Supporting Information

Simplest Homoleptic Metal-Centered Tetrahedrons, $[M(OH_2)_4]^{2+}$, in 1-Ethyl-3-methylimidazolium Tetrafluoroborate Ionic Liquid (M = Co, Ni, Cu)

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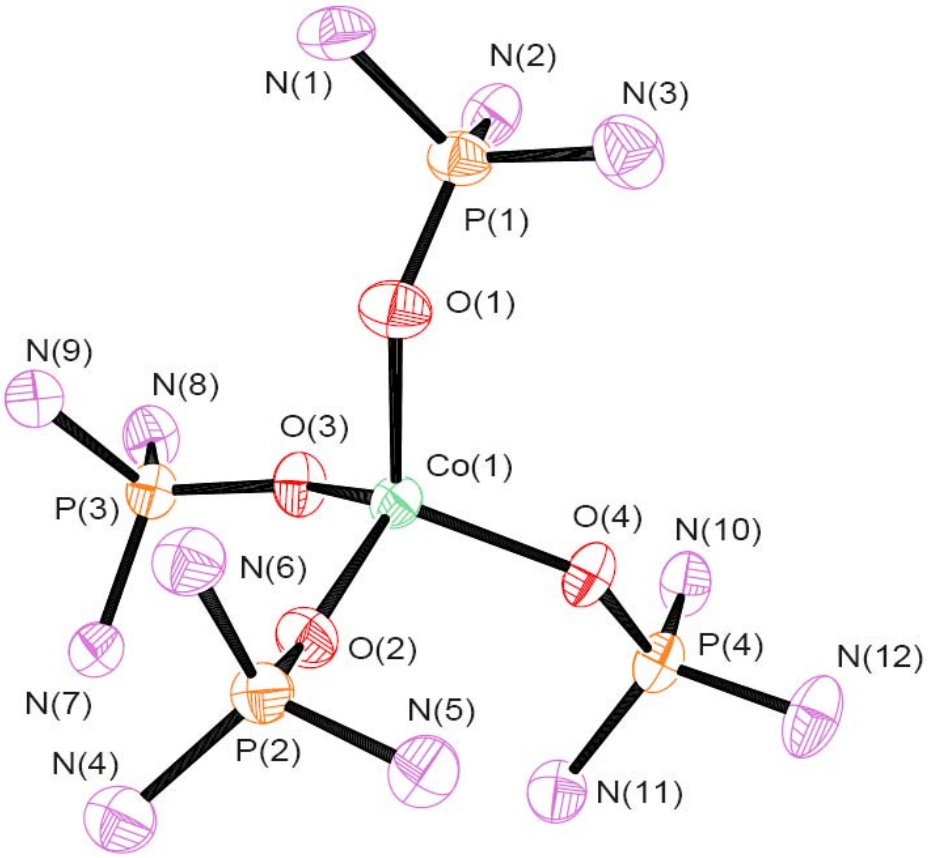

Figure S1. ORTEP drawing of $[Co(HMPA)_4]^{2+}$ in BF_4^- salt showing 50% probability displacement ellipsoids. Methyl groups on N of HMPA were omitted for clarity. Selected bond lengths [Å] and angles [°]: Co(1)–O(1) 1.938(5), Co(1)–O(2) 1.950(5), Co(1)–O(3) 1.945(5), Co(1)–O(4) 1.953(5); O(1)–Co(1)–O(2) 104.0(2), O(1)–Co(1)–O(3) 108.5(2), O(1)–Co(1)–O(4) 113.8(2), O(2)–Co(1)–O(3) 116.7(2), O(2)–Co(1)–O(4) 106.9(2), O(3)–Co(1)–O(4) 107.2(2). $C_{24}H_{72}B_2CoF_8N_{12}O_4P_4$, M_W = 949.35, 0.40×0.54×0.48 mm^3, orthorhombic, *Pbca*, a = 20.74(3), b = 17.03(3), c = 25.84(4) Å, V = 9127(21) $Å^3$, Z = 8, ρ_{calcd} = 1.382 $Mg \cdot m^{-3}$, μ = 0.593 mm^{-1}, Mo-Kα irradiation, λ = 0.71073 Å, T = 123 K, 76755 reflections, 10183 independent, R_{int} = 0.0564, R_1 = 0.1325 ([$F^2 > 2\sigma(F^2)$]), wR_2 = 0.2939 (all data), GOF = 1.320, Θ = 3.03 to 27.48°. $\Delta\rho_{max}$ = 1.030, $\Delta\rho_{min}$ = –0.730 $e^- \cdot Å^{-3}$.

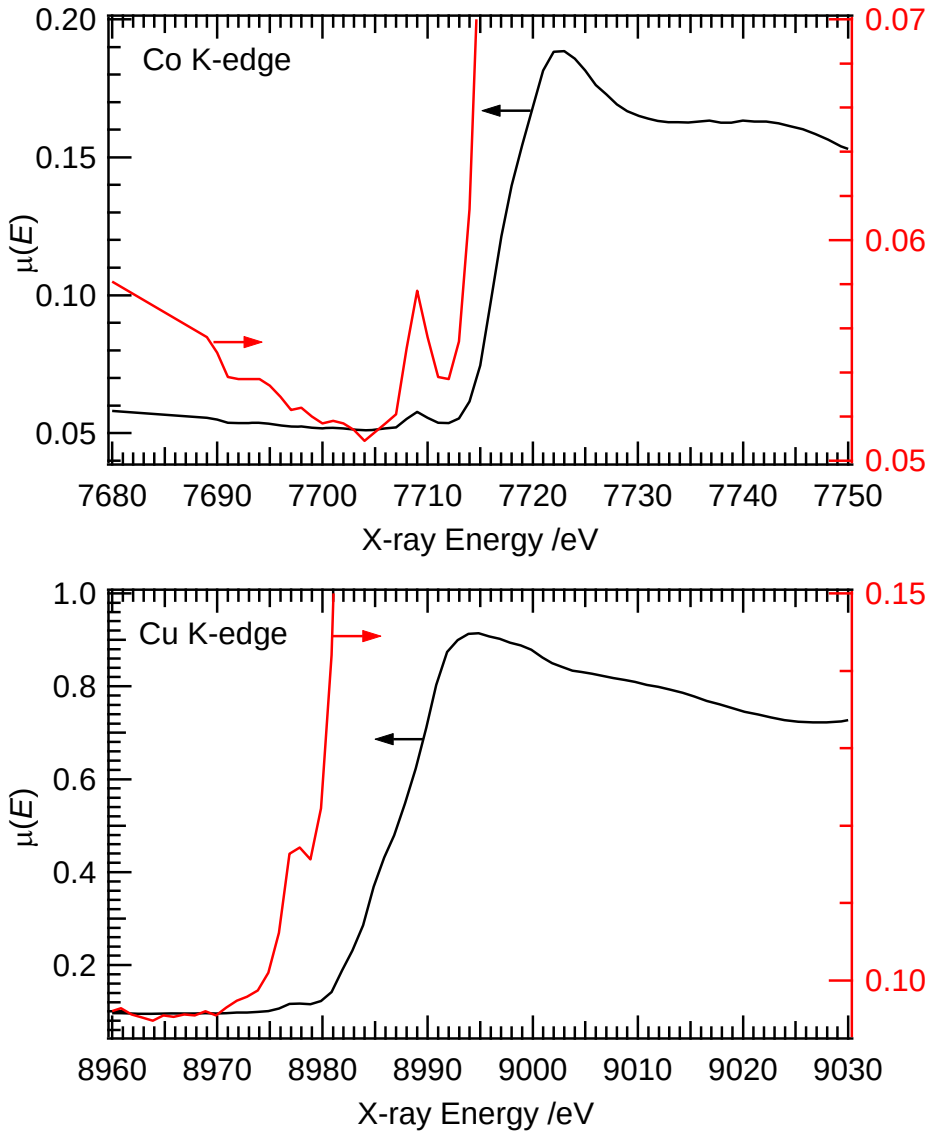

Figure S2. XANES regions in X-ray absorption spectra of Co^{2+} (top, 3.3×10^{-2} M) and Cu^{2+} (bottom, 3.8×10^{-2} M) in [emim]BF_4.

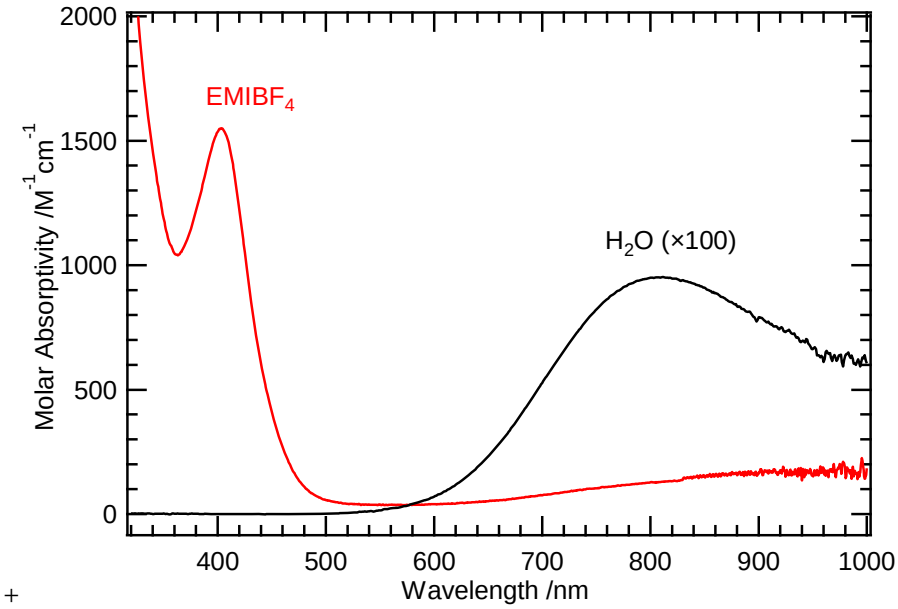

Figure S3. UV-vis absorption spectra of Cu^{2+} in H_2O (black) and [emim]BF_4 (red). The ε axis of the spectra of the H_2O solution was scaled in 100 times.

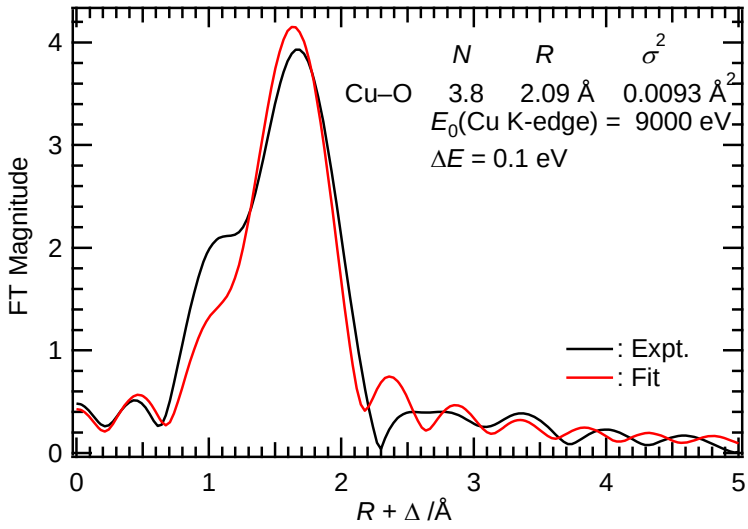

Figure S4. Fourier transformed k^3-weighted Cu K-edge EXAFS spectrum of Cu^{2+} (3.8×10^{-2} M) in [emim]BF_4.

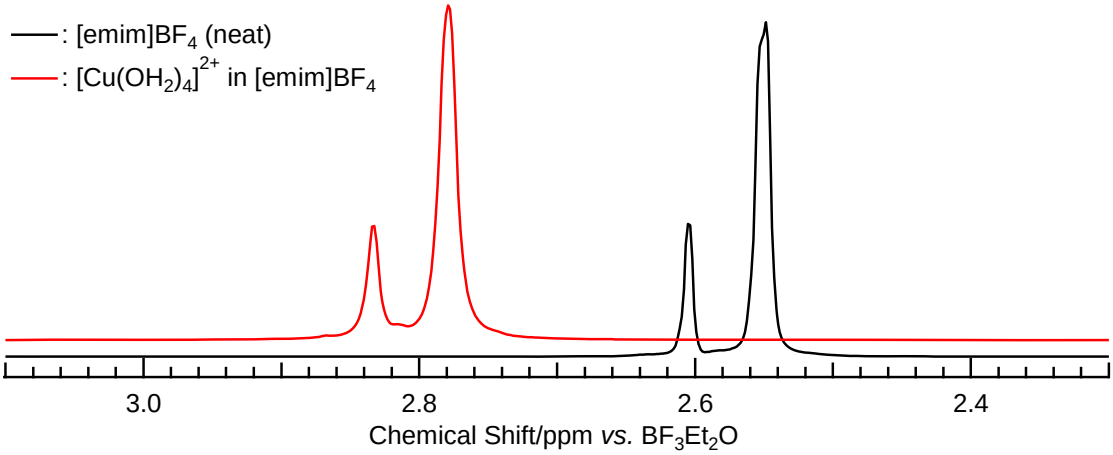

Figure S5. ^{19}F NMR spectra of [emim]BF_4 solution in presence and absence of $[Cu(OH_2)_4]^{2+}$ (3.8×10^{-2} M) at 295 K.

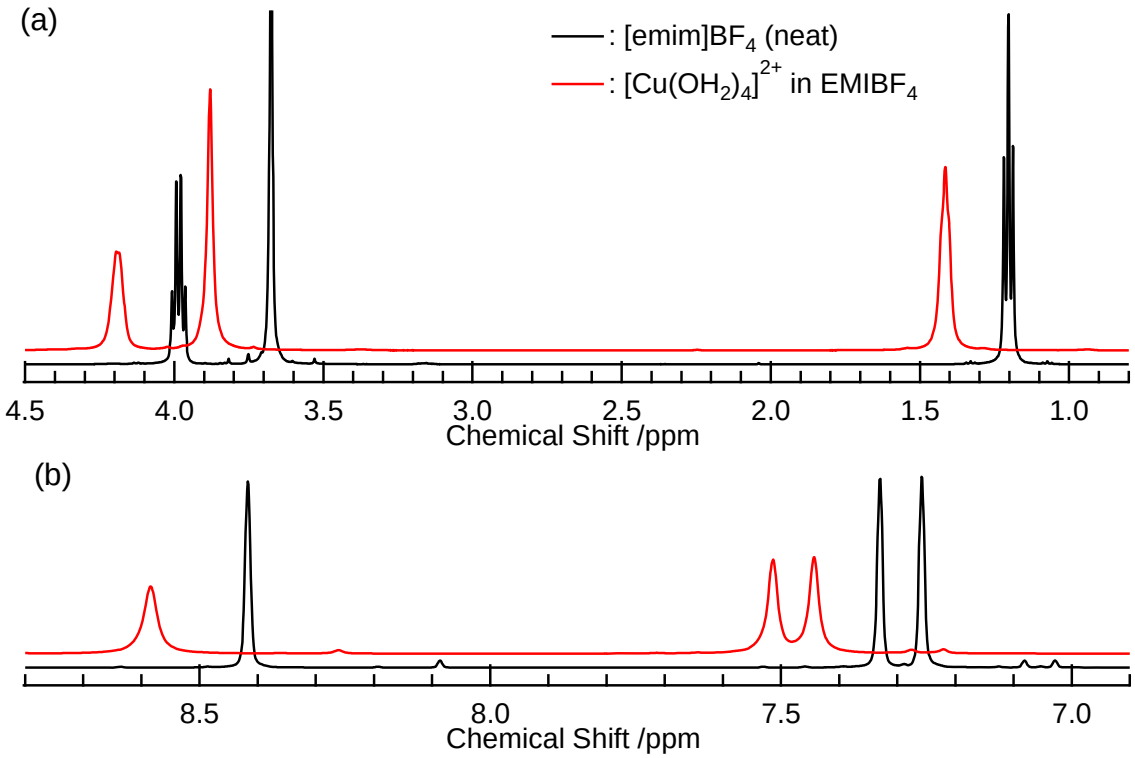

Figure S6. ^{1}H NMR spectra of [emim]BF_4 solution in presence and absence of $[Cu(OH_2)_4]^{2+}$ (3.8×10^{-2} M) at 295 K. Chemical shift range: 0.8-4.5 ppm (a), 6.9-8.8 ppm (b).