-\mu_t(E)z/sin\alpha}\, \omega_x(E)\mu_x(E)e^{-\mu_t(E_f)z/sin\beta}\, dz \quad (1)$$

Where E is the incident photon energy, μ_t(E) is the total photon absorption cross section, μ_x(E) is the photon absorption cross-section of the element of interest, μ_t(E_f) is the total absorption cross-section for emitted photons, and z, α, and β are geometric parameters relevant to incident and emitted beam. I_o(E) accounts for external factors including incident intensity and detector efficiency. This equation can be simplified to

$$PFY(E) = I_0(E) \frac{\mu_x(E)sin\alpha}{\mu_t(E) + \mu_t(E_f)tan\alpha} \quad (2)$$

by assuming that I_o, μ_t(E) and ω_x are constant as well as a 90º angle between incident and emitted beam. In the present scenario μ_t is described as the sum of μ_x(E) and μ_b(E); this requires that μ_x(E) <<< μ_b(E) +$\mu_t(E_f)tan\alpha$, for the measured intensity to be proportional to μ_x(E). One can intuit that in simple standards such as $[NiCl_4]^{2-}$ the metal concentration will be extremely high, resulting in μ_x(E) > μ_b(E) +$\mu_t(E_f)tan\alpha$ and consequently saturation will occur. However, saturation effects can be present in samples containing as low as 1% metal concentration. While this saturation could theoretically be avoided by employing larger counterions, or measuring dilute samples, this is not always a viable option in practice. A more practical way to deal with this issue in solid compounds is by performing a saturation correction using the inverse partial fluorescence yield (IPFY) of an observer element, such as fluorine or oxygen. In order to obtain the equation for inverse partial fluorescent yield we simply replace μ_x(E) with μ_o(E) which gives

$$IPFY(E) = I_0(E)\frac{\mu_o(E)sin\alpha}{\mu_t(E)+ \mu_t(E_o)tan\alpha} \quad (3)$$

Thus, if $\mu_t(E_f)$ is equal to $\mu_t(E_o)$, $\mu_x(E_f)$ is proportional to PFY/IPFY. This correction can be used even in instances when the IPFY signal is extremely low, giving a useful means to correct saturation in species containing even small amounts of observer elements. A full example of a saturation correction is given in below. After the raw Ni $3d \rightarrow 2p$ fluorescence channel (Fig. S10a, grey) is divided by the raw F IPFY channel (Fig, S10a, red). This yields a corrected spectrum (Fig. S10b, red) but introduces additional background from the F IPFY and deviation in raw absorbance from the as collected Ni PFY (Fig. S10b, grey). In order to remove this additional background the resulting spectrum is multiplied by the background of the F IPFY(Fig. S10a, black). The raw saturated (grey) and corrected (red) spectra are shown in Fig. S10c. Note the increase in intensity over the L_3 and L_2 mainlines. Finally, the spectra are normalized, and background corrected as described in the Materials and Methods section. A comparison of the normalized saturated and saturation corrected data for **3** is given in Fig. S10d.

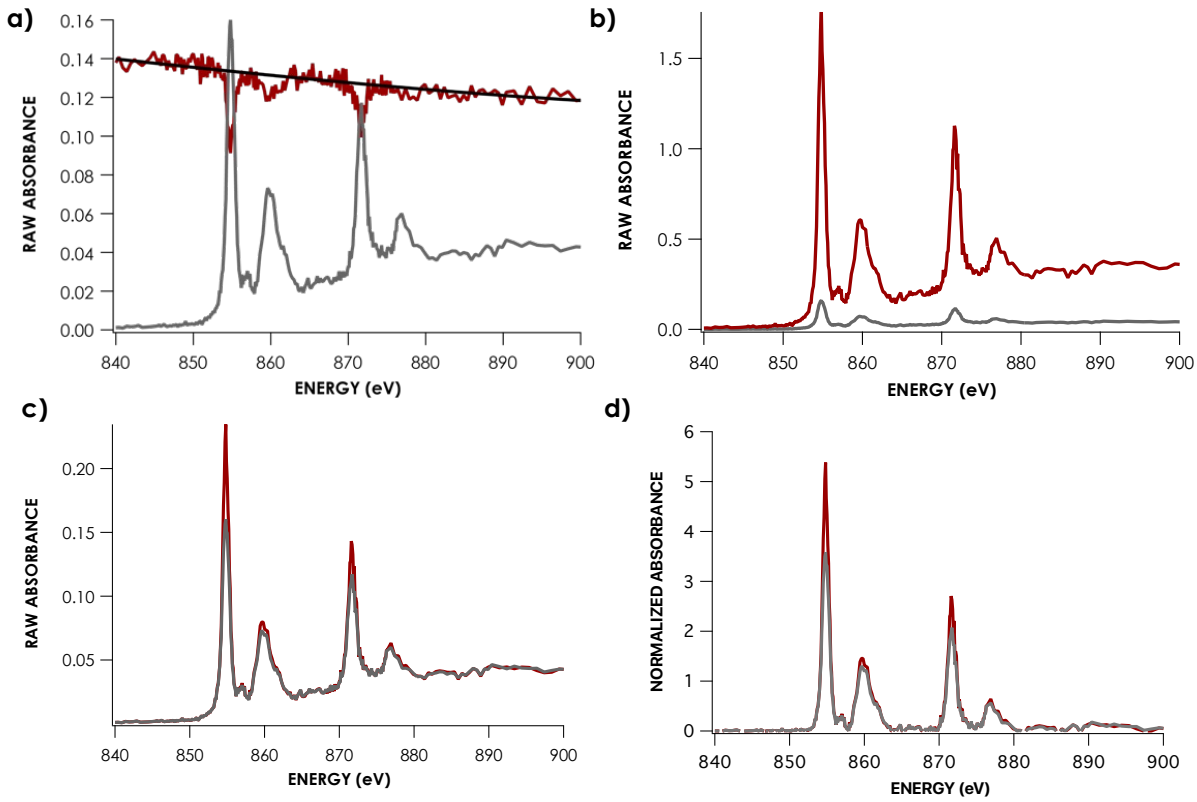

Fig. S10. (a) Raw Ni 3*d* → 2*p* fluorescence (grey), raw F inverse partial fluorescence yield (IPFY) (red) and background for F IPFY (black) for **3** (b) Saturated raw (grey) and corrected raw (red) Ni 3*d* → 2*p* fluorescence prior to F IPFY background correction. (c) Saturated raw (grey) and unsaturated and corrected raw Ni 3*d* → 2*p* fluorescence (red) after F IPFY background correction. (d) Saturated (grey) and corrected (red) Ni 3*d* → 2*p* fluorescence after normalization and background subtraction.

Experimental $L_{2,3}$-Edge XAS and IPFY Desaturation

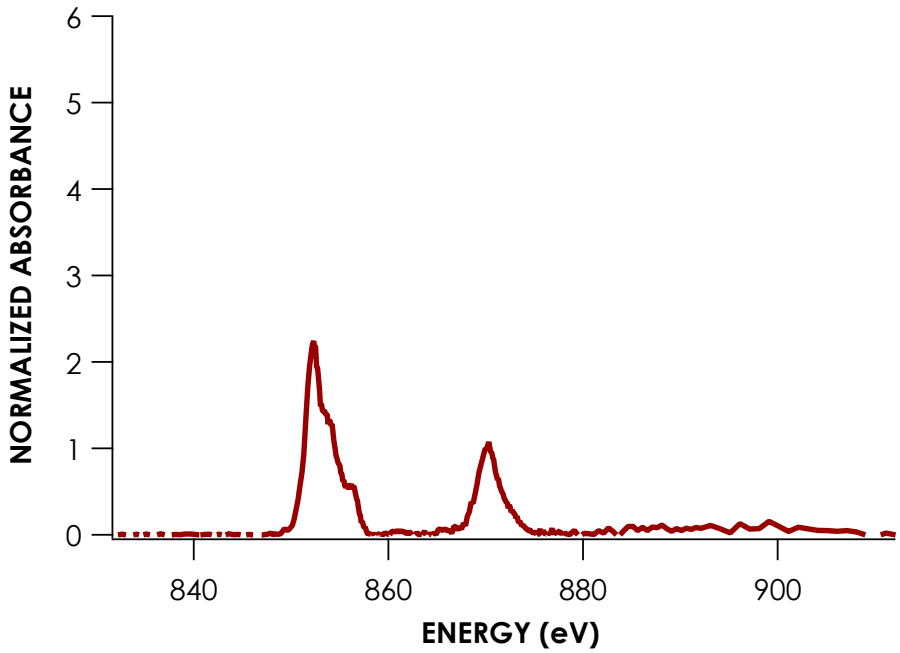

Fig. S11. Saturated normalized and background subtracted $L_{2,3}$-edge for species **1**.

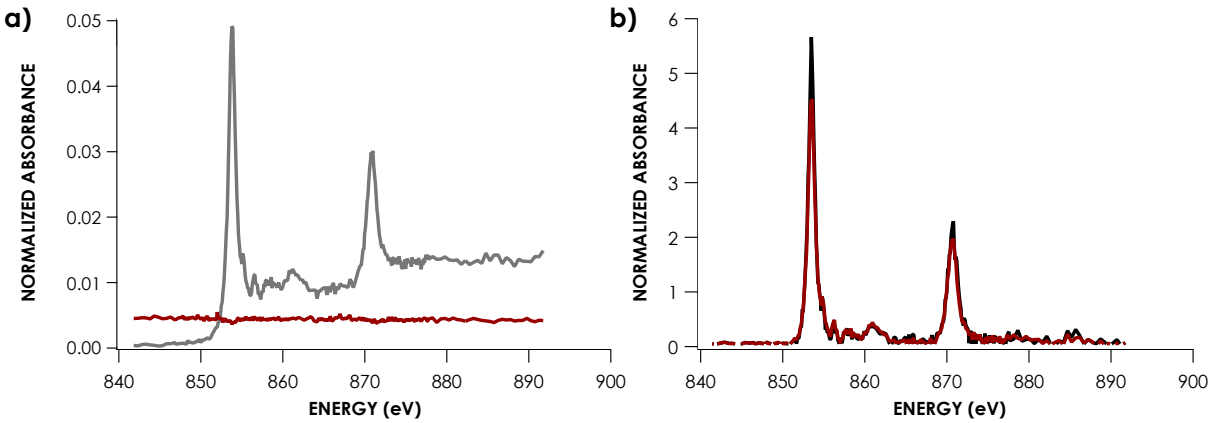

Fig. S12. a) Raw Ni $3d \rightarrow 2p$ fluorescence (grey) Raw F inverse partial fluorescence yield (IPFY) (red). (b) Saturated (red) and saturation-corrected (black) normalized and background subtracted $L_{2,3}$-edge for species **2**.

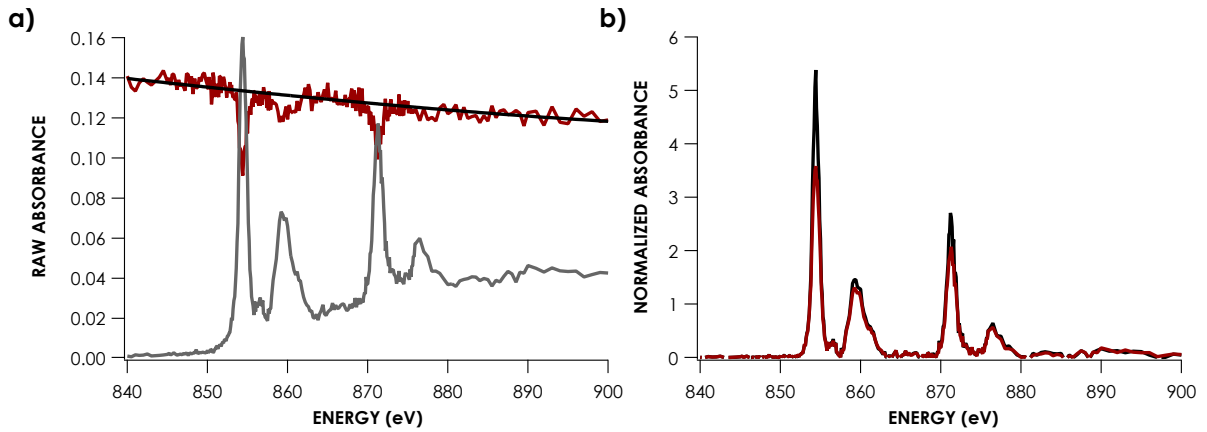

Fig. S13. a) Raw Ni $3d \rightarrow 2p$ fluorescence (grey) Raw F inverse partial fluorescence yield (IPFY) (red). and background for F IPFY (b) Saturated (red) and saturation-corrected (black) normalized and background subtracted $L_{2,3}$-edge for species **3**.

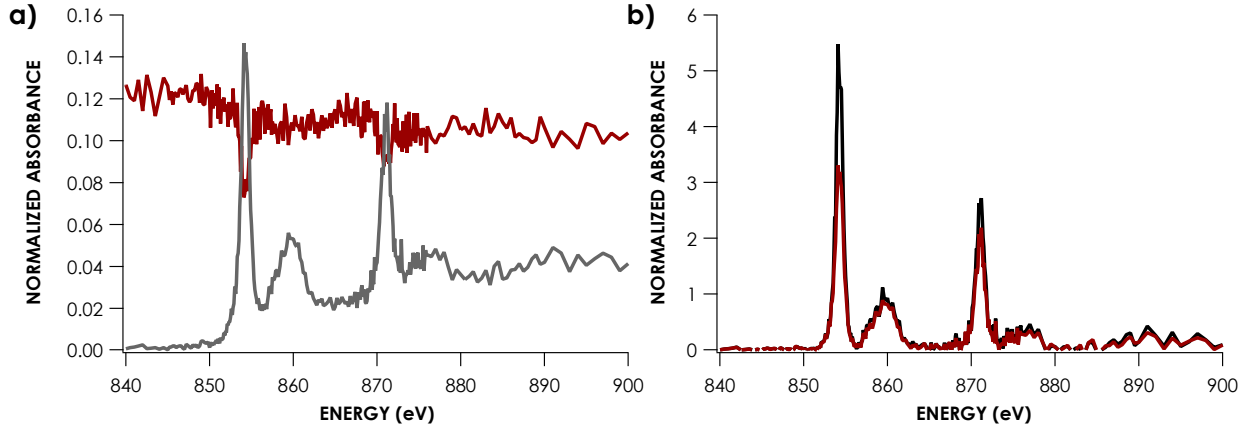

Fig. S14. a) Raw Ni $3d \rightarrow 2p$ fluorescence (grey) Raw F inverse partial fluorescence yield (IPFY) (red). (b) Saturated (red) and saturation-corrected (black) normalized and background subtracted $L_{2,3}$-edge for species **4**.

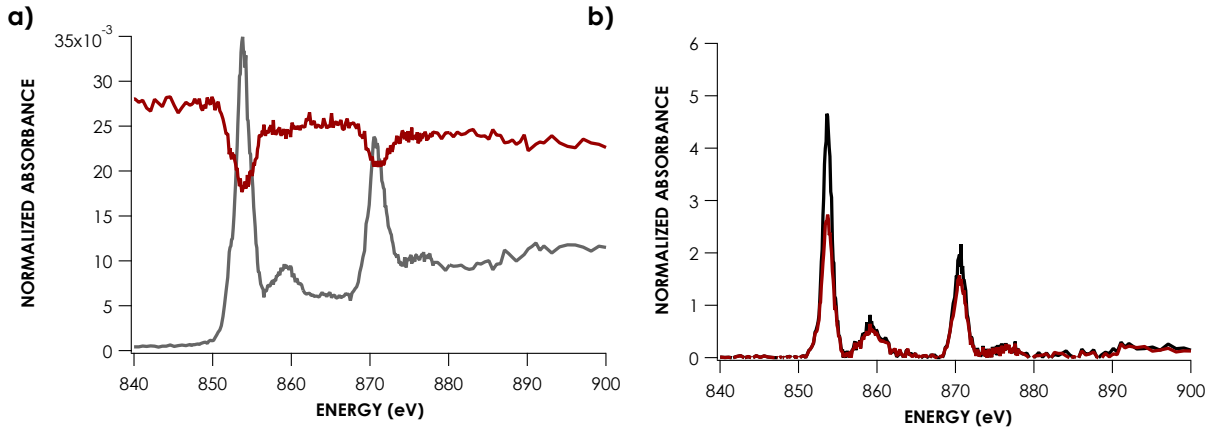

Fig. S15. a) Raw Ni $3d \rightarrow 2p$ fluorescence (grey) Raw F inverse partial fluorescence yield (IPFY) (red). (b) Saturated (red) and saturation-corrected (black) normalized and background subtracted $L_{2,3}$-edge for species **5**.

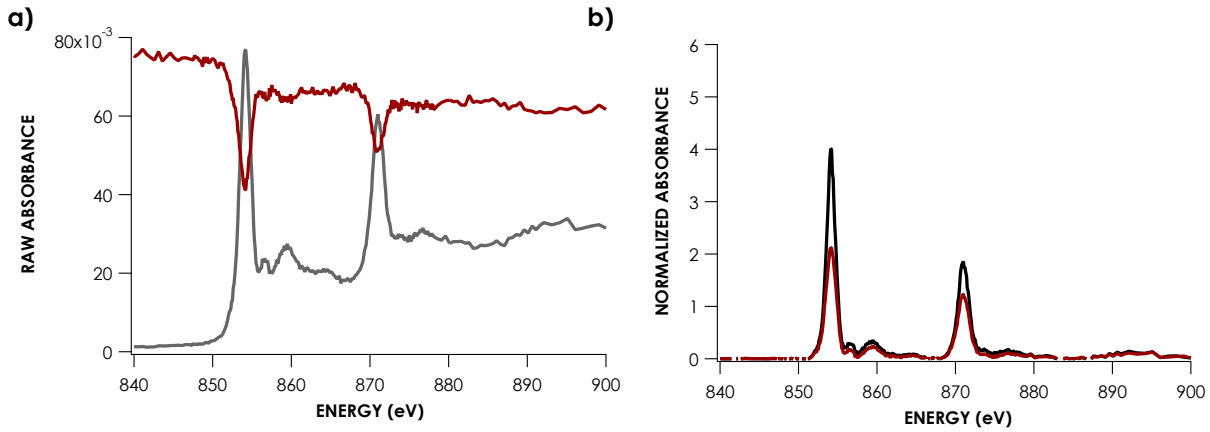

Fig. S16. a) Raw Ni $3d \rightarrow 2p$ fluorescence (grey) Raw F inverse partial fluorescence yield (IPFY) (red). (b) Saturated (red) and saturation-corrected (black) normalized and background subtracted $L_{2,3}$-edge for species **6**.

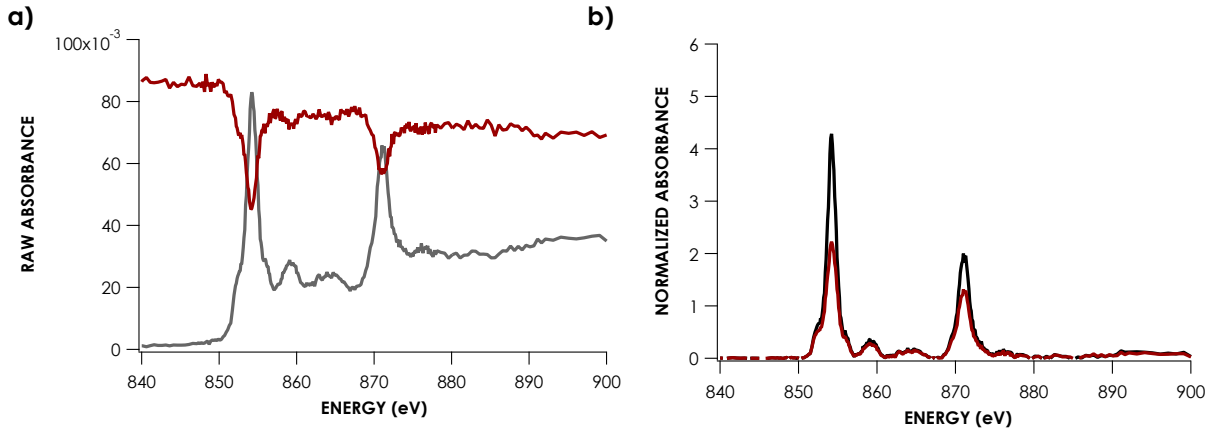

Fig. S17. a) Raw Ni $3d \rightarrow 2p$ fluorescence (grey) Raw F inverse partial fluorescence yield (IPFY) (red). (b) Saturated (red) and saturation-corrected (black) normalized and background subtracted $L_{2,3}$-edge for species **7**.

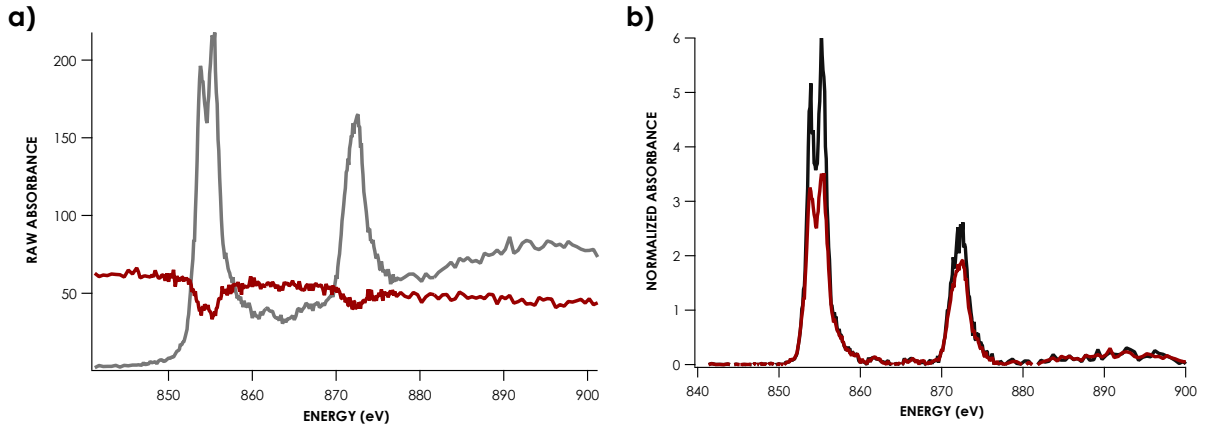

Fig. S18. a) Raw Ni $3d \rightarrow 2p$ fluorescence (grey), raw F inverse partial fluorescence yield (IPFY) (red). (b) Saturated (red) and saturation-corrected (black) normalized and background subtracted $L_{2,3}$-edge for species **8**.

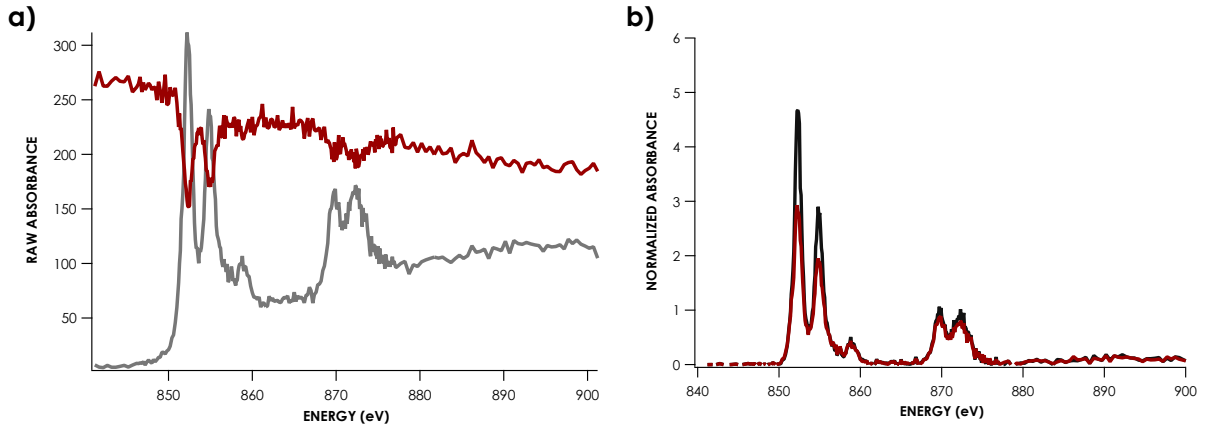

Fig. S19. a) Raw Ni $3d \rightarrow 2p$ fluorescence (grey), raw F inverse partial fluorescence yield (IPFY) (red). (b) Saturated (red) and saturation-corrected (black) normalized and background subtracted $L_{2,3}$-edge for species **9**.

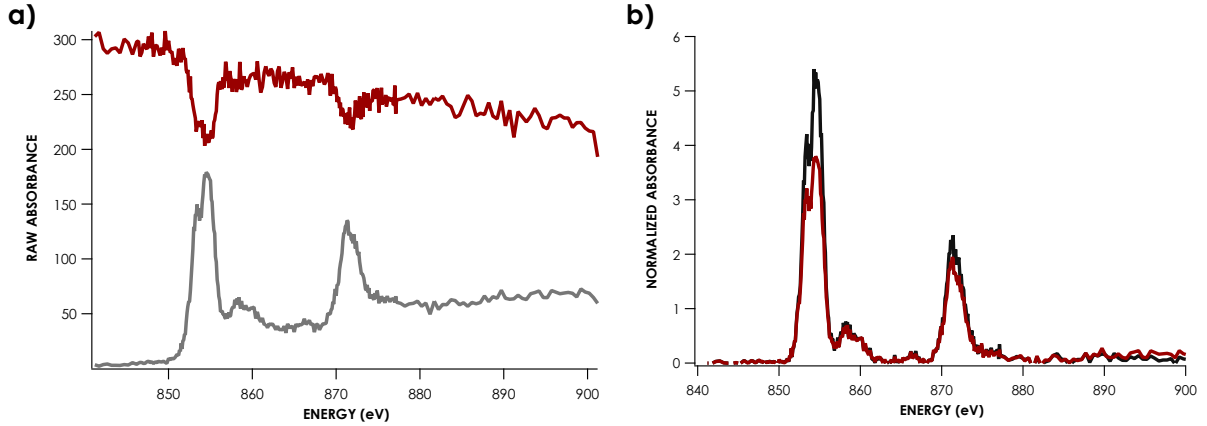

Fig. S20. a) Raw Ni $3d \rightarrow 2p$ fluorescence (grey), raw F inverse partial fluorescence yield (IPFY) (red). (b) Saturated (red) and saturation-corrected (black) normalized and background subtracted $L_{2,3}$-edge for species **10**.

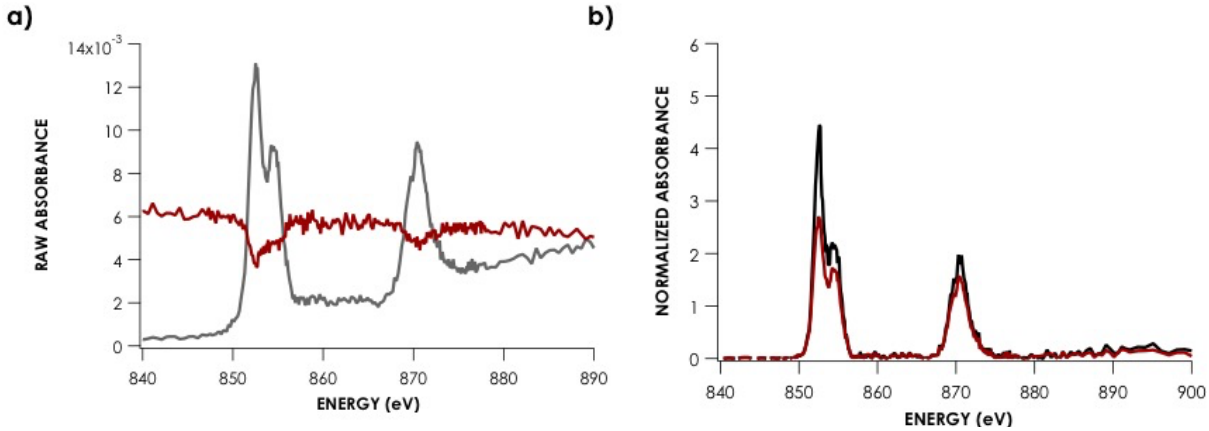

Fig. S21. a) Raw Ni $3d \rightarrow 2p$ fluorescence (grey), raw F inverse partial fluorescence yield (IPFY) (red). (b) Saturated (red) and saturation-corrected (black) normalized and background subtracted $L_{2,3}$-edge for species **11**.

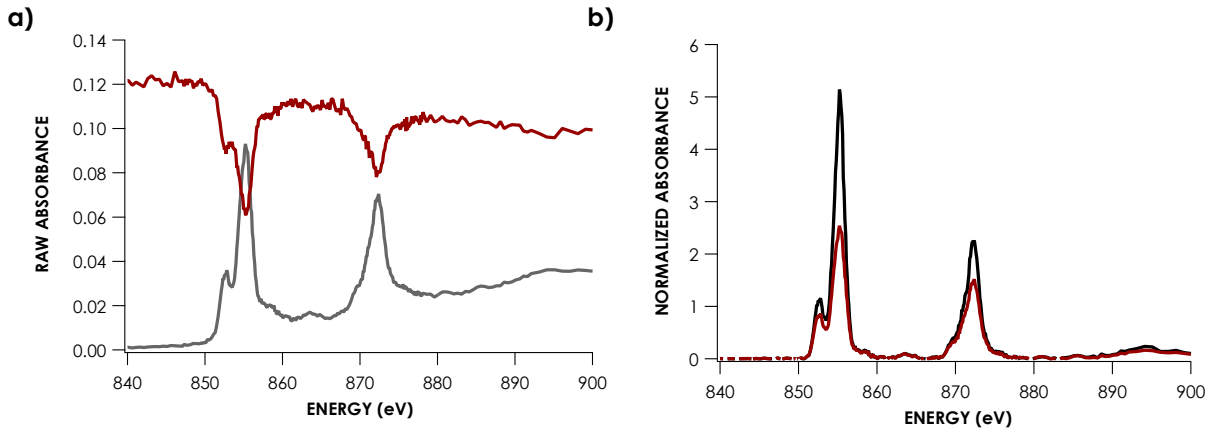

Fig. S22. a) Raw Ni $3d \rightarrow 2p$ fluorescence (grey) Raw F inverse partial fluorescence yield (IPFY) (red). (b) Saturated (red) and saturation-corrected (black) normalized and background subtracted $L_{2,3}$-edge for species **12**.

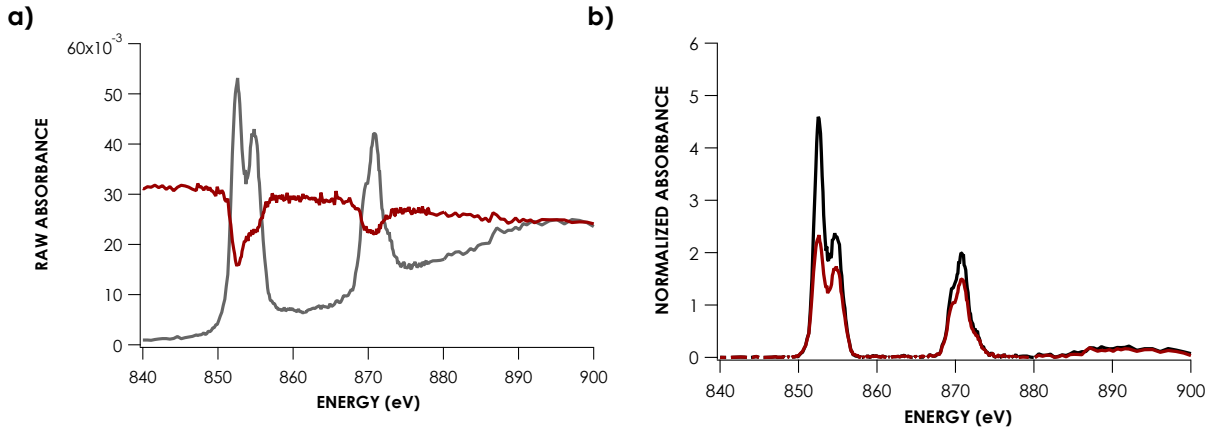

Fig. S23. a) Raw Ni $3d \rightarrow 2p$ fluorescence (grey) Raw F inverse partial fluorescence yield (IPFY) (red). (b) Saturated (red) and saturation-corrected (black) normalized and background subtracted $L_{2,3}$-edge for species **13**.

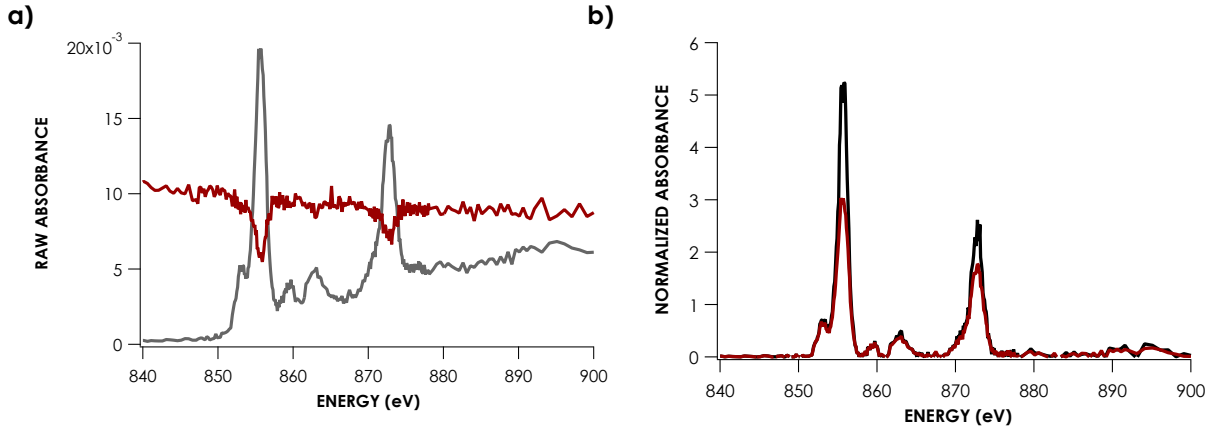

Fig. S24. a) Raw Ni $3d \rightarrow 2p$ fluorescence (grey) Raw F inverse partial fluorescence yield (IPFY) (red). (b) Saturated (red) and saturation-corrected (black) normalized and background subtracted $L_{2,3}$-edge for species **14**.

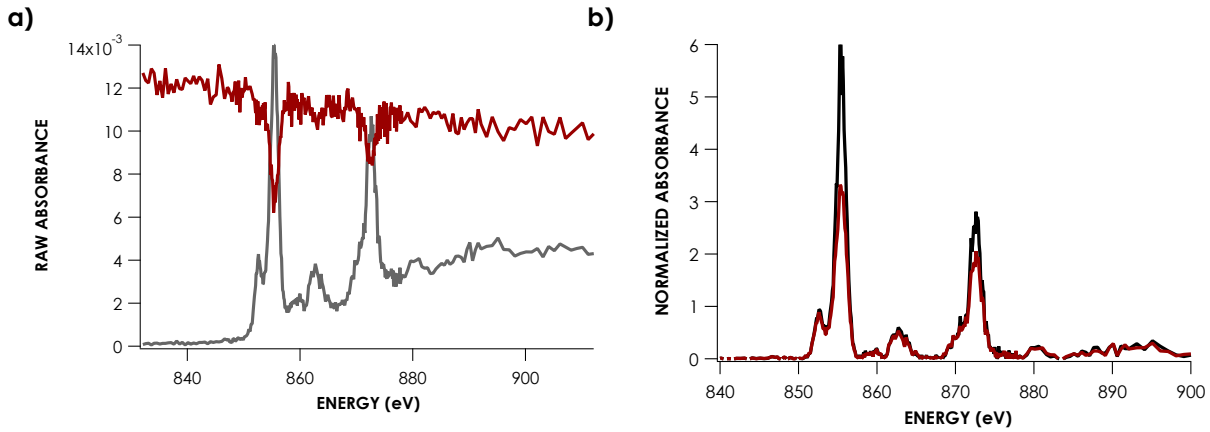

Fig. S25. a) Raw Ni 3*d* → 2*p* fluorescence (grey) Raw F inverse partial fluorescence yield (IPFY) (red). (b) Saturated (red) and saturation-corrected (black) normalized and background subtracted $L_{2,3}$-edge for species **15**.

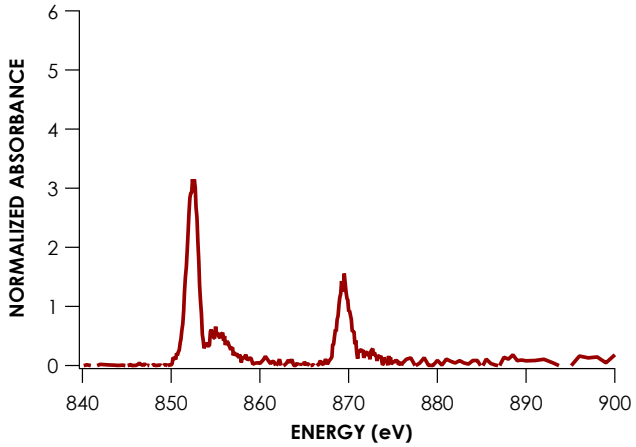

Fig. S26. Saturated normalized and background subtracted $L_{2,3}$-edge for species **16**.

Molecular Orbital Plots for 17-21

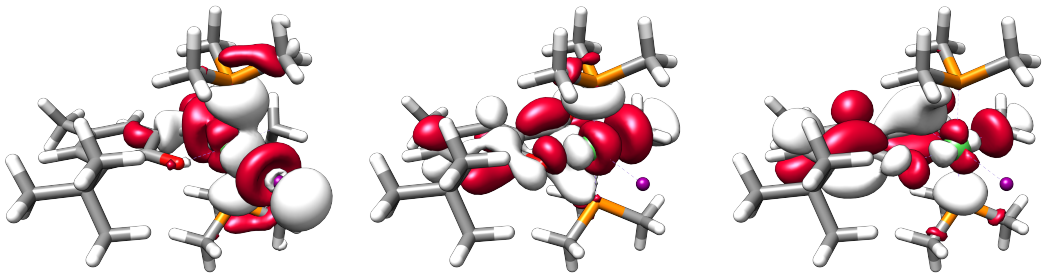

Fig. S27. Ni 3*d*-containing frontier unoccupied molecular orbitals of **17** calculated at the B3LYP/CP(PPP) (on Ni)/SARC-ZORA-TZVPP (on I)/def2-TZVP(-f) level of theory. Orbitals are plotted at an isovalue of 0.03 au.

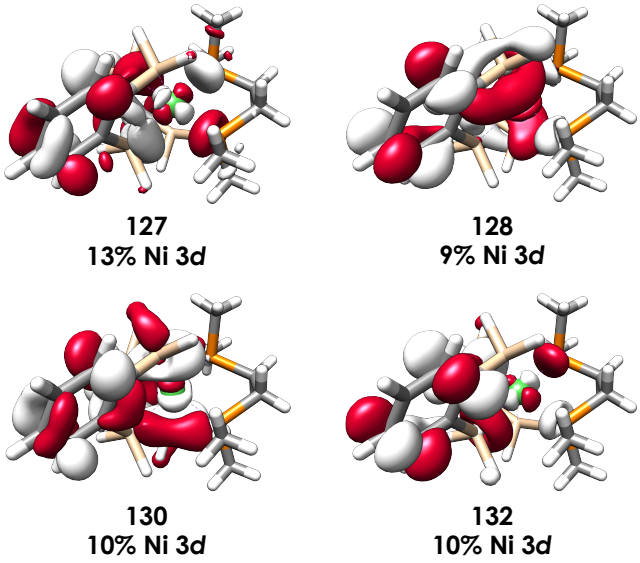

Fig. S28. Ni 3*d*-containing frontier unoccupied molecular orbitals of **18** calculated at the B3LYP/CP(PPP) (on Ni)/def2-TZVP(-f) level of theory. Orbitals are plotted at an isovalue of 0.03 au.

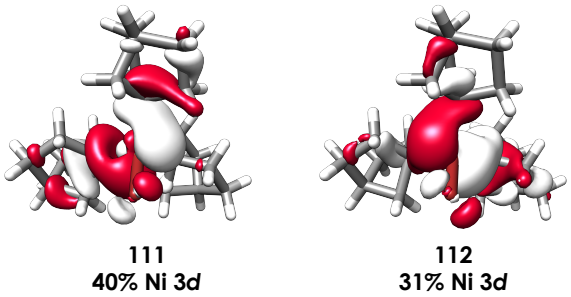

Fig. S29. Ni 3*d*-containing frontier unoccupied molecular orbitals of **19** calculated at the B3LYP/CP(PPP) (on Ni)/def2-TZVP(-f) level of theory. Orbitals are plotted at an isovalue of 0.03 au.

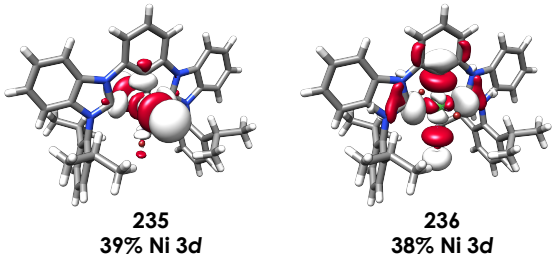

Fig. S30. Ni 3*d*-containing frontier unoccupied molecular orbitals of **20** calculated at the B3LYP/CP(PPP) (on Ni)/def2-TZVP(-f) level of theory. Orbitals are plotted at an isovalue of 0.03 au.

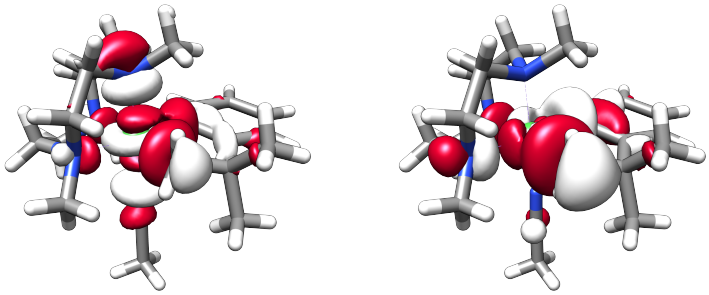

Fig. S31. Ni 3*d*-containing frontier unoccupied molecular orbitals of **21** calculated at the B3LYP/CP(PPP) (on Ni)/def2-TZVP(-f) level of theory. Orbitals are plotted at an isovalue of 0.03 au.

Plots of Calculated Ni K Pre-edge Energy and Calculated 1*s* Binding Energy vs Formal Oxidation State for $Ni(mft)_2^{2-/1-/0}$ Series

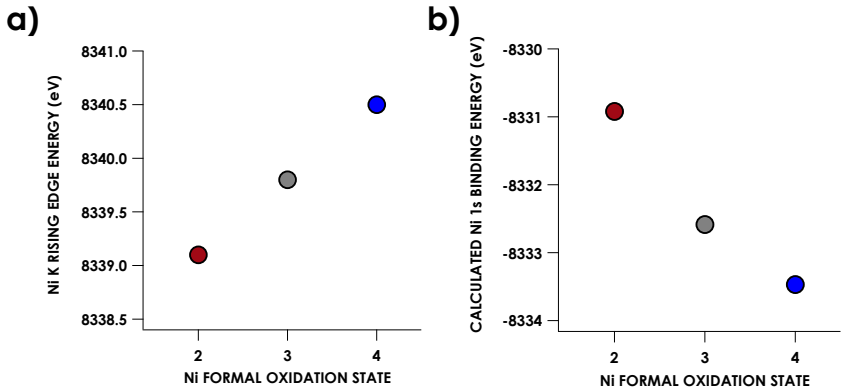

Fig. S32. Plots of (a) Ni K rising edge energy and (b) calculated Ni 1s binding energy vs Ni formal oxidation state for Ni complexes bearing redox-non-innocent mft (mft = maleotrifluoromethyldithiolate) ligands $Ni(mft)_2^{2-/1-/0}$. Data obtained from Ref [48].

Plot of Cu *d*-Vacancy vs. Calculated 1*s* Binding Energy

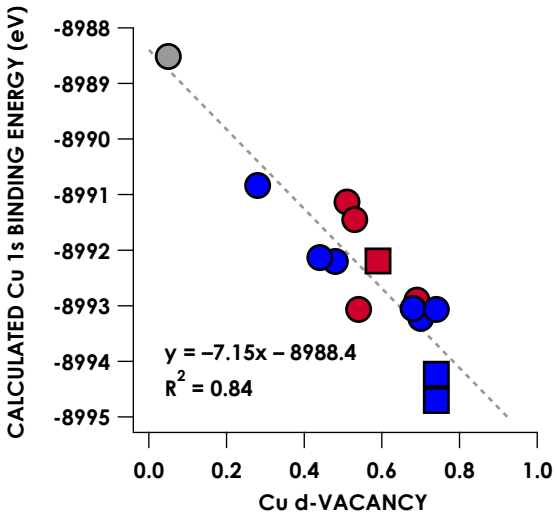

Fig. S33. Plot of Cu *d*-vacancies for Ref. compounds **1–17** (circles) and Ref. compounds "$[Cu^{II}(NHC_2)]^{2+}$", "$[Cu^{III}(NHC_2)]^{3+}$", "$[Cu^{III}(NHC_4)]^{3+}$" (squares) vs Cu 1*s* binding energies calculated at the B3LYP/ZORA-def2-TZVP(-f)/CP(PPP) on Cu level as described in Ref . The *d*-vacancies for the Ref. 49 compounds were obtained experimentally, whereas the values for the Ref. 50 compounds were estimated via DFT calculations using input coordinates from Ref. and the linear relationship in Ref. 49 Fig. 5. Formally Cu^{III} compounds are blue, formally Cu^{II} are red, and the formally Cu^{I} compound is gray.

NEVPT2 Orbitals and State Configurations

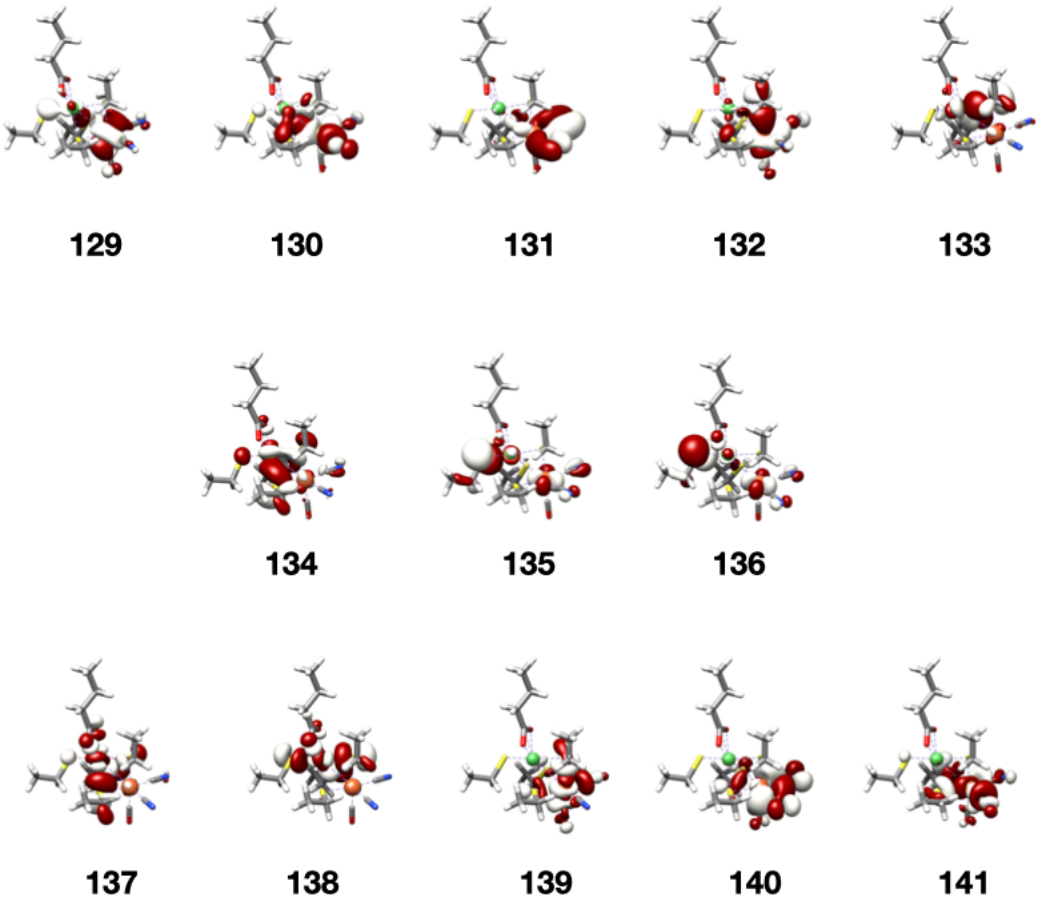

Fig. S34. The 13 molecular orbitals used in the active-space for the FIC-NEVPT2 calculations of [NiFe]H_2ase^{Hex}.

Table S1. Lowest energy triplet state configuration and FIC-NEVPT2 calculated state energy.
FIC-NEVPT2 Energy = -5282.850234 a.u.
0.60192 [199926]: 2222221100000
0.09621 [199808]: 2222201120000
0.06089 [199159]: 2222021102000
0.05524 [199584]: 2222111111000
0.02446 [198673]: 2222001122000
0.00834 [173979]: 2121221100101
0.00668 [196123]: 2220221100200
0.00534 [199905]: 2222212100000
0.00480 [150633]: 2022221100002
0.00478 [199920]: 2222220110000
0.00407 [198447]: 2221221100100
0.00293 [127050]: 1222221100001
0.00290 [199893]: 2222211020000

Table S2. Lowest energy singlet state configuration and FIC-NEVPT2 calculated state energy.
FIC-NEVPT2 Energy = -5282.569704 a.u.
0.31228 [201642]: 2222222000000
0.28803 [201635]: 2222220200000
0.05066 [201531]: 2222202020000
0.04599 [201466]: 2222200220000

0.03170 [200861]: 2222022002000
0.02941 [200796]: 2222020202000
0.02895 [201292]: 2222112011000
0.02654 [201227]: 2222110211000
0.01288 [200400]: 2222002022000
0.01175 [200229]: 2222000222000
0.00943 [201607]: 2222211110000
0.00419 [175253]: 2121222000101
0.00409 [175188]: 2121220200101
0.00405 [201368]: 2222121101000
0.00381 [201608]: 2222211200000
0.00361 [200079]: 2221221100100
0.00342 [197769]: 2220222000200
0.00341 [201640]: 2222221010000
0.00325 [197704]: 2220220200200

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