Supplementary Material

Exploring the limits of redox non-innocence: pseudo square planar [{κ^4-$Me_2C(CH_2N{=}CHpy)_2$}Ni]^n (n = 2+, 1+, 0, -1, -2) favor Ni(II)

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I. UV-vis spectra of $[\{\kappa^4\text{-}Me_2C(CH_2N{=}CHpy)_2\}Ni]^n$ (n = 2+, 1+, 0, -1)

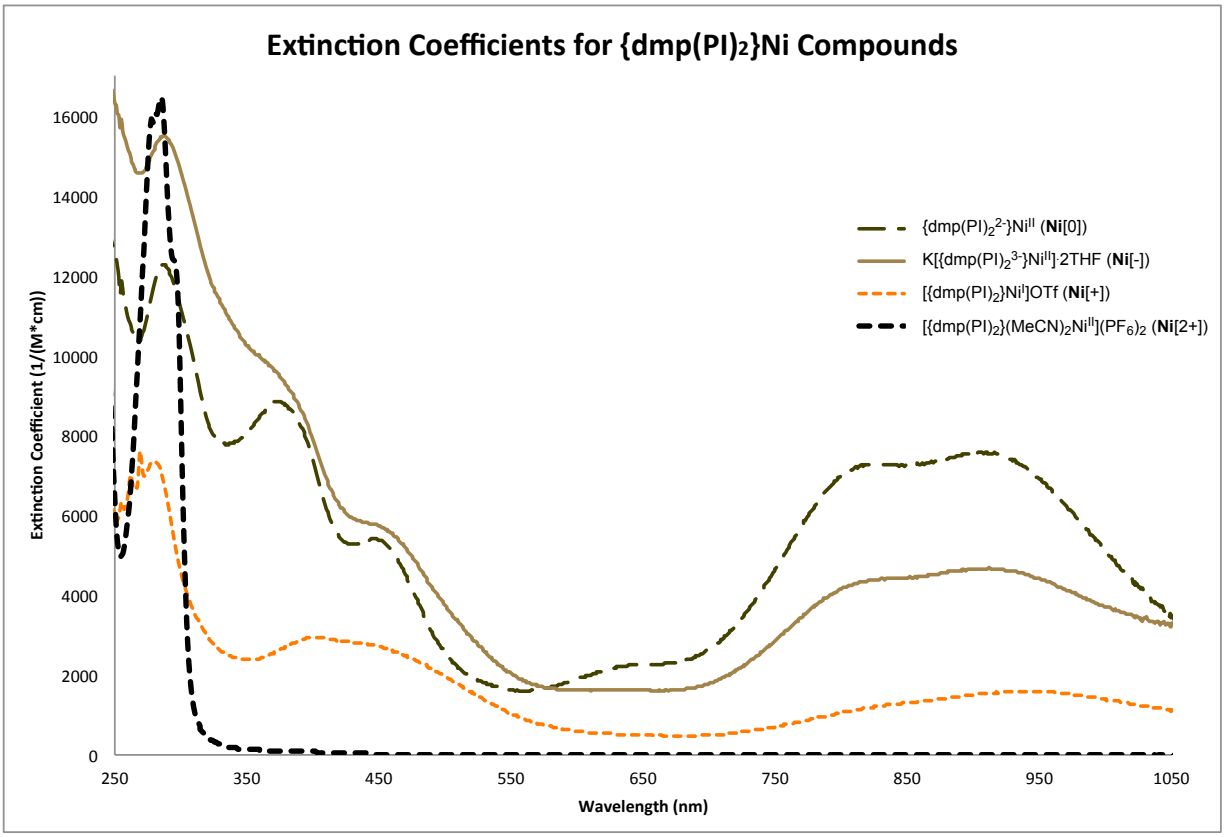


Fig. S1. UV-vis spectra of $\{dmp(PI)_2^{2-}\}Ni^{II}$ (**Ni**[0]), $[\{dmp(PI)_2^{3-}\}Ni^{II}]^-(K(THF)_2)^+$ (**Ni**[-]), and $[\{dmp(PI)_2\}Ni^{I}]^+$ (**Ni**[+]) taken in THF, and $[\{dmp(PI)_2\}(MeCN)_2\,Ni^{II}]^{2+}(PF_6)_2$ (**Ni**[2+]) taken in acetonitrile.

II. BS [2,1] Calculation of [{dmp(PI)$_2^-$}Ni^{II}]$^+$ (Ni[+])

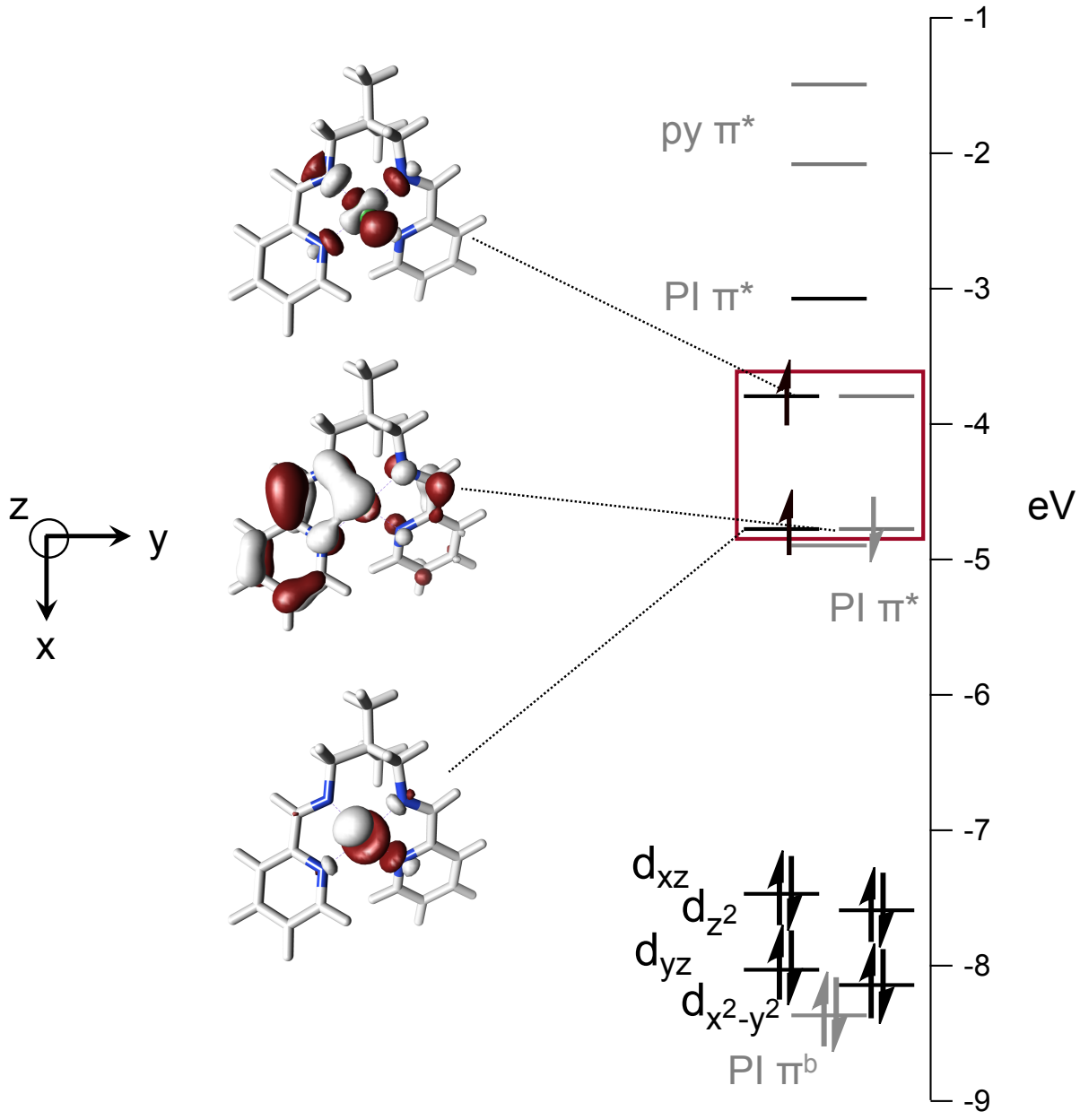


Fig. S2. QRO transformation of the BS[2,1] solution for [{dmp(PI)$_2^-$}Ni^{II}]$^+$ **Ni**[+]. The magnetic, or unrestricted corresponding orbitals (UCOs) are boxed in red (S = 0.36) and positioned at energies from their respective QROs. This solution has a single point energy that is ~5000 cm^{-1} higher than the UKS calculation supporting a [{dmp}(PI)$_2$}Ni^{I}]$^+$ formulation (see Fig. 6).

III. TD-DFT of [{dmp(PI)$_2$}Ni]^n (n = 1+, 0, -1)

A. UV-vis of [{dmp(PI)$_2$}Ni]^n (n = 1+, 0, -1)

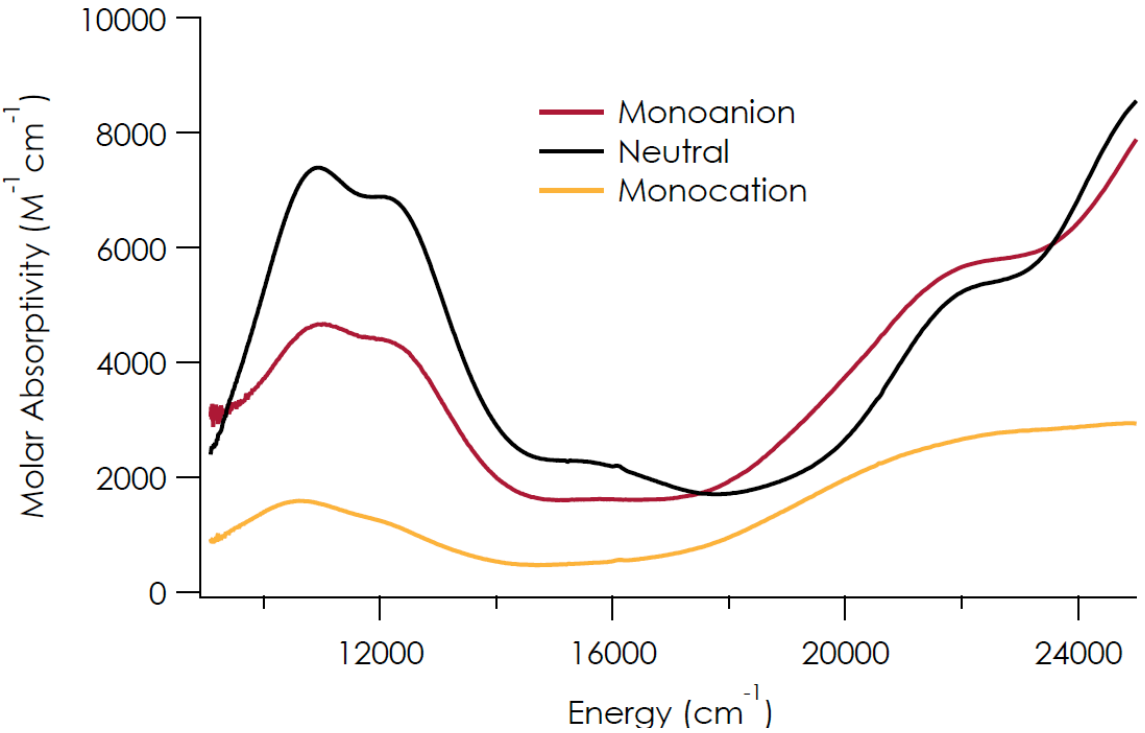


Fig. S3. Uv-vis spectra of [{dmp(PI)$_2$}Ni]^n (n = 1+, **Ni**[+]; 0, **Ni**[0]; -1, **Ni**[-]) taken in THF.

B. TD-DFT of [{dmp(PI)$_2$}Ni]^n (n = 1+, 0, -1)

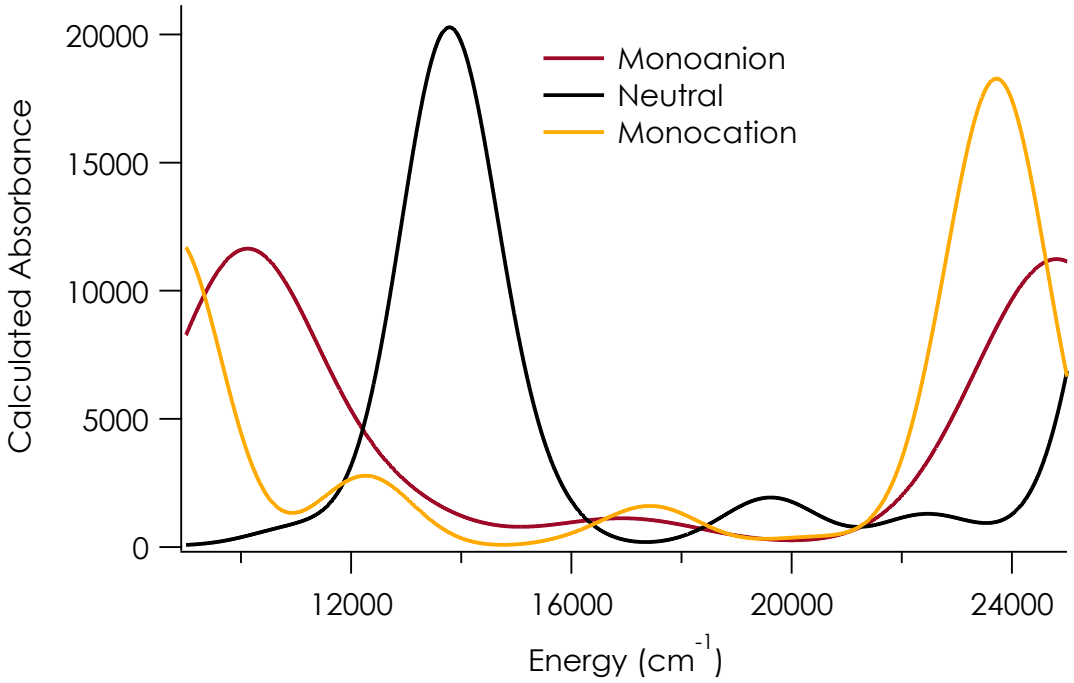


Fig. S4. TD-DFT calculations of UV-vis spectra of [{dmp(PI)$_2$}Ni]^n (n = 1+, **Ni**[+]; 0, **Ni**[0]; -1, **Ni**[-]) derived from QRO transformations of the UKS solutions. The Calculated Absorbances are relative, and do not reflect absolute molar absorptivities.

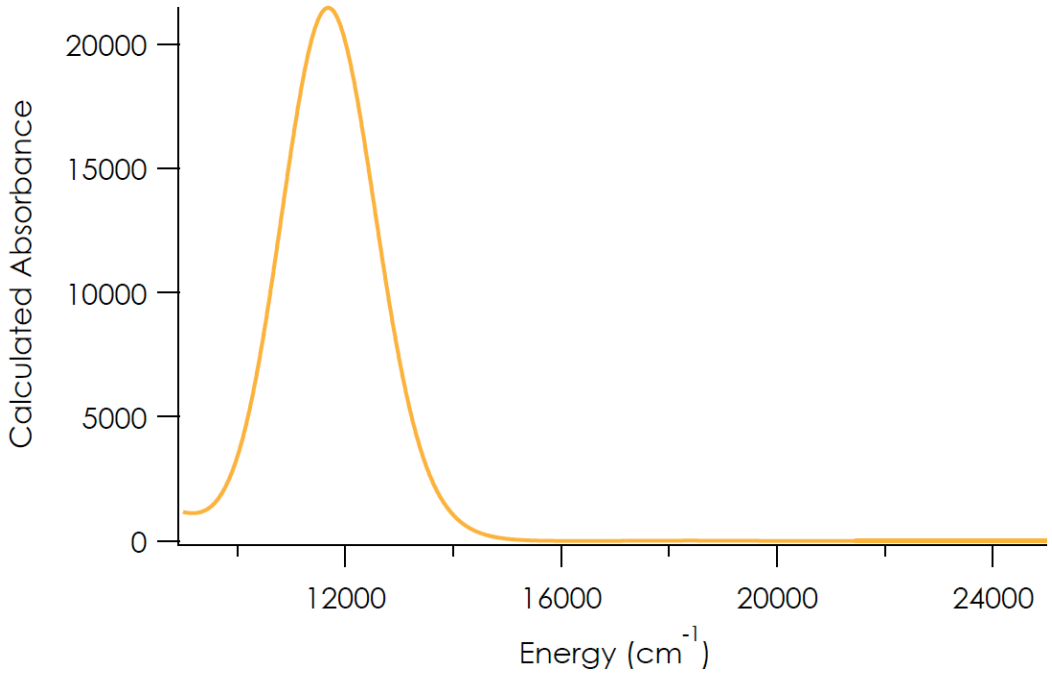


Fig. S5. Spin-orbit corrected SORCI electronic absorption spectrum for **Ni**[+]. The spectrum has been produced with a Gaussian FWHM of 2000 cm^{-1}. The Calculated Absorbance does not reflect the absolute molar absorptivity. Due to the limited number of roots, i.e., excitations, only a limited number of absorbances are indicated. This is why the calculated spectrum is devoid of absorptions at higher energy.

IV. SORCI Calculation of $[\{dmp(PI)_2\}Ni]^+$ (Ni[+])

A SORCI calculation was performed on $[\{dmp(PI)_2\}Ni]^+$ (**Ni**[+]) once the QRO transformation of the UKS solution shown in Fig. 6 did not produce EPR parameters near those of experiment. It was suspected that the omission of critical ground state configurations were responsible hence a multi-reference (MR) calculation was conducted. In support, the modest fit of the TD-DFT to the experimental UV-vis spectrum is likely to be subject to the same difficulties.

Methods. Spectroscopy-oriented configuration interaction (SORCI) calculations were performed using ORCA 2.9.0 as described previously[1] to calculate excitation energies and the g-matrix for **Ni[+]**.[2] These calculations were performed on the BP86/def2-TZVP-ZORA calculated geometry assuming a doublet ground state. Calculations were performed over a CAS(13,11) complete active space, which includes the Ni ligand field as well as proximal pyridine-imine π and π* as well as pyridine π* molecular orbitals. The segmented all-electron relativistically contracted (SARC) def2-TZVP(-f) basis set was used for all atoms.[3] As described elsewhere, individual selection was used in order to ease the computational burden.[1] The size of the first-order interacting space was reduced with a threshold $T_{sel} = 10^{-6}$ Eh. A further approximation involves reduction of the reference space through another selection – all initial references that contribute less than a second threshold ($T_{pre} = 10^{-5}$) to the zeroth-order states are rejected from

the reference space. The initial orbitals from the first step of the SORCI procedure were taken from QROs[4] generated via standard B3LYP/def2-TZVP-ZORA calculations described herein. Ten roots were calculated to generate an electronic absorption spectrum.

The SORCI calculated g-values were: g_1: 2.032, g_2: 2.044, and g_3: 2.181. It is suspected that the low offset from the experimental values (despite the relative accuracy of g_1, g_2 and g_3) is due to the limited number of roots, i.e., excitations, used in this rather lengthy calculation.

The SORCI-calculated ground state consists of one major contributing configuration that places the unpaired electron in an averaged atomic natural orbital (AANO) that is principally of d_{xy} character (printed below). The singly occupied AANOs characterizing two other contributing configurations are also printed below.

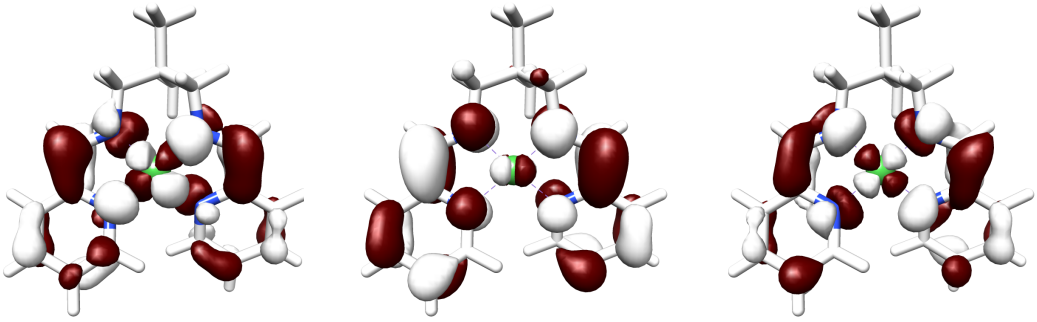
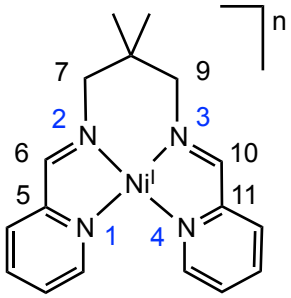


Figure 3. Singly-occupied AANOs in the three major configurations contributing to the electronic ground state of **Ni[+]**. Orbitals are printed at an isolevel of 0.03.

1) Neese, F. *J. Chem. Phys.* **2003**, *119*, 9428-9443.
2) Neese, F. *Magn. Reson. Chem.* **2004**, *42*, S187-S198.
3) Pantazis, D. A.; Chen, X.-Y.; Landis, C. R.; Neese, F., *J. Chem. Theor. Comput.* **2008**, *4*, 908-919.
4) Neese, F., *J. Am. Chem. Soc.* **2006**, *128*, 10213-10222.

V. Comparative Metrics (DFT, X-ray) of [{dmp(PI)$_2$}Ni]^n (n = 1+, 0, -1, -2)

Table S1. Selected bond distances (Å) for [{dmp(PI)$_2$}Ni]^n (n = 1+, **Ni**[+]; 0, **Ni**[0]; -1, **Ni**[-]; -2, **Ni**[2-]) from X-ray crystallography and DFT.[a]



X-Y	**Ni**[2-] **DFT**	**Ni**[-] poly **XRD**	**Ni**[-] crypt **XRD**[b]	**Ni**[-] **DFT**	**Ni**[0] **XRD**	**Ni**[0] **DFT**	**Ni**[+] **DFT**
C5-C6	1.382	1.389	1.372	1.396	1.411	1.415	1.436
C10-C11	1.381	1.377	1.374	1.394	1.410	1.412	1.437
C5-N1	1.442	1.411	1.431	1.420	1.378	1.398	1.379
C6-N2	1.384	1.352	1.383	1.359	1.319	1.332	1.311
C7-N2	1.451	1.456	1.452	1.452	1.460	1.456	1.471
C9-N3	1.446	1.462	1.444	1.457	1.467	1.468	1.458
C10-N3	1.388	1.367	1.365	1.363	1.327	1.337	1.308
C11-N4	1.441	1.418	1.403	1.421	1.382	1.399	1.379
Ni-N1	1.935	1.920	1.910	1.926	1.909	1.921	1.943
Ni-N2	1.915	1.870	1.877	1.891	1.867	1.881	1.907
Ni-N3	1.914	1.873	1.873	1.895	1.875	1.888	1.897
Ni-N4	1.930	1.900	1.918	1.921	1.904	1.916	1.950
Chelate twist (°)	37.1	36.1	31.7	34.4	33.6	32.8	27.5

[a]BP86/def2-TZVP(-f)+COSMO. [b]Averaged metrics of both molecules in asymmetric unit.

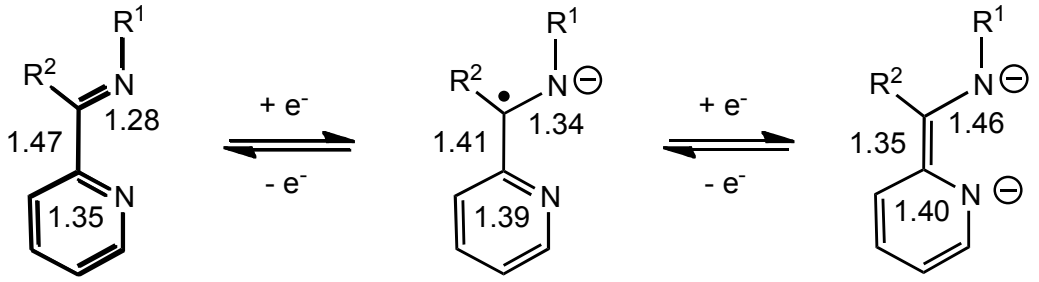


Fig. SX. Redox states of the α-iminopyridine ligand, with characteristic bond lengths (Å).

Using the Wieghardt criteria[15,26] for redox non-innocence in pyridine-imine fragments, the following assignments can be made: 1) by XRD and DFT, {dmp(PI)$_2$}Ni (**Ni**[0]) is {dmp(PI)$_2^{2-}$}Ni^{II}; 2) by DFT, [{dmp(PI)$_2$}Ni]$^+$ (**Ni**[+]) is ambiguous, and could be Ni(II), i.e., [{dmp(PI)$_2^-$}Ni^{II}]$^+$ or [{dmp(PI)$_2$}Ni^I]$^+$ since the distances are roughly between those expected for (PI)^0 and (PI)$^-$; 3) by XRD and DFT, [{dmp(PI)$_2$}Ni]$^-$ (**Ni**[-]) is best considered [{dmp(PI)$_2^{3-}$}Ni^{II}]$^-$ since the distances are roughly between those expected for (PI)$^-$ and (PI)$^{2-}$; 4) by DFT, [{dmp(PI)$_2$}Ni]$^{2-}$ (**Ni**[2-]) is best considered [{dmp(PI)$_2^{4-}$}Ni^{II}]$^{2-}$ (**Ni**[2-]). In the last case, (**Ni**[2-]), the imine distance is not as long as expected for (PI)$^{2-}$ and the C_{im}-C_{py} distance is not as short as predicted, but there is considerable elongation of C_{py}-N_{py} relative to the Wieghardt model. Since all the dπ orbitals are filled for Ni(II), the deviation away from previous model dianion parameters may be due to the lack of any net π-bonding interaction between nickel and ligand, and the greater covalency of the system.

VI. Geometry Optimized Coordinates (DFT) of [{dmp(PI)$_2$}Ni]^n (n = 1+, 0, -1, -2)

Ni[2-]

Ni	-0.007996	0.028387	-0.010581
N	-1.492266	-0.573544	-1.095882
N	-1.350884	0.524186	1.262079
N	1.394569	-0.247421	1.261886
N	1.415617	0.316091	-1.281880
C	-1.534368	-1.085636	-2.345584
C	-2.693096	-1.436967	-3.032626
C	-3.959376	-1.190277	-2.391780
C	-3.973644	-0.654757	-1.125334
C	-2.751780	-0.369372	-0.423841
C	-2.610394	0.110608	0.864466
C	-1.134986	0.656697	2.690913
C	-0.070068	-0.296543	3.301626
C	1.307403	0.018972	2.680453
C	2.645941	-0.038192	0.699989
C	2.709205	0.160955	-0.665507
C	3.885788	0.208734	-1.494052
C	3.798192	0.483512	-2.838471
C	2.503811	0.692178	-3.429705

C	1.384835	0.569133	-2.607901
C	-0.455462	-1.760754	3.053124
H	-1.426847	-1.995724	3.519094
H	0.302384	-2.442039	3.474614
H	-0.527582	-1.943404	1.972000
C	0.006336	-0.020245	4.812618
H	0.267433	1.032760	5.010460
H	0.768400	-0.652894	5.295903
H	-0.960468	-0.225388	5.299828
H	-0.558113	-1.244117	-2.813951
H	0.384729	0.703330	-3.030549
H	-2.087125	0.490797	3.238146
H	3.546058	-0.068857	1.327628
H	-3.463324	0.209380	1.547967
H	-0.804996	1.689005	2.938665
H	1.549333	1.081701	2.934938
H	4.701588	0.526162	-3.453226
H	-2.625592	-1.909667	-4.013361
H	4.856983	0.017984	-1.026838
H	-4.922231	-0.427532	-0.628241
H	2.385044	0.956497	-4.480983
H	-4.896391	-1.407565	-2.911817
H	2.067783	-0.593634	3.216814

Ni[-]

Ni	-0.010471	0.010820	0.011872
N	1.350124	0.298083	-1.313980
N	1.434029	0.036345	1.238116
N	-1.356389	0.439759	1.268788
N	-1.456382	-0.793639	-0.973881
C	1.258962	0.407508	-2.664118
H	0.243719	0.448791	-3.064242
C	2.346272	0.508220	-3.517070
H	2.183781	0.639918	-4.587056
C	3.661693	0.466262	-2.959388
H	4.540431	0.520398	-3.605106
C	3.800332	0.353887	-1.593745
H	4.789956	0.307944	-1.132076
C	2.653538	0.292872	-0.748002
C	2.644925	0.237373	0.645019
H	3.552352	0.369990	1.243103
C	1.368265	0.309059	2.667735
H	1.580150	1.381088	2.872684
H	2.163495	-0.267550	3.181811
C	0.019525	-0.034621	3.329412

C	-1.109833	0.791534	2.655501
H	-2.035469	0.661522	3.249144
H	-0.820343	1.858469	2.728021
C	-2.584843	-0.039448	0.941610
H	-3.421278	0.028273	1.644799
C	-2.705822	-0.626767	-0.319020
C	-3.909494	-1.052878	-0.950822
H	-4.858049	-0.872516	-0.438653
C	-3.876154	-1.672927	-2.180737
H	-4.798128	-2.003776	-2.662721
C	-2.611244	-1.871442	-2.815933
H	-2.527070	-2.395392	-3.768359
C	-1.468564	-1.407738	-2.184627
H	-0.490123	-1.555188	-2.646550
C	0.094609	0.389843	4.806603
H	0.921176	-0.123041	5.322657
H	-0.838921	0.138292	5.333092
H	0.257743	1.475386	4.902701
C	-0.272670	-1.539402	3.235017
H	-0.303244	-1.859510	2.184387
H	-1.240956	-1.780415	3.701708
H	0.509249	-2.117327	3.752927

Ni[0]

Ni	-0.008504	0.025924	0.002056
N	-1.479745	-0.573689	-1.078297
N	-1.354602	0.399641	1.261625
N	1.408033	-0.121696	1.241230
N	1.397236	0.333739	-1.262810
C	-1.493629	-1.079140	-2.340655
C	-2.655134	-1.378517	-3.031784
C	-3.908771	-1.143831	-2.417836
C	-3.928766	-0.643477	-1.128346
C	-2.716482	-0.372869	-0.457983
C	-2.589557	0.082337	0.875872
C	-1.110053	0.657840	2.673653
C	-0.069479	-0.310423	3.296846
C	1.321382	-0.024594	2.703547
C	2.624604	0.021909	0.706761
C	2.667451	0.183218	-0.695449
C	3.835891	0.227774	-1.488849
C	3.739954	0.451660	-2.849699
C	2.454747	0.635304	-3.416359
C	1.337749	0.561778	-2.602637
C	-0.475445	-1.777238	3.084470

H	-1.480363	-1.967015	3.491814
H	0.231173	-2.445801	3.599537
H	-0.479873	-2.039049	2.017276
C	-0.003644	-0.005667	4.804811
H	0.230937	1.054005	4.991009
H	0.772194	-0.615621	5.291694
H	-0.964821	-0.234039	5.288584
H	-0.518750	-1.277849	-2.786723
H	0.342084	0.728365	-3.014616
H	-2.055193	0.575320	3.239340
H	3.525224	0.058617	1.326183
H	-3.438622	0.139211	1.562847
H	-0.731846	1.688465	2.794905
H	1.625687	0.992610	3.016199
H	4.633747	0.492287	-3.472818
H	-2.585983	-1.810555	-4.030169
H	4.803920	0.084173	-1.006182
H	-4.870289	-0.450547	-0.610999
H	2.330122	0.858388	-4.475881
H	-4.837296	-1.360312	-2.947086
H	2.049152	-0.728097	3.146017

Ni[+]

Ni	-0.021800	0.026570	0.002935
N	-1.512815	-0.549210	-1.113880
N	-1.387019	0.315743	1.288393
N	1.411819	-0.037257	1.259422
N	1.407703	0.303322	-1.283470
C	-1.515196	-1.054277	-2.365403
C	-2.687182	-1.346891	-3.057742
C	-3.924764	-1.106354	-2.446166
C	-3.942333	-0.610921	-1.145800
C	-2.729435	-0.353475	-0.495695
C	-2.601902	0.066113	0.873005
C	-1.146478	0.603425	2.697619
C	-0.055393	-0.307566	3.314982
C	1.317067	0.057162	2.724168
C	2.603601	0.012875	0.716500
C	2.652054	0.137933	-0.712964
C	3.826398	0.166828	-1.476101
C	3.742394	0.405705	-2.844122
C	2.480254	0.623408	-3.413989
C	1.347311	0.558110	-2.607613
C	-0.379344	-1.794714	3.101065
H	-1.374063	-2.038159	3.503144

H	0.358778	-2.422181	3.621748
H	-0.365605	-2.067463	2.036150
C	-0.002682	0.002549	4.822598
H	0.182377	1.071380	5.008685
H	0.799865	-0.572049	5.307448
H	-0.951626	-0.270510	5.305731
H	-0.542509	-1.253862	-2.813313
H	0.357526	0.743659	-3.023837
H	-2.085403	0.484990	3.263362
H	3.516479	0.012754	1.319694
H	-3.467796	0.132810	1.538240
H	-0.822640	1.653878	2.787975
H	1.555703	1.096985	3.007795
H	4.642858	0.439217	-3.457723
H	-2.622975	-1.769611	-4.059692
H	4.787871	0.011140	-0.985383
H	-4.880021	-0.426761	-0.620961
H	2.368638	0.853465	-4.473095
H	-4.855918	-1.316508	-2.972182
H	2.090643	-0.589712	3.169572