

MISCELLANEOUS CRYSTAL STRUCTURES

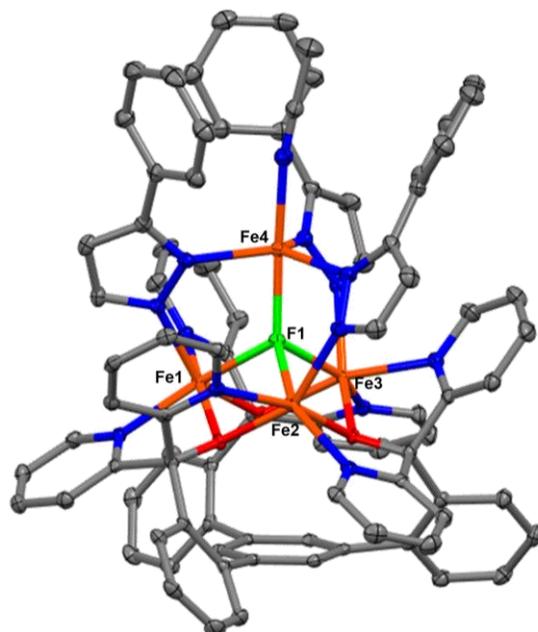


Figure 1. Structure of [LFe₃F(PhPz)₃Fe(MeCN)][OTf], obtained via recrystallization of [LFe₃F(PhPz)₃Fe][OTf] in MeCN/Et₂O vapor diffusion.

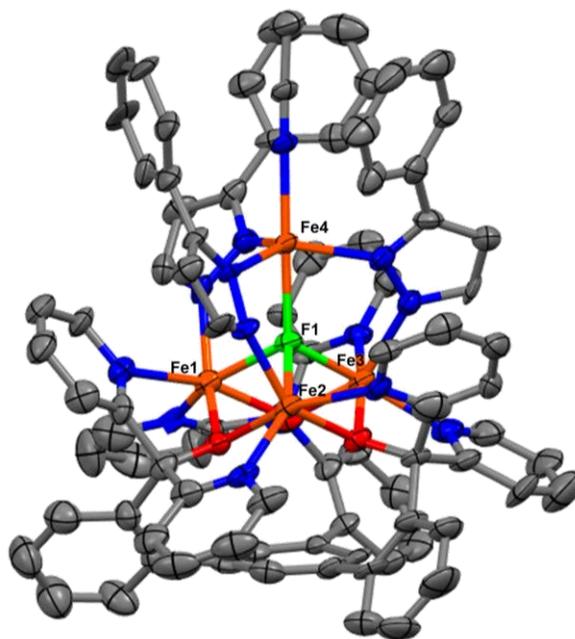


Figure 2. Structure of [LFe₃F(PhPz)₃Fe(MeCN)][OTf]₂, obtained via recrystallization of [LFe₃F(PhPz)₃Fe][OTf]₂ in MeCN/Et₂O vapor diffusion.

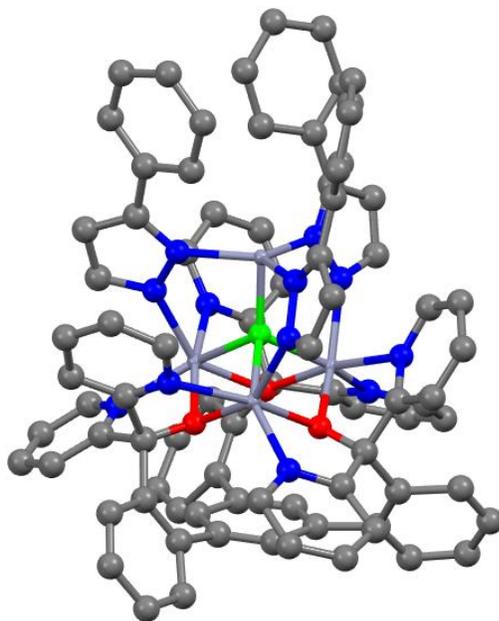


Figure 3. Structure of $[LM_3F(PhPz)_3M][OTf]$, from $LZn_3(OTf)_3$ and $Fe(N(SiMe_3)_2)_2$. The occupancies of the metals are similar at each site: $\sim 130\%$ Fe and $\sim 105\%$ Zn. This is rationalized as Fe scrambling to each position in the cluster.

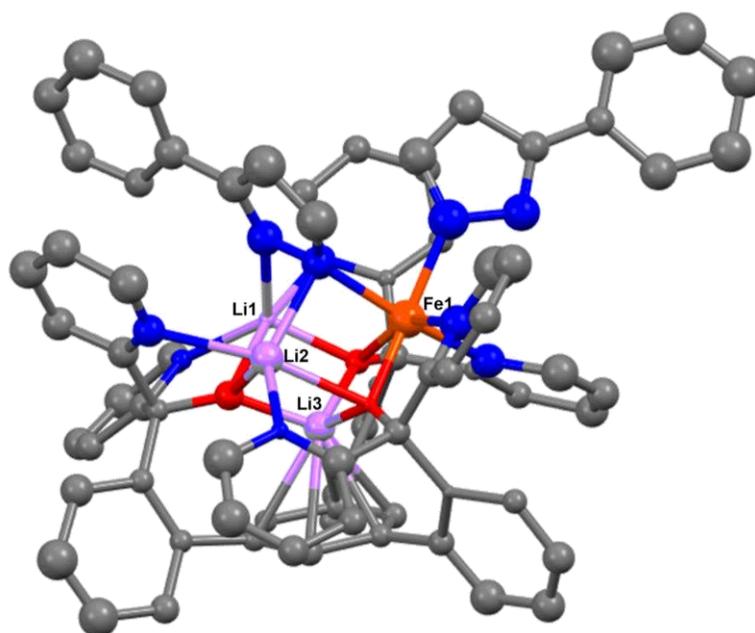


Figure 4. Structure of $LLi_3Fe(PhPz)_2$ (tentative assignment), obtained as a decomposition product of $[NEt_4][Fe_4N_2Cl_{10}]$ (Bennett, et al. *J. Am. Chem. Soc.* **127**, 12378), $KPhPz$, and LLi_3 in THF. The Et_2O soluble product is pink, and gives this structure.

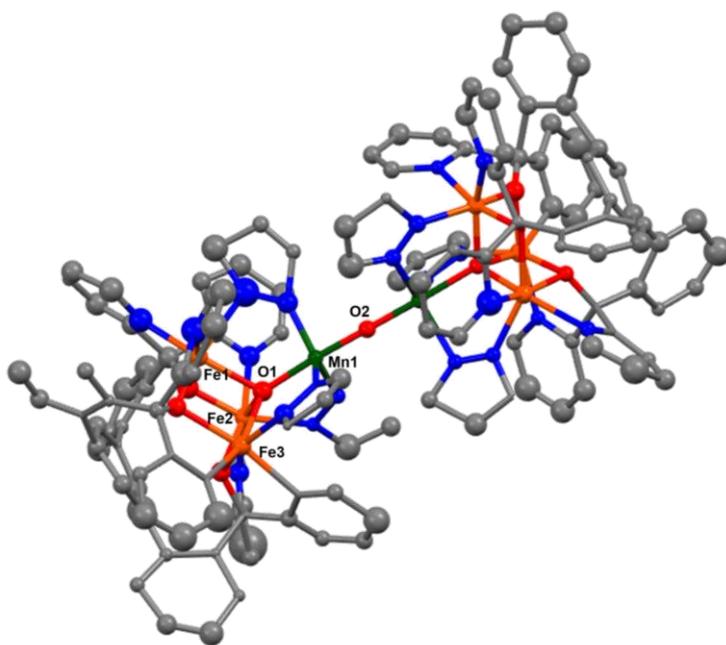


Figure 5. Structure of $[(LFe_3O(Pz)_3Mn)_2O][OTf]_2$, obtained from decomposition of $[LFe_3O(Pz)_3Mn(OH)][OTf]$.

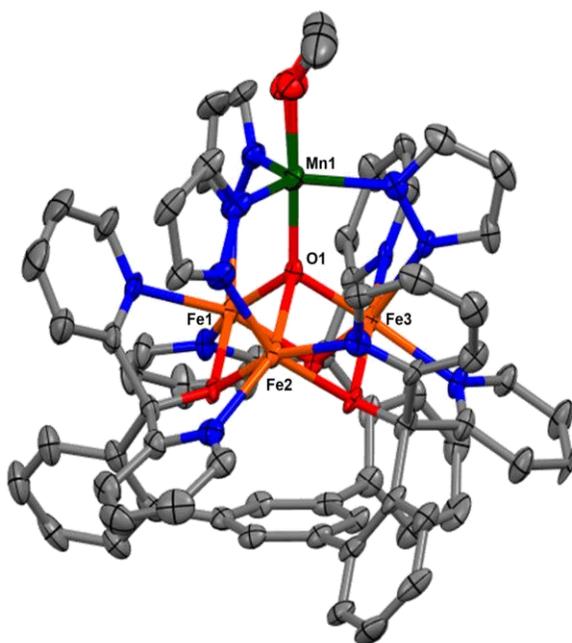


Figure 6. Structure of $[LFe_3O(Pz)_3Mn(OMe)][OTf]$, obtained from addition of methanol solution of sodium methoxide to $[LFe_3O(Pz)_3Mn][OTf]_2$.

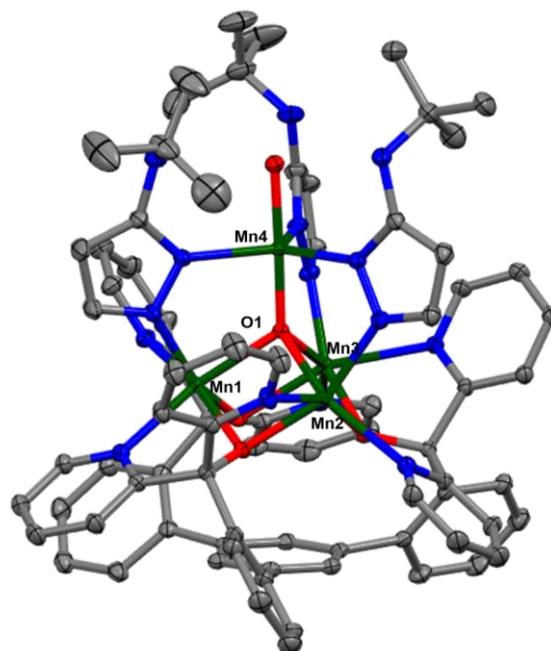


Figure 7. Structure of $\text{LMn}_3\text{O}(\text{PzNHtBu})_3\text{Mn}(\text{OH})$, obtained from the same synthetic route as $\text{LFe}_3\text{O}(\text{PzNHtBu})_3\text{Fe}(\text{OH})$, starting from LMn_3OTf_3 and $\text{Mn}(\text{OTf})_2 \cdot 2 \text{MeCN}$.

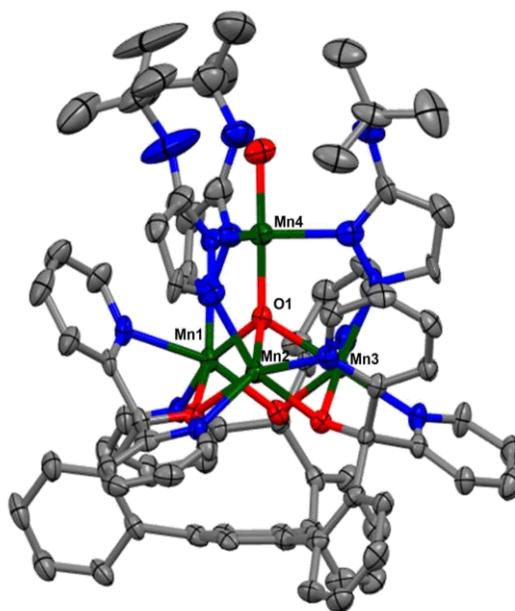


Figure 8. Structure of $[\text{LMn}_3\text{O}(\text{PzNHtBu})_3\text{Mn}(\text{OH})][\text{OTf}]$, obtained from oxidation of $\text{LMn}_3\text{O}(\text{PzNHtBu})_3\text{Mn}(\text{OH})$ with $[\text{Fc}][\text{OTf}]$.

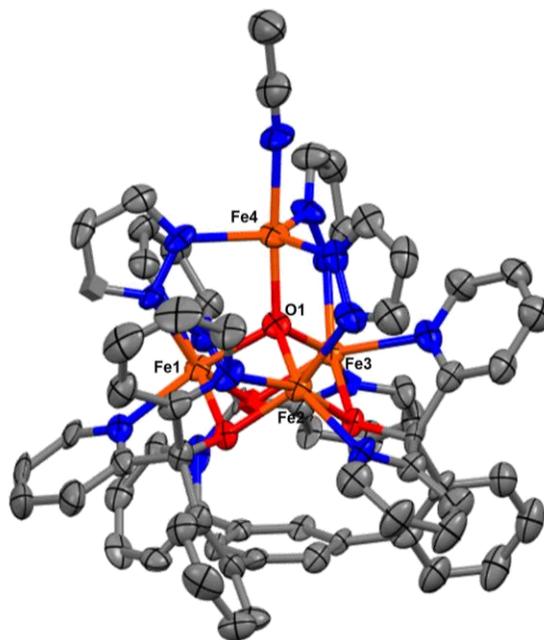


Figure 9. Structure of $[\text{LFe}_3\text{O}(\text{Pz})_3\text{Fe}(\text{MeCN})][\text{OTf}]$, obtained from recrystallization of $[\text{LFe}_3\text{O}(\text{Pz})_3\text{Fe}][\text{OTf}]$ by MeCN/Et₂O vapor diffusion.

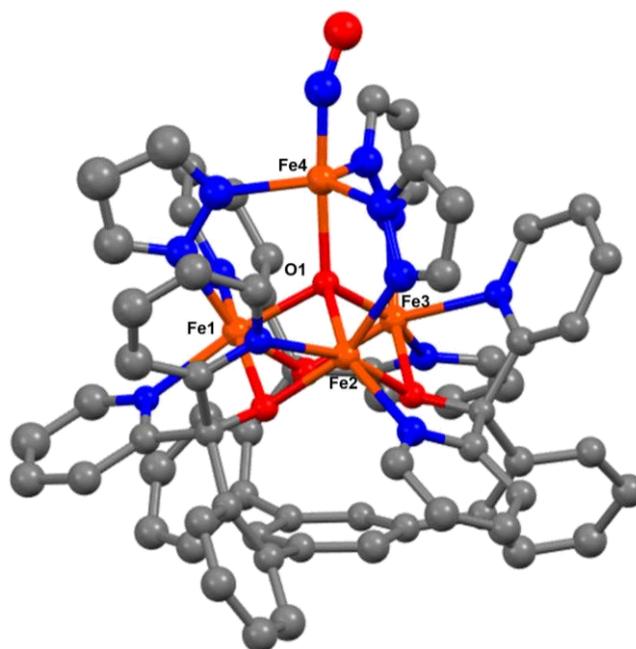


Figure 10. Structure of $[\text{LFe}_3\text{O}(\text{Pz})_3\text{Fe}(\text{NO})][\text{OTf}]_2$, obtained from addition of one equivalent NO gas to $[\text{LFe}_3\text{O}(\text{Pz})_3\text{Fe}][\text{OTf}]_2$.

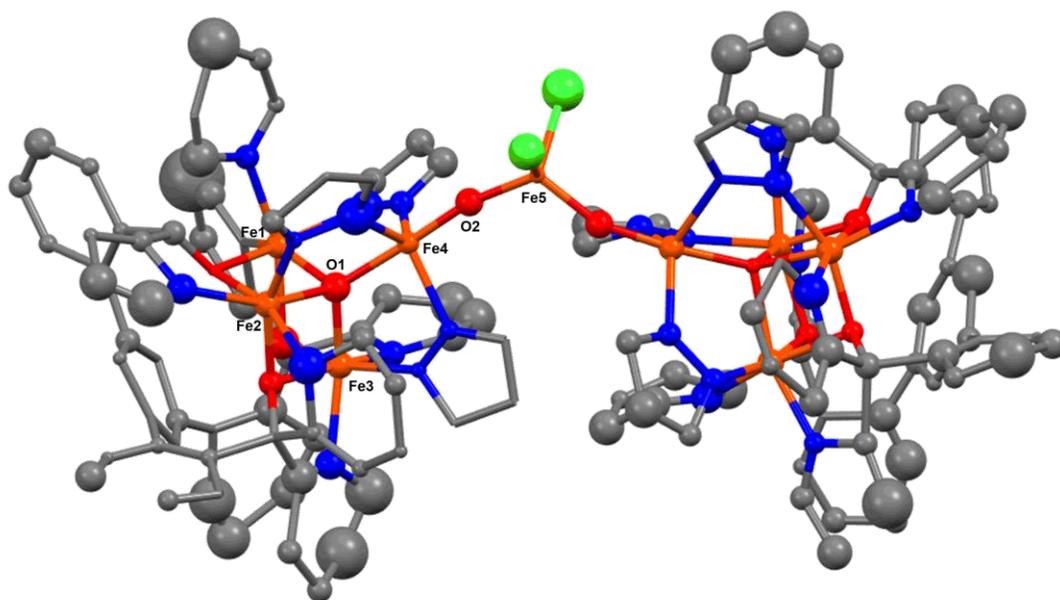


Figure 11. Structure of $[(LFe_3O(Pz)_3FeO)_2FeCl_2]$ (tentative assignment), obtained from addition of one equivalent $[NBu_4][IO_4]$ to $[LFe_3O(Pz)_3FeCl][OTf]$ in THF.

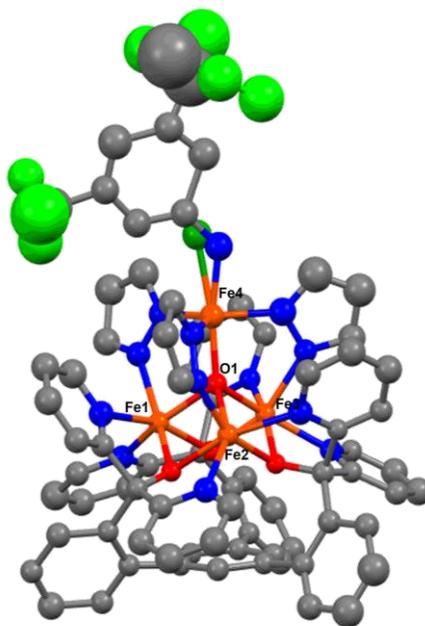


Figure 12. Structure of $[LFe_3O(Pz)_3Fe(NHAr/Cl)][OTf]$ (Ar = 3,5- CF_3 -Ph; ~6:4 amide to chloride), obtained from partial decomposition of the reaction product between $[LFe_3O(Pz)_3Fe][OTf]$ and ArN_3 .

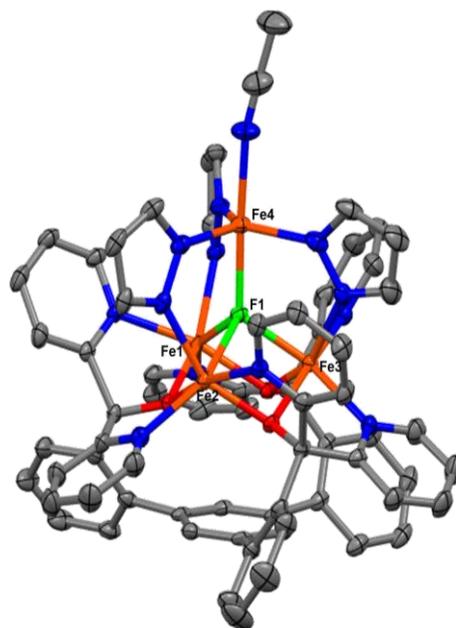


Figure 13. Structure of $[\text{LFe}_3\text{F}(\text{Pz})_3\text{Fe}(\text{MeCN})][\text{OTf}]$, obtained by recrystallization of $[\text{LFe}_3\text{F}(\text{Pz})_3\text{Fe}][\text{OTf}]$ in MeCN/Et₂O vapor diffusion.

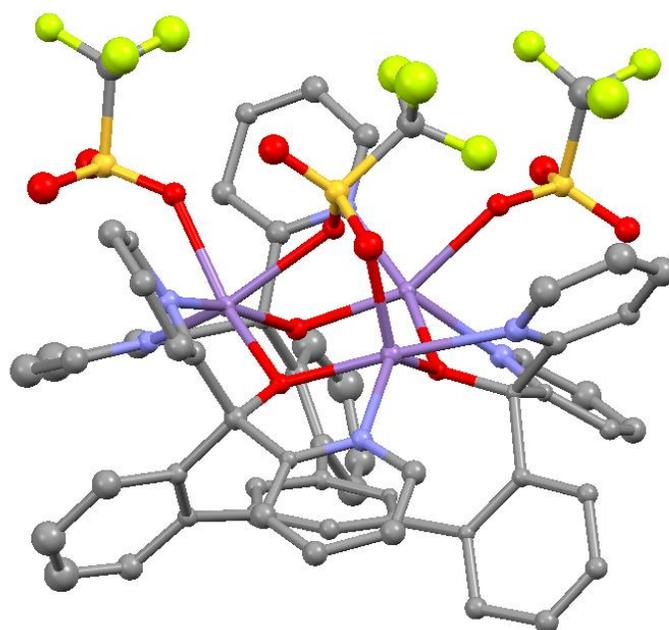


Figure 14. Structure of $\text{LMn}_3(\text{OTf})_3$, obtained by an analogous synthesis to that of $\text{LFe}_3(\text{OTf})_3$ ($\text{LFe}_3(\text{OAc})_3$ and 10 equivalents Me_3SiOTf ; Arnett, et al. *J. Am. Chem. Soc.* **140**, 5569).

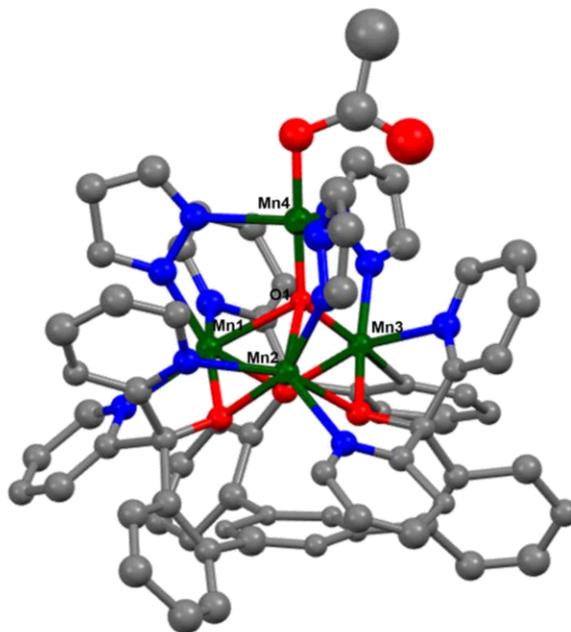


Figure 15. Structure of [LMn₃O(Pz)₃Mn(OAc)][OTf], obtained by an analogous synthesis to that of [LFe₃O(Pz)₃Fe(OAc)][OTf].

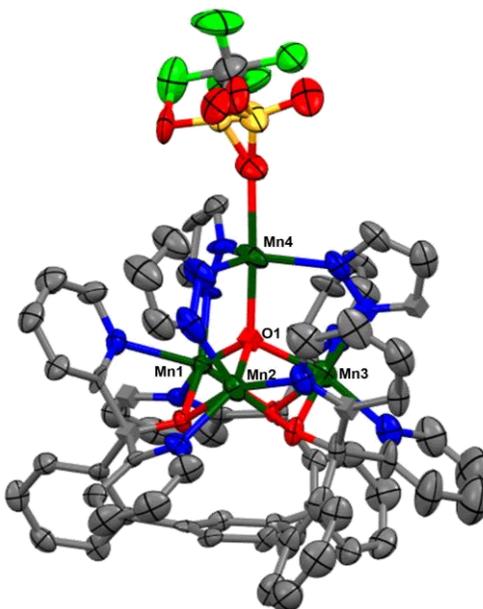


Figure 16. Structure of [LMn₃O(Pz)₃Mn][OTf]₂, obtained by an analogous synthesis to that of [LFe₃O(Pz)₃Fe][OTf]₂.

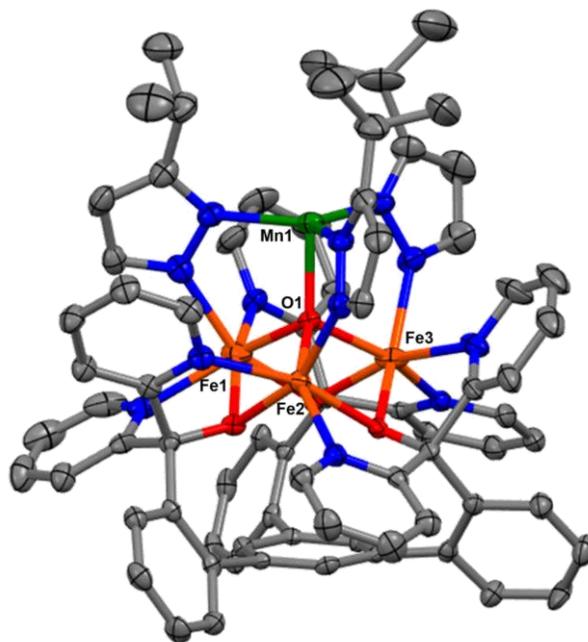


Figure 17. Structure of $[\text{LFe}_3\text{O}(\text{iPrPz})_3\text{Mn}][\text{OTf}]_2$, obtained by addition of KiPrPz , PhIO , and $\text{Mn}(\text{OTf})_2 \cdot 2 \text{MeCN}$ to $\text{LFe}_3(\text{OTf})_3$.

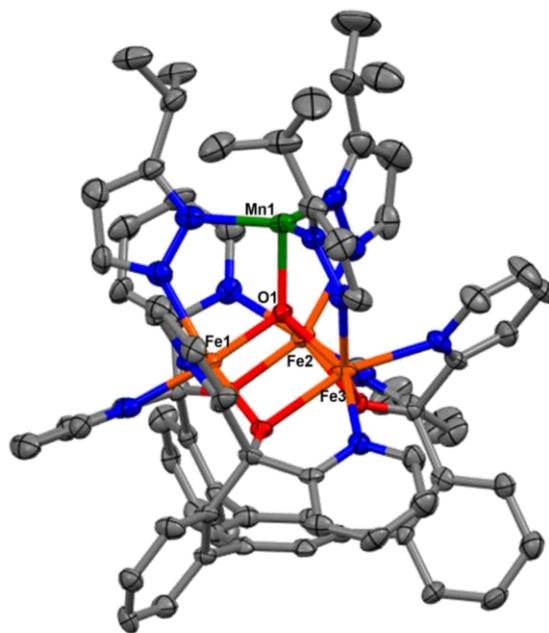


Figure 18. Structure of $[\text{LFe}_3\text{O}(\text{iPrPz})_3\text{Mn}][\text{OTf}]$, obtained by reduction of $[\text{LFe}_3\text{O}(\text{iPrPz})_3\text{Mn}][\text{OTf}]_2$ with CoCp_2 .

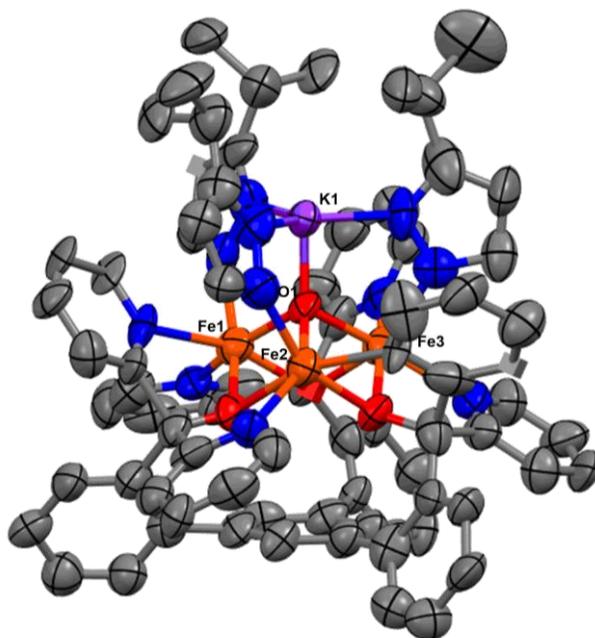


Figure 19. Structure of $[\text{LFe}_3\text{O}(\text{iPrPz})_3\text{K}][\text{OTf}]$, obtained by addition of KiPrPz , PhIO , and $\text{Fe}(\text{OTf})_2$ to $\text{LFe}_3(\text{OTf})_3$. Full metalation of Fe was not observed by NMR, and this byproduct was crystallized out instead of the desired compound.

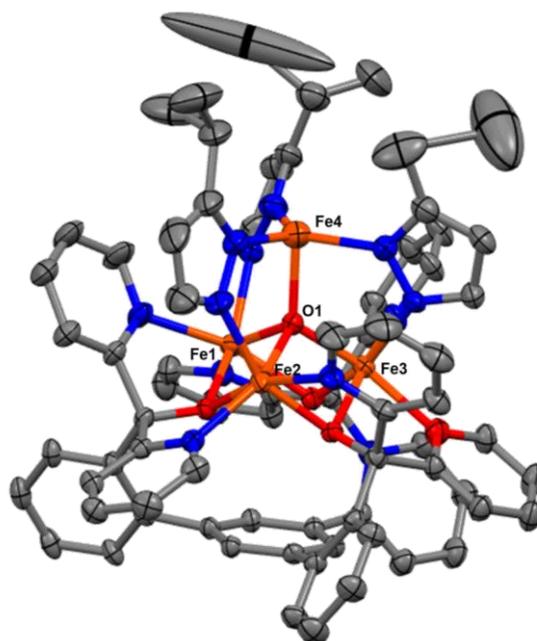


Figure 20. Structure of $[\text{LFe}_3\text{O}(\text{iPrPz})_3\text{Fe}][\text{OTf}]_2$, obtained by addition of KiPrPz , PhIO , and $\text{Fe}(\text{OTf})_2 \cdot 2 \text{MeCN}$ to $\text{LFe}_3(\text{OTf})_3$. Full metalation of Fe was observed with this reagent by NMR.

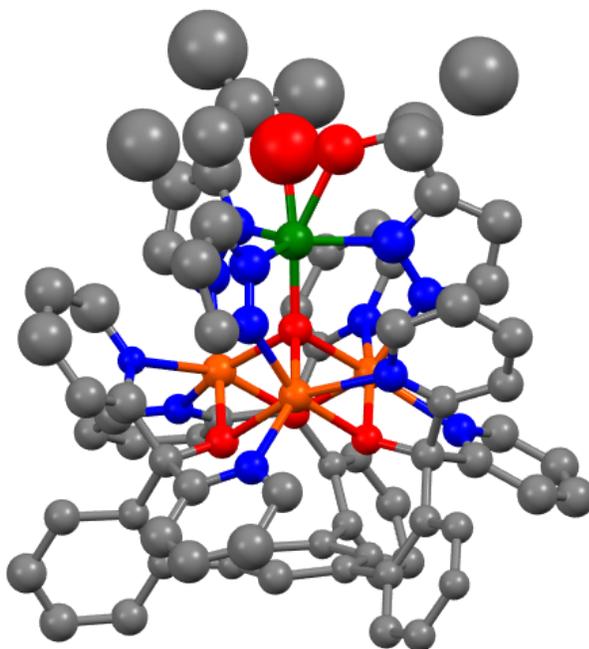


Figure 21. Structures of a mixture of $[\text{LFe}_3\text{O}(\text{iPrPz})_3\text{Mn}(\text{OH})][\text{OTf}]$ and $[\text{LFe}_3\text{O}(\text{iPrPz})_2(\text{OiPrPz})\text{Mn}][\text{OTf}]$ (roughly 50:50; tentative assignments), obtained by addition of (2-tert-butyl-sulfonyl)-iodosylbenzene to $[\text{LFe}_3\text{O}(\text{iPrPz})_3\text{Mn}][\text{OTf}]$.