Supplementary Information

New Types of Cu and Ag Clusters Supported by the Pyrrole-based NNN-Pincer Type Ligand

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Contents

$^1$H, $^{13}$C, $^{19}$F NMR, FTIR, and UV spectra
**Figure S1.** $^1$H NMR (200 MHz, 25 °C) spectrum of [Cu(μ-Cl)(μ-C$_4$H$_3$N-2,5-(CH$_2$Me$_2$pz)$_2$–N,N,N)]$_2$, 1a in CDCl$_3$.

**Figure S2.** IR spectrum of [Cu(μ-Cl)(μ-C$_4$H$_3$N-2,5-(CH$_2$Me$_2$pz)$_2$–N,N,N)]$_2$, 1a recorded as KBr disc.
Figure S3. $^1$H NMR (200 MHz, 25 °C) spectrum of [Cu(μ-Br)(μ-C$_4$H$_3$N-2,5-(CH$_2$Me$_2$pz)$_2$–N,N,N], 1b in CDCl$_3$.

Figure S4. IR spectrum of [Cu(μ-Br)(μ-C$_4$H$_3$N-2,5-(CH$_2$Me$_2$pz)$_2$–N,N,N)]$_2$, 1b recorded as KBr disc.
Figure S5. $^1$H NMR (200 MHz, 25 °C) spectrum of [Cu(µ-I)(µ-C$_4$H$_3$N-2,5-(CH$_2$Me$_2$pz)$_2$–N,N,N)]$_2$, 1c in CDCl$_3$.

Figure S6. IR spectrum of [Cu(µ-I)(µ-C$_4$H$_3$N-2,5-(CH$_2$Me$_2$pz)$_2$–N,N,N)]$_2$, 1c recorded as KBr. disc.
Figure S7. IR spectrum of [Cu₄(μ-I)₂(μ-C₄H₂N-2,5-(CH₂Me₃pz)₂-N,N,N)]₂, 2 recorded as KBr disc. The band around 3500 cm⁻¹ is due to the presence of water in KBr used.

Figure S8. IR spectrum of [Cu₄(μ-I)₂(μ-C₄H₂N-2,5-(CH₂Me₃pz)₂-N,N,N)]₂, 2 recorded as a Nujol mull.
Figure S9. IR spectrum of [Cu{μ-C₄H₂N-2,5-(CH₂Me₂pz)₂–N,N,N}], 3 recorded as KBr disc. The band around 3400 cm⁻¹ is due to the presence of water in KBr used.

Figure S10. IR spectrum of [Cu{μ-C₄H₂N-2,5-(CH₂Me₂pz)₂–N,N,N}], 3 recorded as a Nujol mull.
Figure S11. $^1$H NMR (400 MHz, 25 °C) spectrum of [Ag(μ-C₄H₃N-2,5-(CH₂Me₂pz)₂–N,N,N)(CF₃SO₃)]ₙ, 4a in CDCl₃.

Figure S12. $^{19}$F NMR (376.3 MHz, 25 °C) spectrum of [Ag(μ-C₄H₃N-2,5-(CH₂Me₂pz)₂–N,N,N)(CF₃SO₃)]ₙ, 4a in CDCl₃.
Figure S13. IR spectrum of [Ag(μ-C₄H₃N-2,5-(CH₂Me₂pz)₂–N,N,N(CF₃SO₃)]ₙ, 4a recorded as KBr disc.

Figure S14. ¹H NMR (200 MHz, 25 °C) spectrum of [Ag(μ-C₄H₃N-2,5-(CH₂Me₂pz)₂–N,N,N(BF₄)]ₙ, 4b in CD₃CN.
**Figure S15.** $^{13}$C NMR (102.6 MHz, 25 °C) spectrum of $[Ag(\mu-C_4H_3N-2,5-(CH_2Me_2pz)_2-N,N,N)(BF_4)]_n$, 4b in CD$_3$CN.

**Figure S16.** $^{19}$F NMR (376.3 MHz, 25 °C) spectrum of $[Ag(\mu-C_4H_3N-2,5-(CH_2Me_2pz)_2-N,N,N)(BF_4)]_n$, 4b in CD$_3$CN.
**Figure S17.** IR spectrum of [Ag(μ-C₄H₃N-2,5-(CH₂Me₂pz)₂–N,N,N(BF₄)₃, 4b recorded as KBr disc.

**Figure S18.** ¹H NMR (200 MHz, 25 °C) spectrum of [Ag[(μ-C₄H₂N-2,5-(CH₂Me₂pz)₂–N,N,N](BF₄)₃, 5 in CD₃CN.
Figure S19. $^{13}$C NMR (153.9 MHz, 25 °C) spectrum of [Ag{($\mu$-C$_4$H$_2$N-2,5-(CH$_2$Me$_2$pz)$_2$−$N,N,N$}]$_3$, 5 in CD$_3$CN.
Figure S20. IR spectrum of [Ag{(μ-C₆H₄N-2,5-(CH₃Me₂pz)₂–N,N,N}]₃, 5 recorded as KBr disc. The band around 3400 cm⁻¹ is due to the presence of water in KBr used.
**Figure S21.** IR spectrum of [Ag{((μ-CH₂)N-2,5-(CH₂Me₂pz)₂–N,N,N}₃, 5 recorded as a Nujol mull.
Figure S22. ORTEP diagram of complex 1c with 50% probability ellipsoids; most H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): N13–Cu11 2.051(11), N14–Cu12 2.027(10), Cu11–I10 2.7063(17), Cu12–I10 2.7205(17); Cu12–I10–Cu11 85.29(6), N13′–Cu11–N13 109.5(6), I10′–Cu12–I10 94.39(7), N13–Cu11–I10 102.0(3). Symmetry transformations used to generate equivalent atoms: (i) 1−y,1−x, 3/2−z; (ii) −y, −x, 3/2−z.
Figure S23. UV-vis spectrum of the tetranuclear copper(I) complex [Cu₄(μ-I)₂(μ-C₄H₂N-2,5-(CH₂Me₂pz)₂-N,N,N)₂] 2 with concentration of 10⁻⁵ M solution in CH₃CN. 0.0003 g of this complex dissolved in 25 mL of CH₃CN and then UV recorded within 1 hr. The color of the solution appeared almost colorless.
**Figure S24.** UV-vis spectrum of the NNN pincer ligand, 2,5-Bis(3,5-dimethylpyrazolylmethyl)pyrrole LH, with concentration of $10^{-4}$ M solution in CH$_3$CN.