MS22-P06 | Insights into the Origin of Magnetic Anisotropy in Linear Iron Complexes from the Experimental Electron Density

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In 2013, Zadrozny *et al*. [1,2] discovered zero-field slow magnetic relaxation and hysteresis for the linear iron(I) complex $[Fe(C(SiMe_3)_3)_2]^-$, which has one of the largest spin-reversal barriers reported for mononuclear transition-metal single-molecule magnets. Theoretical calculations suggested that the magnetic anisotropy is due to pronounced stabilization of the iron $3d_z{}^2$ orbital in this complex compared to the neutral iron(II) complex $Fe(C(SiMe_3)_3)_2$ [3]. Experimental support for this interpretation has however remained lacking. In the present study[4], we have determined the experimental electron density from high-resolution single-crystal X-ray diffraction data in $Fe(C(SiMe_3)_3)_2]^-$ and $Fe(C(SiMe_3)_3)_2$, which shows that the $d_z{}^2$ orbital is indeed more populated in $Fe(C(SiMe_3)_3)_2]^-$ than in $Fe(C(SiMe_3)_3)_2$. This can be interpreted as arising from a greater stabilization of the $d_z{}^2$ orbital in $Fe(C(SiMe_3)_3)_2]^-$ than in $Fe(C(SiMe_3)_3)_2$, thus providing unprecedented experimental evidence for the origin of magnetic anisotropy in $[Fe(C(SiMe_3)_3)_2]^-$ and the corresponding slow magnetic relaxation.

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