Supporting Information for

Quantification of Ni-N-O bond angles and NO activation by X-ray emission spectroscopy

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1. XES details

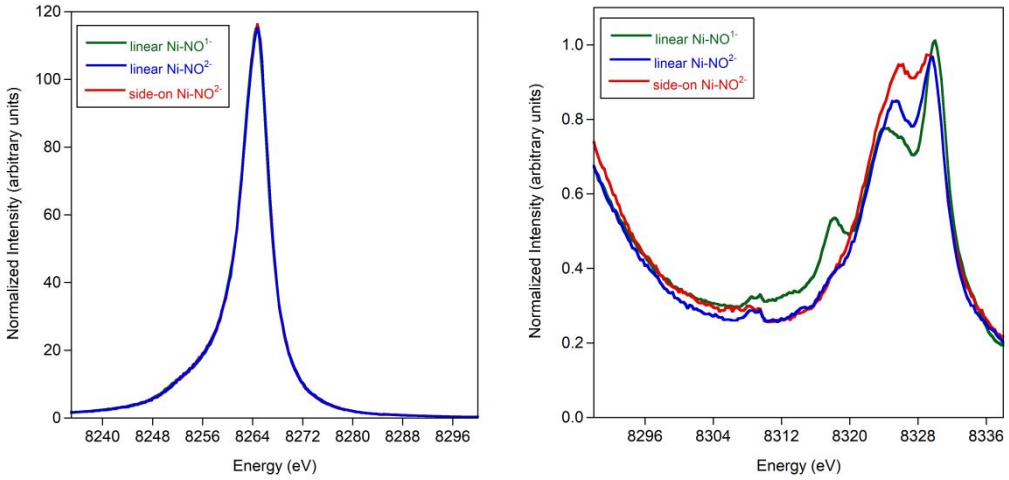

Figure S1. Kβ main line (left) and VtC (right) XES of [^{i}Pr$_2$NN$_{F6}$]NiNO (linear Ni-(NO^{1-}), green), [^{i}Pr$_2$NN$_{F6}$]Ni(μ-η^1:η^1-NO)K[2.2.2-cryptand] (linear Ni-(NO^{2-}), blue), and [^{i}Pr$_2$NN$_{F6}$]Ni(μ-η^2:η^2-NO)K(18-crown-6)(THF) (side-on Ni-(NO^{2-}), red).

2. Computational details

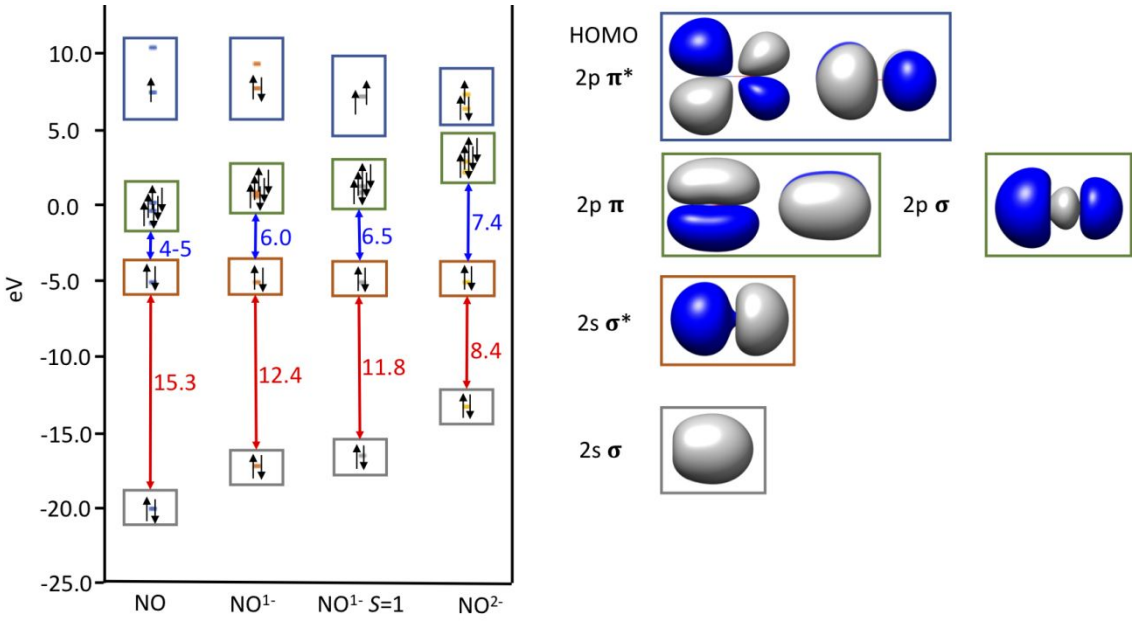

Figure S2. Qualitative MO energy diagram for NO, NO^{1-} (S = 0), NO^{1-} (S = 1), and NO^{2-} from DFT geometry optimization, along with visualization of corresponding orbitals. The energy scale was calibrated to the 2s σ* orbital to reflect the small change in energy of the NO 2s σ* orbital observed for the studied nickel nitrosyl complexes.

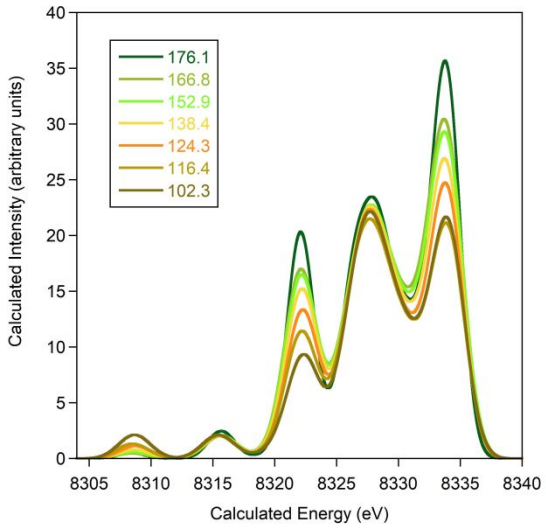

Figure S3. Calculated VtC XES spectrum of Ni-(NO^{1-}) with varying the Ni-N-O angle from 102-176°. A shift of 217.0 eV and a broadening of 2.5 eV were applied to the computed data.

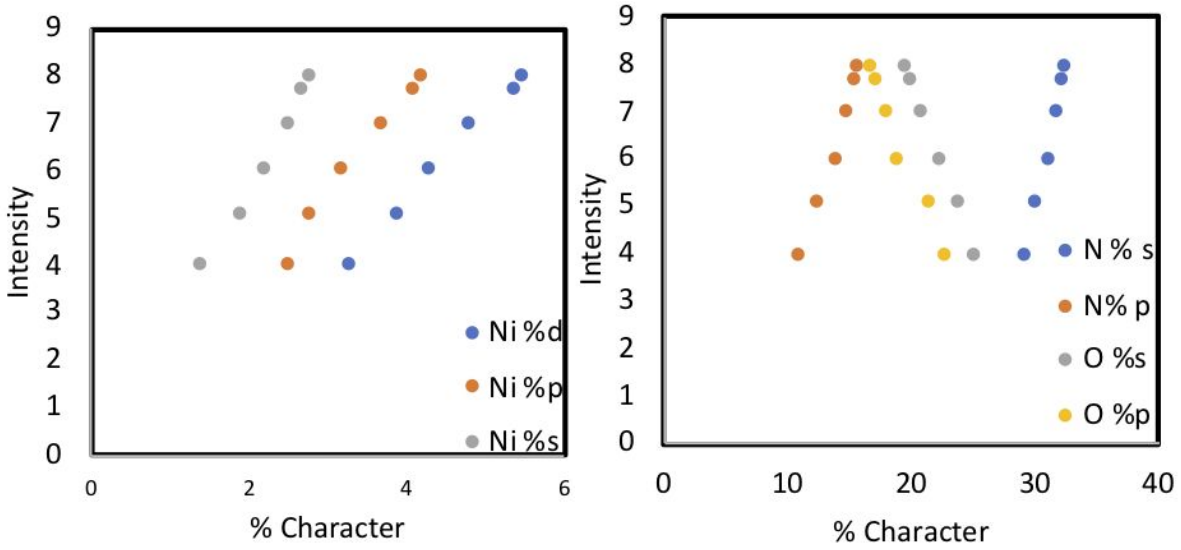

Figure S4. Total intensity versus calculated nickel character (left) and NO character (right) in transitions contributing to XES VtC spectral feature around 8322 eV for the calculated VtC XES spectrum of Ni-(NO^{1-}) with varying the Ni-N-O angle from 102-176°.

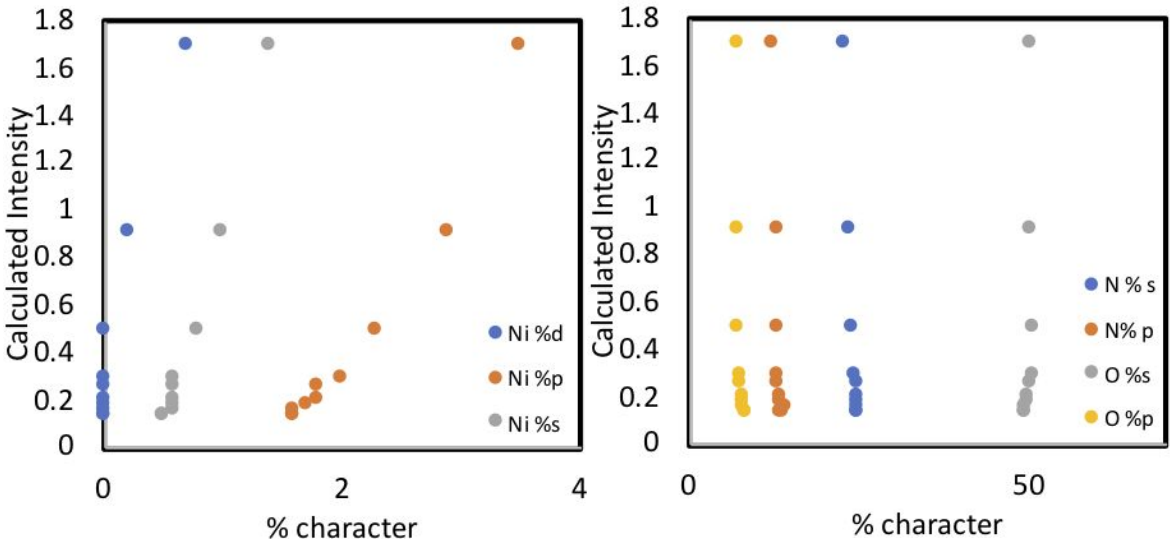

Figure S5. Total intensity versus calculated nickel character (left) and NO character (right) in transitions contributing to XES VtC spectral feature around 8310.7 eV for the calculated VtC XES spectrum of Ni-(NO^{2-}) with varying the Ni-N-O angle from 80-160°.

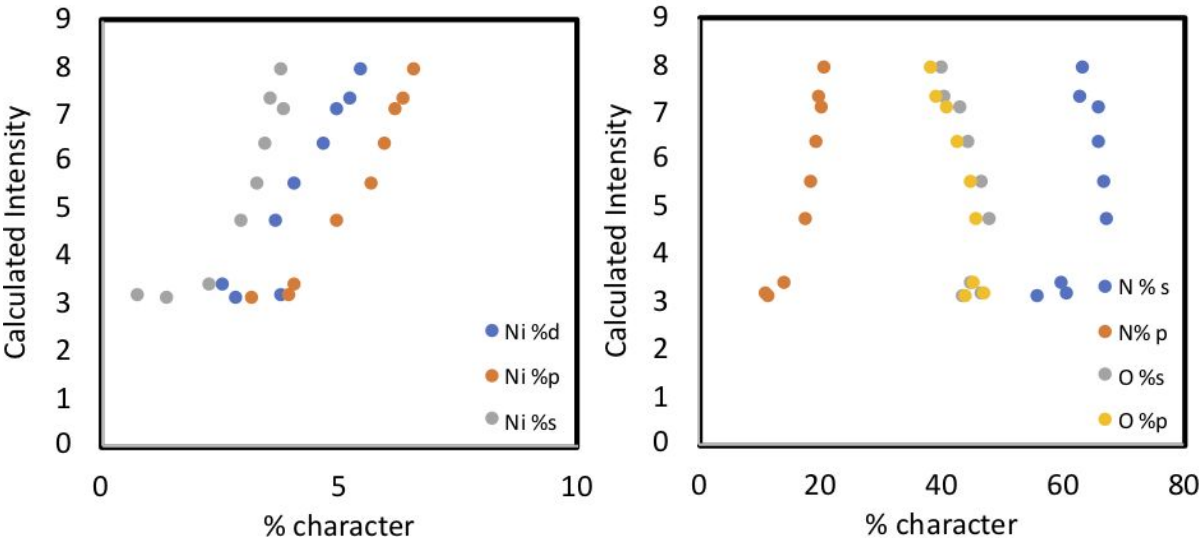

Figure S6. Total intensity versus calculated nickel character (left) and NO character (right) in transitions contributing to XES VtC spectral feature around 8322 eV for the calculated VtC XES spectrum of Ni-(NO^{2-}) with varying the Ni-N-O angle from 80-160°.

Table S1. Ni-NO bond angles (deg.) and distances (Å) resulting from geometry optimizations with fixed Ni-N-O bond angles for [$^{i}Pr_2NN_{F6}$]NiNO, Ni-(NO^{1-}).

Ni-N-O angle (deg.)	Ni-N distance (Å)	Ni-O distance (Å)	N-O distance (Å)
176.1	1.632	2.784	1.153
166.8	1.635	2.772	1.155
152.9	1.64	2.772	1.158
138.4	1.654	2.639	1.163
124.3	1.675	2.526	1.17
116.4	1.701	2.457	1.173
102.3	1.718	2.283	1.184

Table S2. Ni-NO bond angle (deg.) and distances (Å) resulting from geometry optimizations with fixed Ni-N-O bond angles for Ni-(NO^{2-}).

Ni-N-O angle (deg.)	Ni-N distance (Å)	Ni-O distance (Å)	N-O distance (Å)
160	1.771	2.944	1.217
150	1.784	2.905	1.22
140	1.801	2.848	1.222
130	1.827	2.78	1.227
120	1.849	2.688	1.234
110	1.897	2.6	1.244
100	1.877	2.427	1.247
90	1.847	2.232	1.253
80	1.83	2.036	1.265

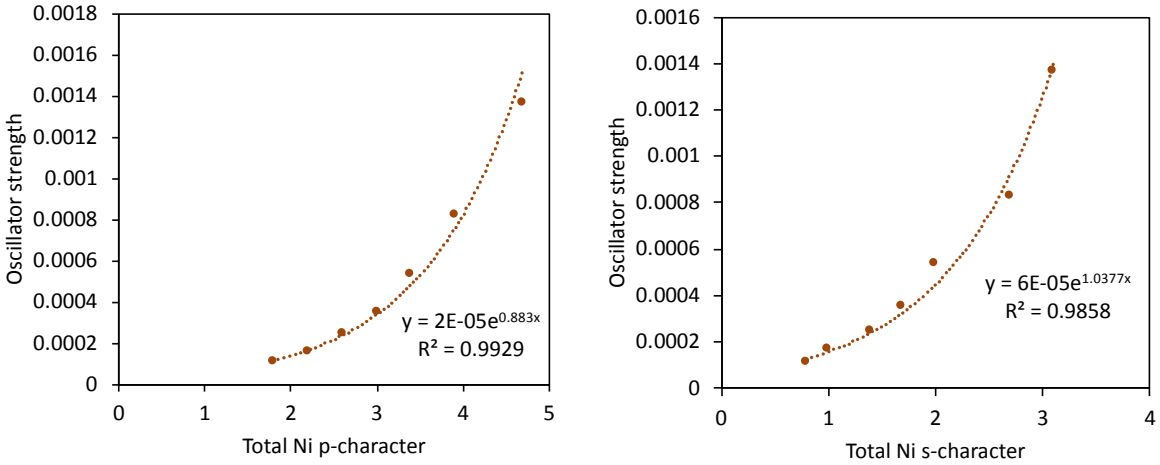

Figure S7. Total oscillator strength versus calculated nickel *p*-character (left) and *s*-character (right) in transitions contributing to XES VtC spectral feature around 8322 eV for linear Ni-(NO^{1-}) with fixed Ni-N distances.

Table S3. Total oscillator strength versus calculated percent nickel *p*-character and *s*-character in transitions contributing to XES VtC spectral feature around 8322 eV for linear Ni-(NO^{1-}) with fixed Ni-N distances.

Energy (eV)	Ni-N distance (Å)	Total Ni *p*-character (%)	Total Ni *s*-character (%)
8321.99	1.527	4.7	3.1
8322.07, 8322.20	1.627	3.9	2.7
8322.21	1.727	3.4	2.0
8322.24	1.827	3.0	1.7
8322.25, 8322.68	1.927	2.6	1.4
8322.23, 8322.57	2.027	2.2	1.0
8322.19, 8322.46	2.127	1.8	0.8

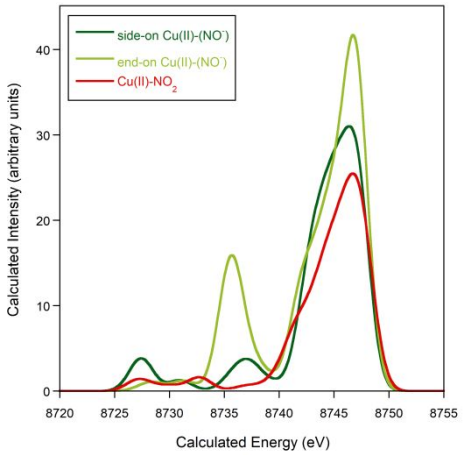

Figure S8. Calculated VtC XES spectrum of NiR for side-on Cu(II)-(NO^-), end-on Cu(II)-(NO^-), and Cu(II)-NO_2. The energy scale is not calibrated, and a broadening of 2.5 eV was applied.

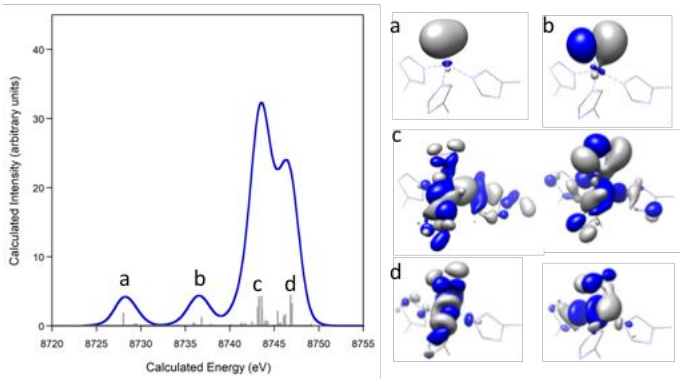

Figure S9. Calculated VtC XES spectrum of NiR for side-on Cu(I)-(NO^+) with the molecular orbitals that strongly contribute to the observed transitions. The energy scale is not calibrated, and a broadening of 2.5 eV was applied.

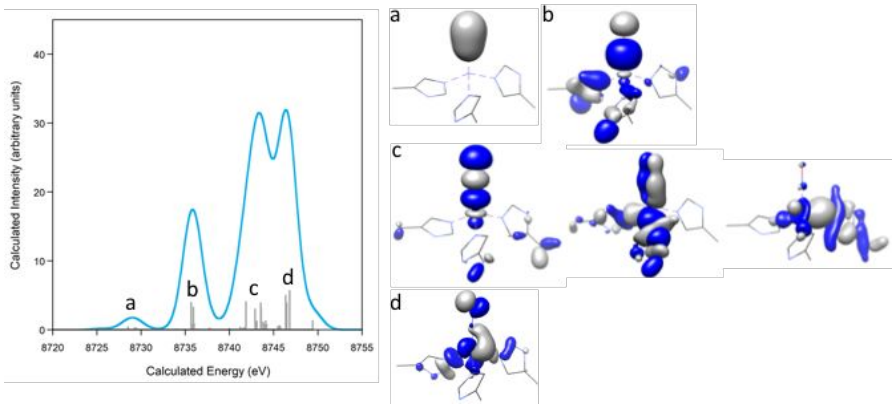

Figure S10. Calculated VtC XES spectrum of NiR for end-on Cu(I)-(NO^+), with the molecular orbitals that strongly contribute to the observed transitions. The energy scale is not calibrated, and a broadening of 2.5 eV was applied.

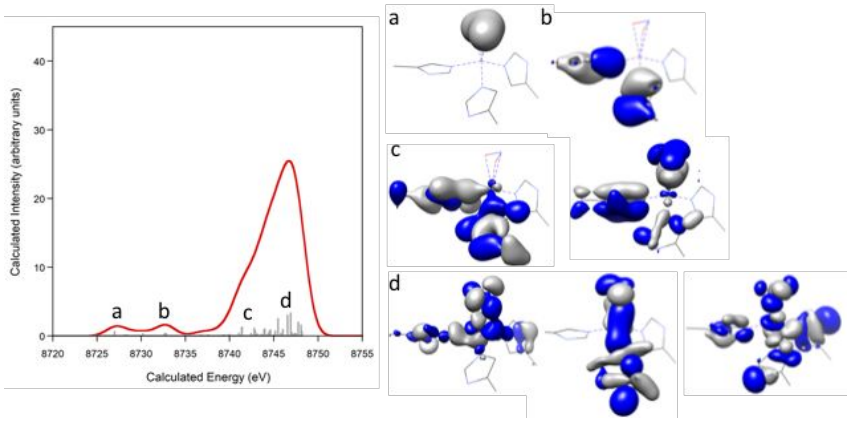

Figure S11. Calculated VtC XES spectrum of NiR for Cu(II)-NO_2 with the molecular orbitals that strongly contribute to the observed transitions. The energy scale is not calibrated, and a broadening of 2.5 eV was applied.

<u>Representative geometry optimization input file for fixed Ni-N-O angle of 150° (ORCA):</u>

```
! UKS B3LYP RIJCOSX SlowConv TightSCF def2-SV(P) def2-SVP/J Normalprint OPT PAL8
%geom Constraints
        { A 0 2 4 150.0 C }
        end
        end

%basis  NewGTO 28 "def2-TZVP(-f)" end
        NewGTO 7 "def2-TZVP(-f)" end
        NewGTO 8 "def2-TZVP(-f)" end
        NewAuxGTO 28 "def2-TZVP/J" end
        NewAuxGTO 7 "def2-TZVP/J" end
```

```
        NewAuxGTO 8 "def2-TZVP/J" end
        end

%scf    MaxIter 3000
        TolE 1E-7
        TolErr 1E-6
        end

* xyz 0 1 coordinates.xyz
```

Representative XES input file (ORCA):

```
! UKS BP86 TZVP def2-TZV/J TightSCF SlowConv COSMO SCFConv7 PAL8
! Normalprint
! grid4 nofinalgrid

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

%method         SpecialGridAtoms 28
                SpecialGridIntAcc 7
                end

%scf            MaxIter 1000
                TolE 1e-7
                TolErr 1e-6
                end

* xyzfile 0 1 coordinates.xyz

%xes
                CoreOrb 0,0
                OrbOp 0,1
                End
```

Atomic coordinates used in calculations (xyz format):

1. Previously published geometry optimized coordinates for linear Ni-NO^{1-}, linear Ni-NO^{2-}, and side-on Ni-NO^{2-} were used from reference 3.
2. All other geometry optimized coordinates and atomic coordinates can be found on the Zenodo repository under DOI: 10.5281/zenodo.3911324