The Influence of Redox-Innocent Donor Groups in Tetradentate Ligands Derived from o-Phenylenediamine: Electronic Structure Investigations with Nickel

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**Table S1.** Crystallographic data for H₂(MeNNNNMe)-DAB (L1) and nickel complexes with L1.

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<th>L1</th>
<th>I</th>
<th>I[BF₄]</th>
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<td>R₁ [I &gt; 2σ(I)]ᵃ</td>
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<td>0.0339</td>
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<td>wR₂ (all data)ᵇ</td>
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<td>-</td>
<td>-</td>
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ᵃ. R₁ = \sum |F_o| - |F_c| / \sum |F_o| for reflections with F_o² > 2σ(F_o²) ᵇ. wR₂ = \[\sum w(F_o² - F_c²)^2 / \sum (F_o²)^2\]¹/² for all reflections.
Table S2. Crystallographic data for nickel complexes with L2 and L3.

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<th>2[NTf]₂</th>
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<td>C₂₀H₁₈BF₄N₂NiS₂</td>
<td>C₂₂H₁₈F₆N₂NiO₆S₄</td>
<td>C₂₄H₁₈F₁₂N₄NiO₈S₈</td>
<td>C₁₆H₁₈N₂NiS₂</td>
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<td><strong>FW (g mol⁻¹)</strong></td>
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<td>C₂/c</td>
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<td><strong>b (Å)</strong></td>
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<td><strong>R₁ [I &gt; 2σ(I)]a</strong></td>
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<tr>
<td><strong>wR₂ (all data)b</strong></td>
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<td>0.0974</td>
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<td><strong>Ext. Coeff.</strong></td>
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<td>-</td>
<td>-</td>
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<tr>
<td><strong>Largest Peak/Hole (e · Å⁻³)</strong></td>
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<td>1.620/-1.321</td>
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<td>1.273/-0.646</td>
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<tr>
<td><strong>Temp (K)</strong></td>
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<td>190(2)</td>
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---

a. \( R₁ = \frac{\sum |F_o| - |F_c|}{|\sum F_o|} \) for reflections with \( F_o^2 > 2 \sigma(F_o^2) \)

b. \( wR₂ = \left[ \frac{\sum w(F_o^2 - F_c^2)^2}{\sum (F_o^2)^2} \right]^{1/2} \) for all reflections.
Figure S1. Molecular structure of H$_2$(MeNNNNMe)-DAB (L1). Ellipsoids are drawn at 50% probability level.
Figure S2. Molecular structure of Ni(SNNS)-DAE (3). Hydrogen atoms are omitted from the figure and ellipsoids are drawn at the 50% probability level.
**Figure S3.** Molecular structure of 1[BF₄]. Hydrogen atoms are omitted from the figure and ellipsoids are drawn at the 50% probability level.
Figure S4. Molecular structure of $2[\text{NTf}_2]_2$. Hydrogen atoms omitted from the figure and ellipsoids are drawn at the 50% probability level.
Figure S5. UV-Vis spectrum of 1[NTf₂] (red) and 2[NTf₂] (black). Data were collected at: 50 μM (UV) and 250 μM (vis-NIR) solutions in DCM at 298 K.
Figure S6. Sulfur K-edge XAS spectrum of 2 (red) and 3 (blue).
Figure S7. Complete background subtracted and normalized S K-edge XAS spectrum of 3.
Figure S8. Complete background subtracted and normalized S K-edge XAS spectrum of 2.
Figure S9. Complete background subtracted and normalized S K-edge XAS spectrum of 2[BF₄].
Figure S10. Complete background subtracted and normalized S K-edge XAS spectrum of 2[NTf$_2$]$_2$. 
Figure S11. Complete background subtracted and normalized S K-edge XAS spectrum of 2[OTf]$_2$. 
NMR Data

Figure S12. $^1$H NMR spectrum of H$_2$(NNN) in CDCl$_3$. Residual NMR solvent is marked with an asterisk.
Figure S13. $^{13}$C NMR spectrum of $\text{H}_2(\text{NNNN})$ in CDCl$_3$. Spectrometer artifact is marked with †.
Figure S14. $^1$H NMR spectrum of $N,N'$-bis[2-(methylthio)phenyl]ethanediylidene. Residual water is marked with an asterisk.
Figure S15. $^1$H NMR spectrum of $\text{H}_2(\text{SNNS})$-DAE in CDCl$_3$. Residual NMR solvent is marked with an asterisk.
Figure S16. $^{13}$C NMR spectrum of H$_2$(SNNS)-DAE in CDCl$_3$. Spectrometer artifact is marked with ‡.
Figure S17. $^1$H NMR spectrum of 1 in THF-D$_8$. Residual NMR solvent is marked with an asterisk.
Figure S18. $^{13}$C NMR spectrum of 1 in THF-$d_8$. 
Figure S19. $^{19}$F NMR spectrum of $1[BF_4]$ in CH$_2$Cl$_2$. 
Figure S20. $^{11}$B NMR spectrum of $1[BF_4]$ in CH$_2$Cl$_2$. 
Figure S21. $^{19}$F NMR spectrum of $1\text{[NTf}_2\text{]}$ in CH$_2$Cl$_2$. 
Figure S22. $^1$H NMR spectrum of $1[\text{OTf}]_2$ in CD$_2$Cl$_2$. 
Figure S23. $^{19}$F NMR spectrum of $1[OTf]_2$ in CD$_2$Cl$_2$. 
Figure S24. $^1$H NMR spectrum of 2 in C$_6$D$_6$. Residual NMR solvent is marked with an asterisk.
Figure S25. $^{13}$C NMR spectrum of 2 in C₆D₆.
Figure S26. \(^{11}\)B NMR spectrum of 2[BF\(_4\)] in CH\(_2\)Cl\(_2\).
Figure S27. $^{19}$F NMR spectrum of 2|BF$_4$| in CH$_2$Cl$_2$. 

50 0 -50 -100 -150 -200 [ppm]
Figure S28. $^{19}$F NMR spectrum of $2[\text{NTf}_2]$ in CH$_2$Cl$_2$. 
Figure S29. $^1$H NMR spectrum of 2[OTf]$_2$ in CD$_2$Cl$_2$. 
Figure S30. $^{19}$F NMR spectrum of 2[OTf]$_2$ in CH$_2$Cl$_2$. 
Figure S31. $^1$H NMR spectrum of 2[NTf$_2$]$_2$ in CD$_2$Cl$_2$. 
Figure S32. $^{19}$F NMR spectrum of $2\text{[NTf}_2\text{]}_2$ in THF.
Figure S33. $^1$H NMR spectrum of 3 in C$_6$D$_6$. Residual NMR solvent is marked with an asterisk.
Figure S34. $^{13}$C NMR spectrum of 3 in C$_6$D$_6$. 
Figure S35. Variable temperature EPR experiment of $2\text{[BF}_4\text{]}$ (0.95 mM, 3:1 mixture of DCM:2-methyl THF) from 155 (grey) to 109 K (red) with spectra collected at 10 K increments. Frequency: 9.50 GHz. Power: 40 mW. Modulation: 10.0 G/100 kHz.
Figure S36. EPR spectrum of $\text{1[BF}_4\text{]}$ (0.77 mM, DCM) recorded at 298 K. Frequency: 9.50 GHz. Power: 20 mW. Modulation: 10.0 G/100 kHz.
Figure S37. EPR spectrum of $1\text{[BF}_4\text{]}$ (0.77 mM, DCM) with 3000 equiv. of pyridine recorded at 298 K. Frequency: 9.50 GHz. Power: 20 mW. Modulation: 10.0 G/100 kHz.
**Figure S38.** EPR spectrum of 1[NTf2] (0.92 mM, DCM) recorded at 298 K. Frequency: 9.50 GHz. Power: 20 mW. Modulation: 10.0 G/100 kHz.
Figure S39. EPR spectrum of $\mathbf{1[NTf_2]}$ (0.92 mM, DCM) recorded at 109 K. Frequency: 9.50 GHz. Power: 20 mW. Modulation: 10.0 G/100 kHz.
**Figure S40.** EPR spectrum of $\mathbf{1[NTf_2]}$ (0.92 mM, DCM) with 3000 equiv. of pyridine recorded at 298 K. Frequency: 9.50 GHz. Power: 20 mW. Modulation: 10.0 G/100 kHz.
Figure S41. EPR spectrum of 1[NTf₂] (0.92 mM, DCM) with 3000 equiv. of pyridine recorded at 109 K (black). Simulated spectrum in red. Frequency: 9.50 GHz. Power: 20 mW. Modulation: 10.0 G/100 kHz.
Figure S42. EPR spectrum of $2[\text{BF}_4]$ (0.91 mM, DCM) with 3000 equiv. of pyridine recorded at 298 K. Frequency: 9.50 GHz. Power: 20 mW. Modulation: 10.0 G/100 kHz.
Figure S43. EPR spectrum of $2\text{[NTf}_2]$ (0.83 mM, DCM) recorded at 298 K. Frequency: 9.50 GHz. Power: 20 mW. Modulation: 10.0 G/100 kHz.
Figure S44. EPR spectrum of $2\{\text{NTf}_2\}$ (0.83 mM, DCM) recorded at 109 K. Frequency: 9.50 GHz. Power: 20 mW. Modulation: 10.0 G/100 kHz.
Figure S45. EPR spectrum of 2|NTf₂| (0.83 mM, DCM) with 3000 equiv. of pyridine recorded at 298 K. Frequency: 9.50 GHz. Power: 20 mW. Modulation: 10.0 G/100 kHz.
Figure S46. EPR spectrum of 2[NTf₂] (0.83 mM, DCM) with 3000 equiv. of pyridine recorded at 109 K. Simulated spectrum in red. Frequency: 9.50 GHz. Power: 20 mW. Modulation: 10.0 G/100 kHz.
Figure S47. EPR spectrum of 1[OTf]$_2$ (unknown concentration, 3:1 mixture of DCM:2-methyl THF) recorded at 298 K. Frequency: 9.49 GHz. Power: 1 mW. Modulation: 5.0 G/100 kHz.
Figure S48. EPR spectrum of 2[OTf]$_2$ (unknown concentration, 3:1 mixture of DCM:2-methyl THF) recorded at 298 K. Frequency: 9.49 GHz. Power: 1 mW. Modulation: 5.0 G/100 kHz.
Figure S49. EPR spectrum of $2\text{[OTf]}_2$ (unknown concentration, 3:1 mixture of DCM:2-methyl THF) recorded at 109 K. Simulated spectrum in red. Frequency: 9.50 GHz. Power: 1 mW. Modulation: 5.0 G/100 kHz.
Figure S50. EPR spectrum of 2[NTf$_2$]$_2$ (unknown concentration, 3:1 mixture of DCM:2-methyl THF) recorded at 298 K. Frequency: 9.49GHz. Power: 1 mW. Modulation: 5.0 G/100 kHz.
Figure S51. Curie-Weiss plot of VT Evans method experiment for $2[\text{NTf}_2]_2$ (4.9 µM in DCM with a DCM capillary insert). Collected using a DRX Bruker 400 MHz. Temp: -80 °C (193 K) to 30 °C (300 K).

\[
y = 0.3343x + 90.255
\]

\[
R^2 = 0.9852
\]
Figure S52. Cyclic voltammograms of 1 in DCM, \textit{left}- full window and \textit{right}- truncated window. WE: Glassy Carbon, RE: Pt wire, CE: Pt wire, Fc: reference, solvent: DCM, electrolyte: TBAPF₆. T: 298 K. Arrows signify scan start and direction.
**Figure S53.** Cyclic voltammograms of 2 in DCM, *left-* full window and *right-* truncated window. WE: Glassy Carbon, RE: Pt wire, CE: Pt wire, Fc: reference, solvent: DCM, electrolyte: TBAPF$_6$. T: 298 K. Arrows signify scan start and direction.
### Table S3. Parameters for simulated EPR data selected by easyspin least squares fit for singly oxidized (S = ½) compounds. EPR data collected in DCM unless otherwise noted.

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<th>Ni(III) region</th>
<th>Ligand radical region</th>
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<td>A₁</td>
<td>A₂</td>
</tr>
<tr>
<td>1[BF₄]</td>
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<tr>
<td>1-py[BF₄]</td>
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<td>1-py[NTf₂]</td>
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<tr>
<td>2[BF₄]* (2-MeTHF/DCM)</td>
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A tensors are reported as MHz. LW broadenings are reported as mT. *Fluorine splitting was modeled as a separate S = ½ species with giso = 2.186 and A = 11.62, 8.45 and 777.41 MHz.

### Table S4. Parameters for simulated EPR data selected by easyspin least squares fit for double oxidized (S = 1) compounds. EPR data collected in DCM.

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<th>gzz</th>
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<th>A₁</th>
<th>A₂</th>
<th>A₃</th>
<th>LW</th>
<th>LW</th>
<th>D</th>
<th>E</th>
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<td>2.016</td>
<td>0.012</td>
<td>14.997</td>
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A tensors are reported as MHz. LW broadenings are reported as mT. D and E parameters are reported as MHz.
Table S5. Bond distances (Å) and angles (deg) from DFT calculations.

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<th>1⁺</th>
<th>1[BF₄]</th>
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<th>2[NTf₂]₂⁺</th>
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<th>2-py[BF₄]</th>
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¹Calculated with atom positions constrained to match those from XRD studies. All other structures optimized.
Figure S54. Spin density plot for calculated structure of 2[BF₄] with axially positioned BF₄⁻. Spin density isovalue is 0.002. Hydrogen atoms were omitted from the figure.
**Figure S55.** Optimized structure of $2[BF_4]$ that started with two pyridine ligands bound to Ni. The resulting Ni-pyridine distances are 2.183 and 4.553 Å. Hydrogen atoms were omitted from the figure.