Supporting Information

Role of structures of the Cu(II) complexes in deciding the mechanistic pathway of reduction of Cu(II) by nitric oxide

Pankaj Kumar, Apurba Kalita, Biplab Mondal*

Department of Chemistry, Indian institute of Technology Guwahati, Assam 781039, India
Figure S1: FT-IR spectrum of L₁ in KBr pellet

Figure S2: ¹H-NMR spectrum of L₁ in CDCl₃
Figure S3: $^{13}$C-NMR spectrum of L$_1$ in CDCl$_3$.

Figure S4: ESI-Mass spectrum of L$_1$ in methanol
Figure S5: FT-IR spectrum of L₂ in KBr pellet

Figure S6: ¹H-NMR spectrum of L₂ in CDCl₃
Figure S7: $^{13}$C-NMR spectrum of L$_2$ in CDCl$_3$

Figure S8: ESI-Mass spectrum of L$_2$ in methanol
Figure S9: FT-IR spectrum of L₃ in KBr pellet

Figure S10: ¹H-NMR spectrum of L₃ in CDCl₃
Figure S11: $^{13}$C-NMR spectrum of L$_3$ in CDCl$_3$

Figure S12: ESI-Mass spectrum of L$_3$ in methanol
Figure S13: FT-IR spectrum of L₄ in KBr pellet

Figure S14: ¹H-NMR spectrum of L₄ in CDCl₃
Figure S15: $^{13}$C-NMR spectrum of $L_4$ in CDCl$_3$

Figure S16: ESI-Mass spectrum of $L_4$ in methanol
Figure S17: FT-IR spectrum of complex 1 in KBr pellet

Figure S18: UV-visible spectrum of complex 1 in methanol
Figure S19: FT-IR spectrum of complex 2 in KBr pellet

Figure S20: UV-visible spectrum of complex 2 in methanol
Figure S21: FT-IR spectrum of complex 3 in KBr pellet

Figure S22: UV-visible spectrum of complex 3 in methanol
Figure S23: FT-IR spectrum of the complex 4 in KBr pellet

Figure S24: UV-visible spectrum of complex 4 in methanol
Figure S25: FT-IR spectrum of complex $L_1\text{-ClO}_4$ in KBr pellet

Figure S26: $^1$H-NMR spectrum of $L_1\text{-ClO}_4$ in D$_2$O
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Figure S30: FT-IR spectrum of L$_2^{1}$/ClO$_4$ in KBr pellet

Figure S31: $^1$H-NMR spectrum of L$_2^{1}$/ClO$_4$ in D$_2$O
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Figure S39: ¹H-NMR spectrum of L₄⁻ClO₄⁻ in D₂O
Figure S40: ESI-Mass spectrum of L₄⁻ClO₄⁻ in methanol

Figure S41: $^{13}$C-NMR spectrum of L₄⁻ClO₄⁻ in D₂O and CD₃CN mixture.
Figure S42. UV-visible spectra of complex 1 in methanol before (solid line), after (dash line) addition of one equivalent of sodium ethoxide and after (dotted line) purging nitric oxide.

Figure S43. X-Band EPR spectra of complex 1 in methanol before (solid line), after (dash line) addition of one equivalent of sodium ethoxide and after (dotted line) purging nitric oxide.
Figure S44. UV-visible spectra of complex 2 in methanol before (solid line), after (dash line) addition of one equivalent of sodium ethoxide and after (dotted line) purging nitric oxide.

Figure S45. X-Band EPR spectra of complex 2 in methanol before (solid line), after (dash line) addition of one equivalent of sodium ethoxide and after (dotted line) purging nitric oxide.
Figure S46. UV-visible spectra of complex 3 in methanol before (solid line), after (dash line) addition of one equivalent of sodium ethoxide and after (dotted line) purging nitric oxide

Figure S47. X-Band EPR spectra of complex 3 in methanol before (solid line), after (dash line) addition of one equivalent of sodium ethoxide and after (dotted line) purging nitric oxide
Figure S48. UV-visible spectra of complex 4 in methanol before (solid line), after (dash line) addition of one equivalent of sodium ethoxide and after (dotted line) purging nitric oxide

Figure S49. X-Band EPR spectra of complex 4 in methanol before (solid line), after (dash line) addition of one equivalent of sodium ethoxide and after (dotted line) purging nitric oxide
Figure S50: X-Band EPR spectra of complex 1 before (solid line) and after (dashed line) one equivalent of NaOEt in methanol medium at 77K

Figure S51: X-Band EPR spectra of complex 2 before (solid line) and after (dashed line) one equivalent of NaOEt in methanol medium at 77K
Figure S52: X-Band EPR spectra of complex 3 before (solid line) and after (dashed line) one equivalent of NaOEt in methanol medium at 77K

Figure S53: X-Band EPR spectra of complex 4 before (solid line) and after (dashed line) one equivalent of NaOEt in methanol medium at 77K
Figure S54: UV-visible spectra of complex 1 in methanol before (black line), after (red line) purging excess nitric oxide in absence of NaOEt.

Figure S55: UV-visible spectra of complex 2 in methanol before (black line), after (red line) purging excess nitric oxide in absence of NaOEt.
Figure S56: UV-visible spectra of complex 3 in methanol before (black line), after (red line) purging excess nitric oxide in absence of NaOEt.

Figure S57: UV-visible spectra of complex 4 in methanol before (black line), after (red line) purging excess nitric oxide in absence of NaOEt.
Figure S58: Time scan plot of complex 1 ($\lambda_{\text{max}}$ = 642 nm) after reaction with nitric oxide in presence of one equivalent NaOEt at room temperature.

Figure S59: Time scan plot of complex 2 ($\lambda_{\text{max}}$ = 664 nm) after reaction with nitric oxide in presence of one equivalent NaOEt at room temperature.
Figure S60: Time scan plot of complex 3 ($\lambda_{\text{max}}=668$) after reaction with nitric oxide in presence of one equivalent NaOEt at room temperature.

Figure S61: Time scan plot of complex 4 ($\lambda_{\text{max}}=640$) after reaction with nitric oxide in presence of one equivalent NaOEt at room temperature.
Figure S62: Cyclic voltammogram of complex 1 in acetonitrile solvent. Working electrode, Pt; Reference electrode, Ag/Ag+; TBAP supporting electrolyte; scan rate 50 mv/s.

Figure S63: Cyclic voltammogram of complex 2 in acetonitrile solvent. Working electrode, Pt; Reference electrode, Ag/Ag+; TBAP supporting electrolyte; scan rate 50 mv/s.
Figure S64: Cyclic voltammogram of complex 3 in acetonitrile solvent. Working electrode, Pt; Reference electrode, Ag/Ag+; TBAP supporting electrolyte; scan rate 50 mv/s.

Figure S65: Cyclic voltammogram of complex 4 in acetonitrile solvent. Working electrode, Pt; Reference electrode, Ag/Ag+; TBAP supporting electrolyte; scan rate 50 mv/s.
Figure S66: Cyclic voltammogram of complex 1 in methanol solvent. Working electrode, Pt; Reference electrode, Ag/Ag+; TBAP supporting electrolyte; scan rate 50 mv/s.

Figure S67: Cyclic voltammogram of complex 1 + one equivalent NaOEt in methanol solvent. Working electrode, Pt; Reference electrode, Ag/Ag+; TBAP supporting electrolyte; scan rate 50 mv/s.
Figure S68: Cyclic voltammogram of complex 2 in methanol solvent. Working electrode, Pt; Reference electrode, Ag/Ag+; TBAP supporting electrolyte; scan rate 50 mv/s.

Figure S69: Cyclic voltammogram of complex 2 + one equivalent NaOEt in methanol solvent. Working electrode, Pt; Reference electrode, Ag/Ag+; TBAP supporting electrolyte; scan rate 50 mv/s.
Figure S70: Cyclic voltammogram of complex 3 in methanol solvent. Working electrode, Pt; Reference electrode, Ag/Ag+; TBAP supporting electrolyte; scan rate 50 mv/s.

Figure S71: Cyclic voltammogram of complex 3 + one equivalent NaOEt in methanol solvent. Working electrode, Pt; Reference electrode, Ag/Ag+; TBAP supporting electrolyte; scan rate 50 mv/s.
Figure S72: Cyclic voltammogram of complex 4 in methanol solvent. Working electrode, Pt; Reference electrode, Ag/Ag+; TBAP supporting electrolyte; scan rate 50 mv/s.

Figure S73: Cyclic voltammogram of complex 4 + one equivalent NaOEt in methanol solvent. Working electrode, Pt; Reference electrode, Ag/Ag+; TBAP supporting electrolyte; scan rate 50 mv/s.
Table S1: X-Band EPR data of the complexes after addition of one equivalent NaOEt at 77K.

<table>
<thead>
<tr>
<th>Compound</th>
<th>g</th>
<th>g_II</th>
<th>A X 10^4 (cm⁻¹)</th>
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<tr>
<td>1+base</td>
<td>2.027</td>
<td>2.256</td>
<td>161</td>
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<tr>
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<td>2.025</td>
<td>2.256</td>
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<tr>
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<tr>
<td>4+base</td>
<td>2.025</td>
<td>2.221</td>
<td>136</td>
</tr>
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</table>

Figure S74: ORTEP diagram of complex 2 (50% thermal ellipsoid plot; H-atoms removed for clarity).
Figure S75. $^1$H-NMR spectrum of complex 3 after addition of one equivalent of sodium ethoxide and then purging of excess of nitric oxide in CD$_3$OD.

Figure S76. UV-visible spectra of complex 1 in methanol (black), after addition of 1 equivalent of HCl (red) and then addition of excess NO (green).
Figure S77. UV-visible spectra of complex 2 in methanol (black), after addition of 1 equivalent of HCl (red) and then addition of excess NO (green).

Figure S78. UV-visible spectra of complex 3 in methanol (black), after addition of 1 equivalent of HCl (red) and then addition of excess NO (green).
Figure S78. UV-visible spectra of complex 4 in methanol (black), after addition of 1 equivalent of HCl (red) and then addition of excess NO (green).

Figure S79. UV-visible spectra of complex 1 in methanol (black), after addition of four equivalent of triethylamine (red) and then addition of excess NO (green).
Figure S80. UV-visible spectra of complex 2 in methanol (black line), after addition of four equivalent of triethylamine (red) and then addition of excess NO (green).

Figure S81. UV-visible spectra of complex 3 in methanol (black), after addition of four equivalent of triethylamine (red) and then addition of excess NO (green).
Figure S82. UV-visible spectra of complex 4 in methanol (black), after addition of four equivalent of triethylamine (red) and then addition of excess NO (green).