Supplementary information

The Supplementary Information contains the structures and summaries of the X-ray structures (see attached cif), the Slant Fourier map of the iron-aquo environment indicating the electron density attributed to the protons of the aquo ligand and a histogram of the Fe-OR_2 (ether) distances from the CCDC.

Figure SI1 Slant fourier map of the iron-aquo environment indicating the electron density attributable to the protons on the aquo ligand of complex $[\{Fe(II)(H_2O)L^{1b}\}_2][Fe(III)Cl_4]_2$ **16**.

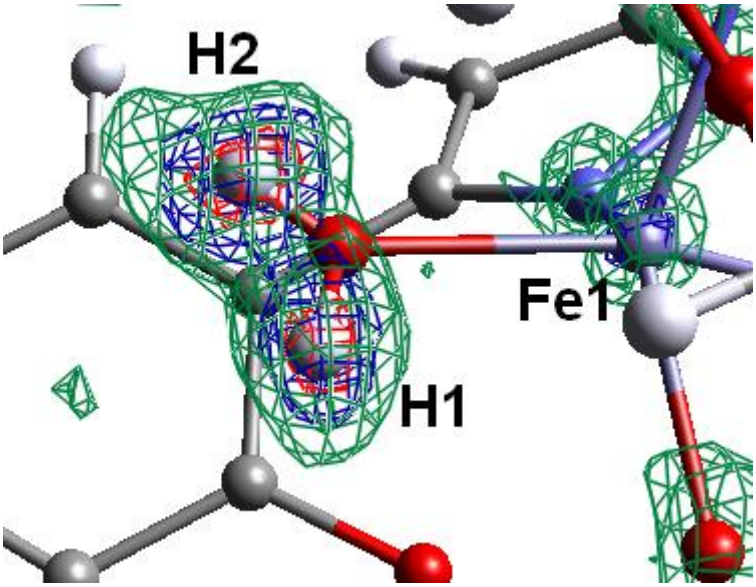
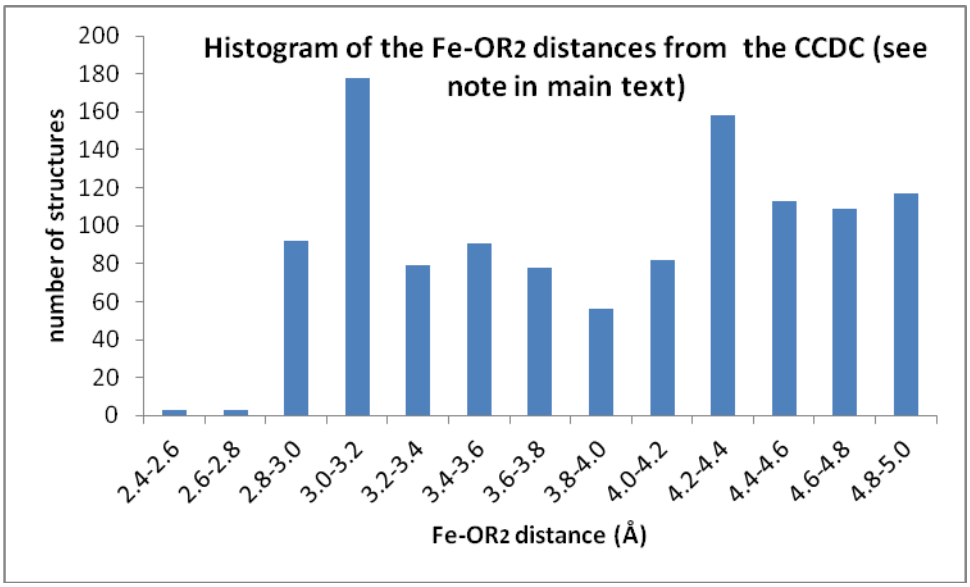


Figure SI2 A histogram of the Fe-OR_2 (metal-ether) distances as found in the Cambridge Crystallographic Data Centre.



Below are Ortep depictions of the single crystal X-ray diffraction data were obtained for compounds **HL^{1b}**, **HL^{1c}**, **4b**, **12**-**22**, **27** and **32** (Fig. SI3-SI18).

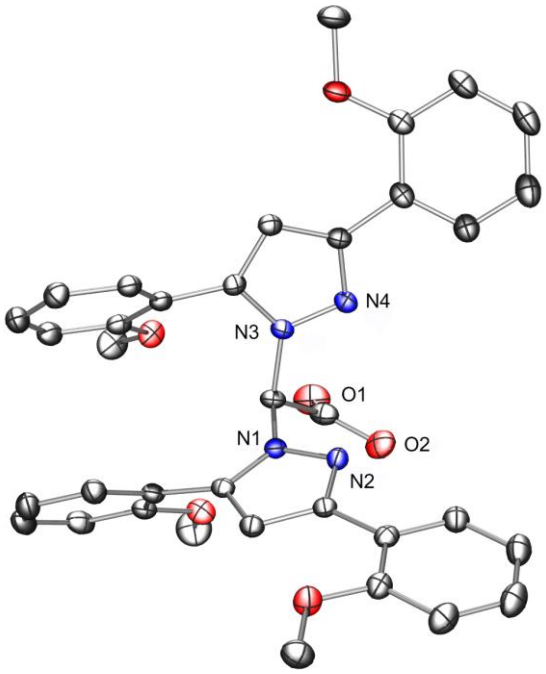


Figure SI3. X-ray crystal structures of ligand **HL**[1b]. Thermal ellipsoids drawn at 50% probability and hydrogen atoms removed for clarity.

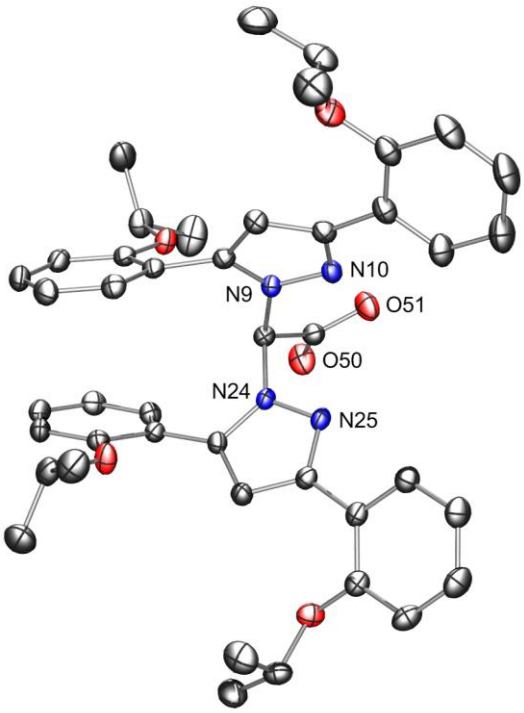


Figure SI4. X-ray crystal structure of ligand **HL**[1c]. Thermal ellipsoids drawn at 50% probability and hydrogen atoms removed for clarity.

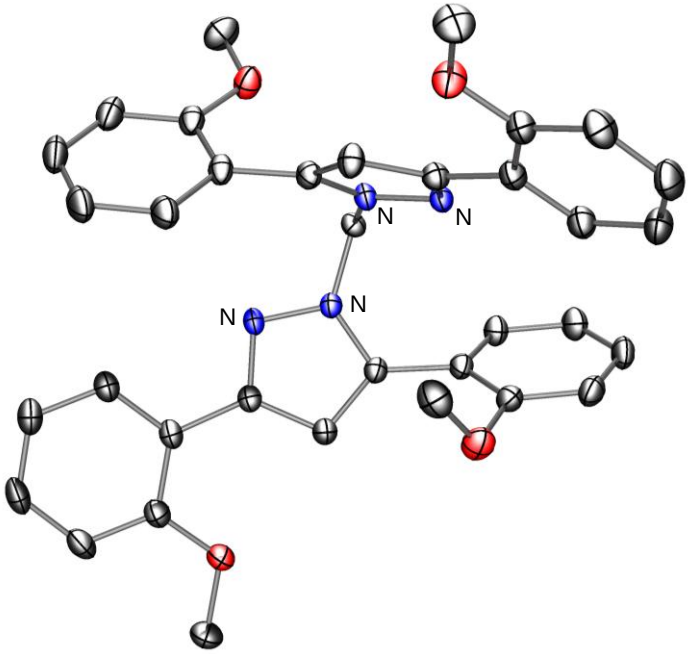


Figure SI5. X-ray crystal structure of bis(3,5-bis(2-methoxyphenyl)-1H-pyrazol-1-yl) **4b**. Thermal ellipsoids drawn at 50% probability and hydrogen atoms removed for clarity.

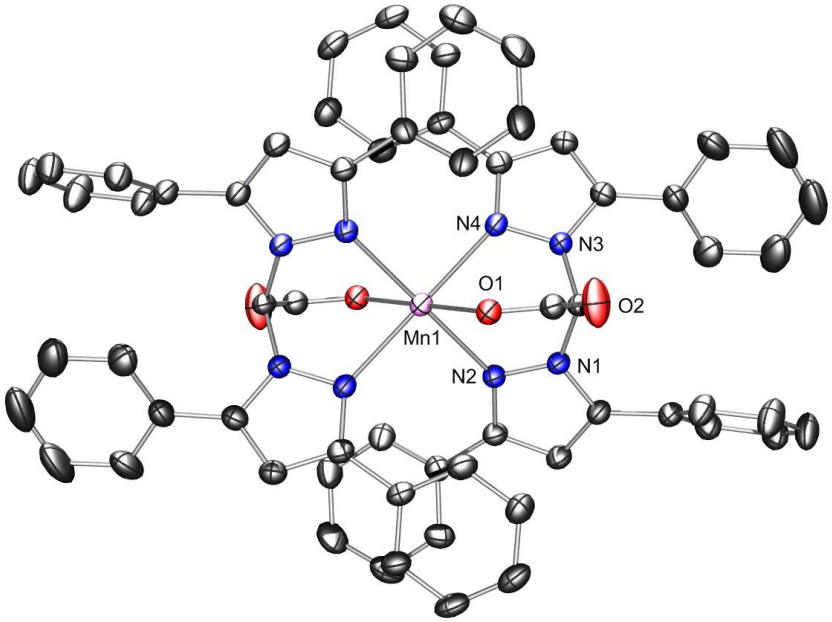


Figure SI6. X-ray crystal structure of complex [Mn(L^{1a})$_2$] **12**. Thermal ellipsoids drawn at 50% probability and hydrogen atoms, solvent and disorder removed for clarity.

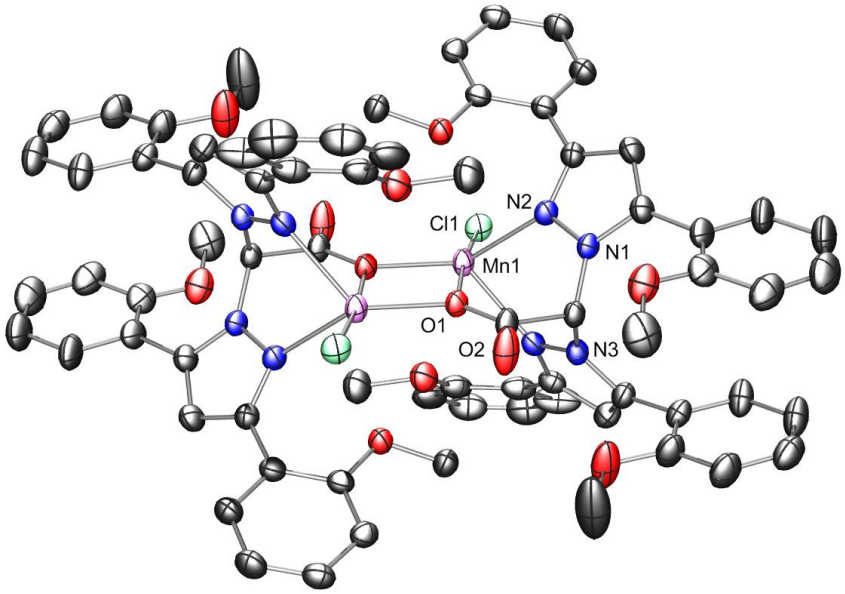


Figure SI7. X-ray crystal structure of complex $[\{MnL^{1b}Cl\}_2]$ **13**. Thermal ellipsoids drawn at 40% probability and hydrogen atoms and solvent removed for clarity.

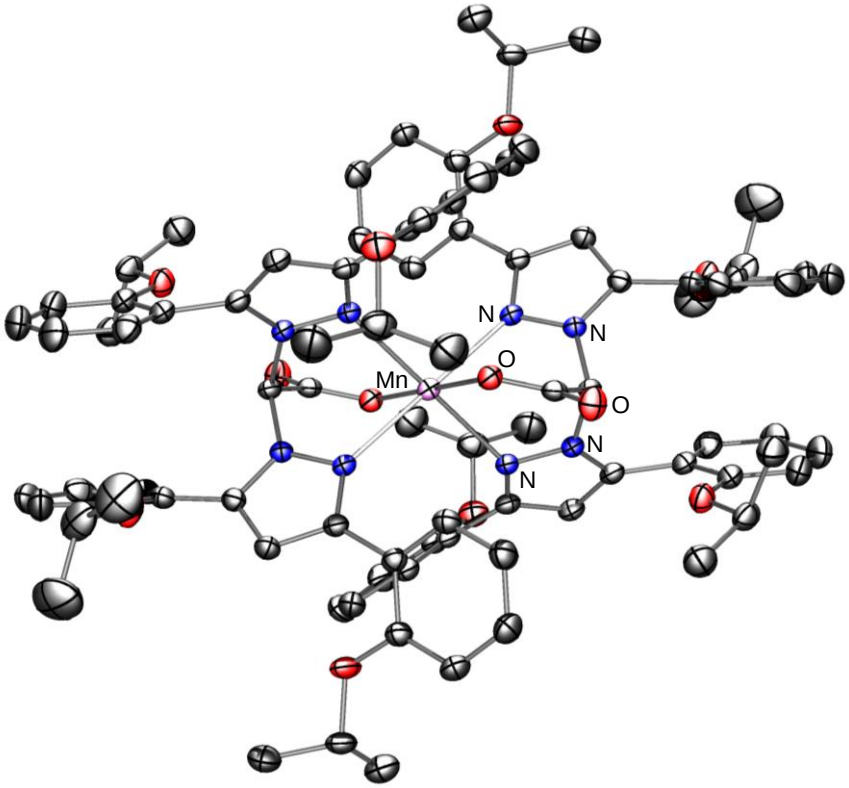


Figure SI8. X-ray crystal structure of complex $[Mn(L^{1c})_2]$ **14**. Thermal ellipsoids drawn at 50% probability and hydrogen atoms, solvent and disorder removed for clarity.

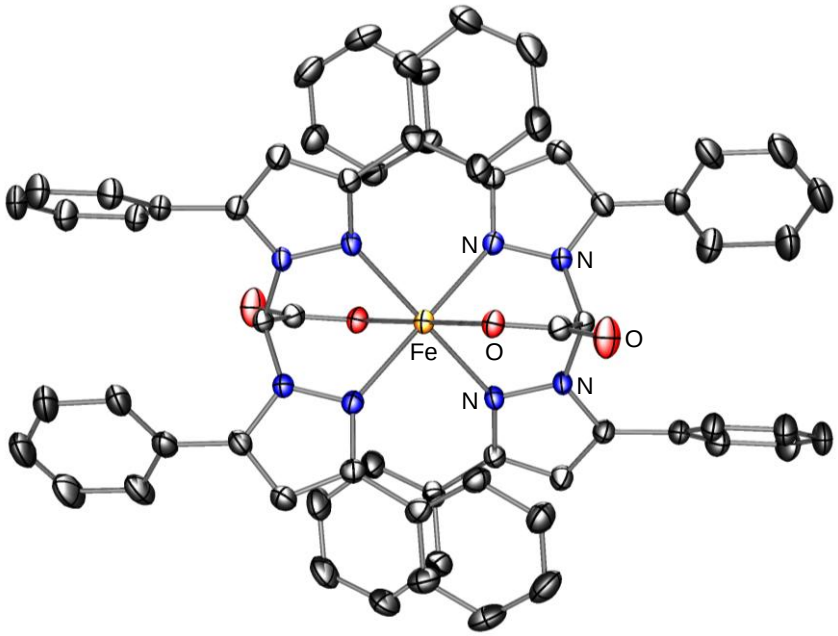


Figure SI9. X-ray crystal structure of complex [Fe(L^{1a})$_2$] **15**. Thermal ellipsoids drawn at 50% probability with the minor component of disorder in a phenyl ring and the hydrogen atoms removed for clarity.

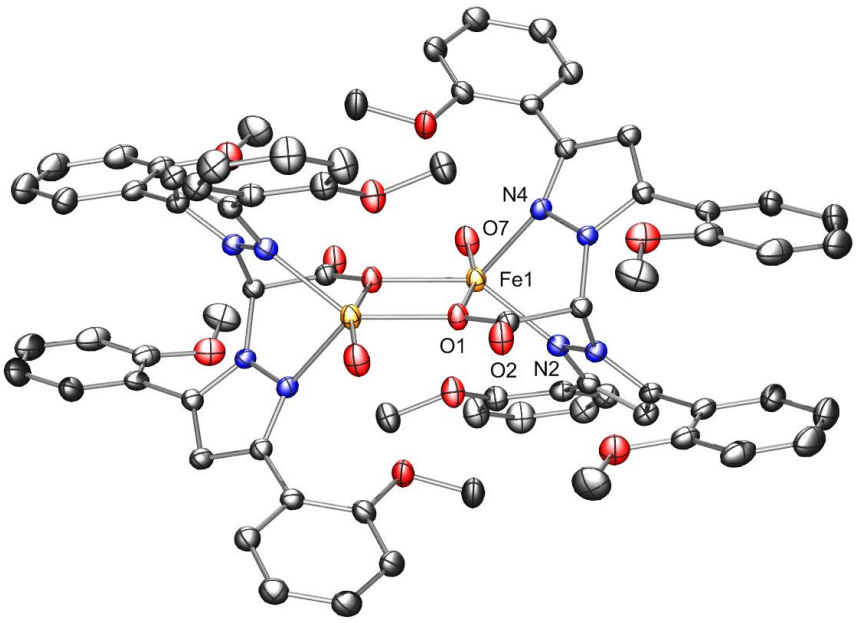


Figure SI10. X-ray crystal structure of complex [{Fe(H_2O)L^{1b}}$_2$][$FeCl_4$]$_2$ **16**. Thermal ellipsoids drawn at 50% probability and hydrogen atoms, solvent and counterions removed for clarity.

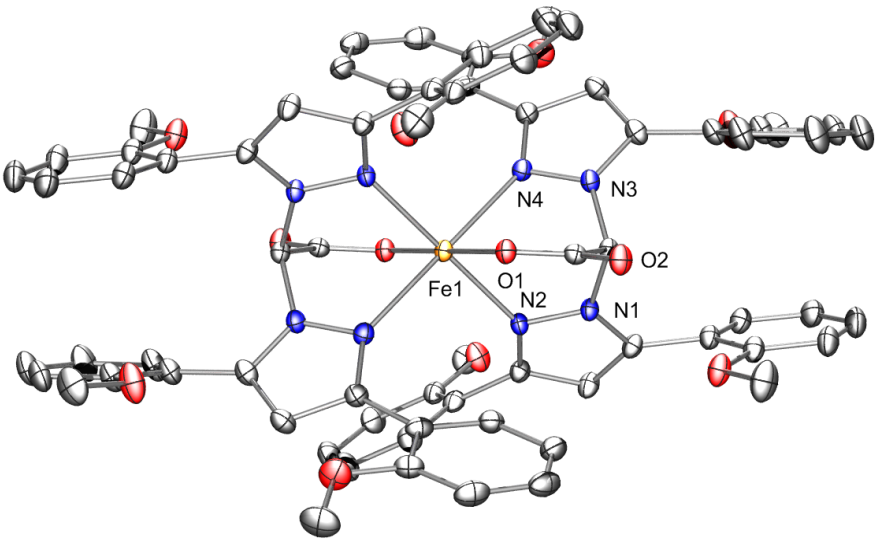


Figure SI11. X-ray crystal structure of complex [Fe(L^{1b})$_2$] **17**. Thermal ellipsoids drawn at 50% probability and hydrogen atoms removed for clarity.

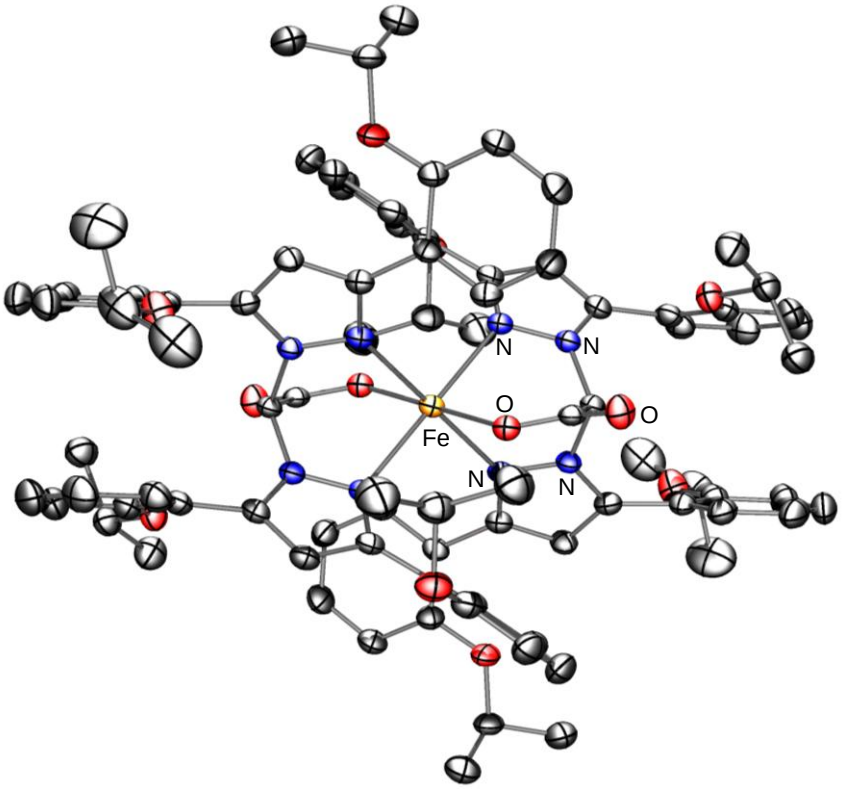


Figure SI12. X-ray crystal structure of complex [Fe(L^{1c})$_2$] **18**. Thermal ellipsoids drawn at 50% probability and hydrogen atoms removed for clarity.

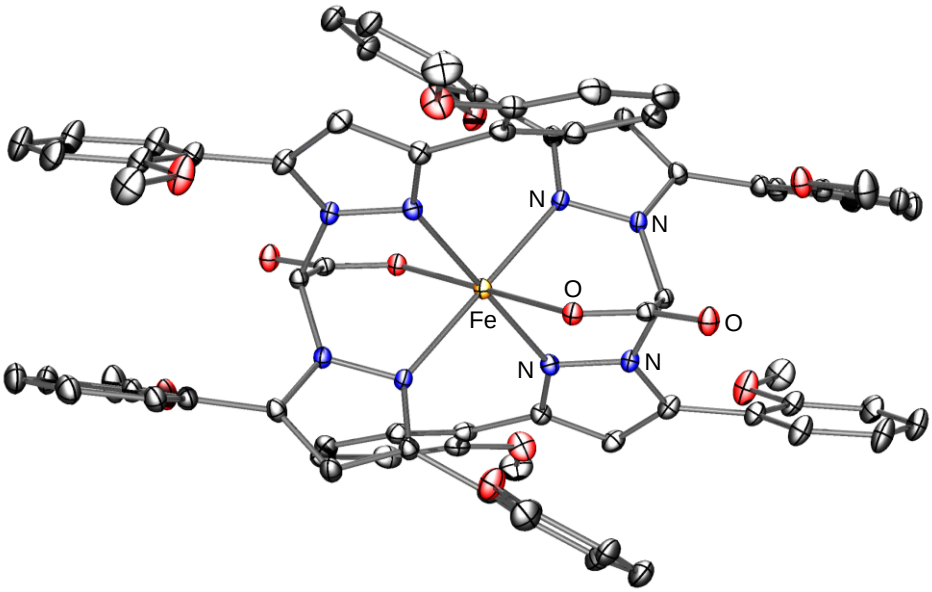


Figure SI13. X-ray crystal structure of complex $[Fe(III)(L^{1b})_2][Fe(III)Cl_4]$ **19**. Thermal ellipsoids drawn at 30% probability and the counterions, solvent and hydrogen atoms are omitted for clarity.

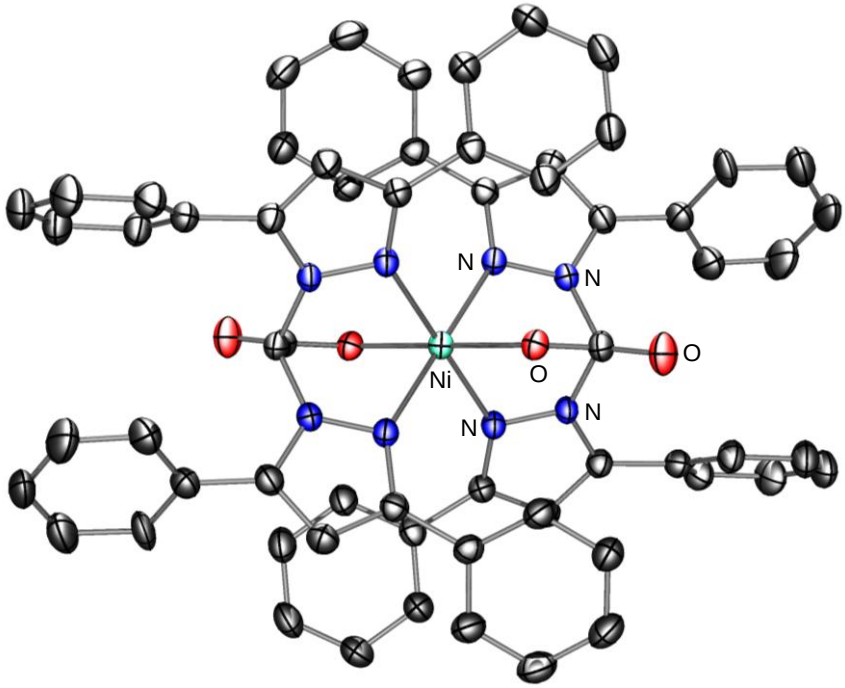


Figure SI14. X-ray crystal structure of complex $[Ni(L^{1a})_2]$ **20**. Thermal ellipsoids drawn at 50% probability with the minor component of disorder in a phenyl ring and the hydrogen atoms removed for clarity.

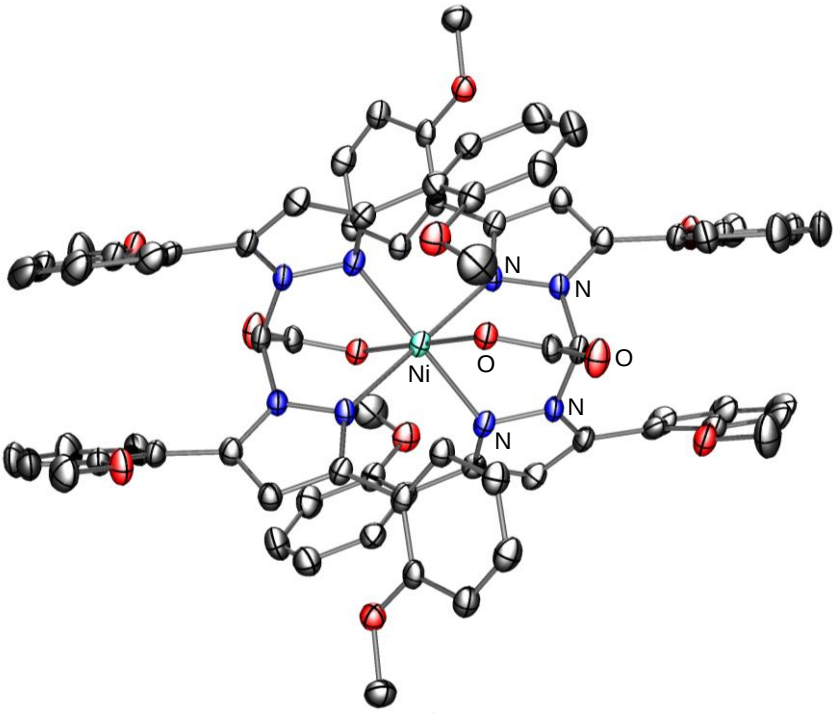


Figure SI15. X-ray crystal structure of complex $[Ni(L^{1b})_2]$ **21**. Thermal ellipsoids drawn at 30% probability with the hydrogen atoms removed for clarity.

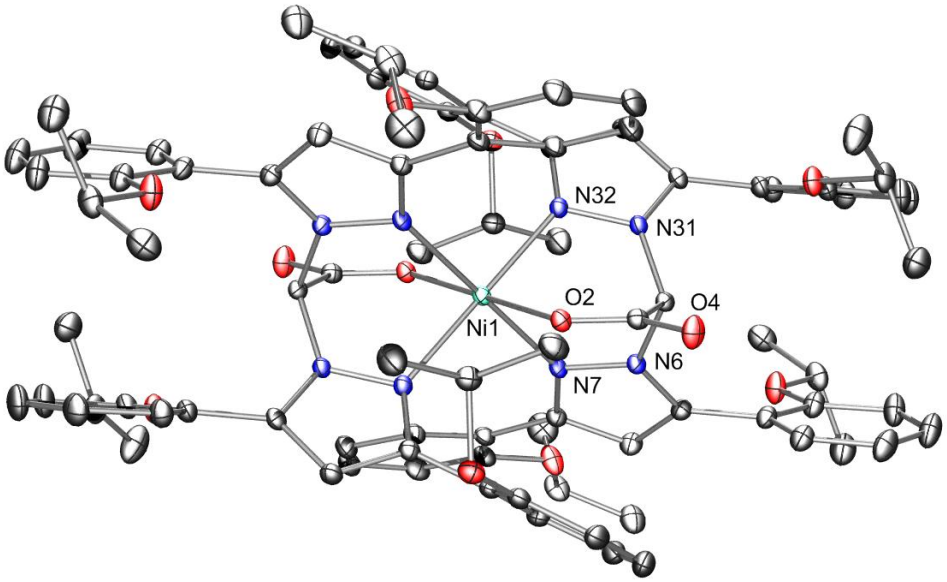


Figure S16. X-ray crystal structure of complex $[Ni(L^{1c})_2]$ **22**. Thermal ellipsoids drawn at 30% probability and the molecule of THF and the hydrogen atoms removed for clarity.

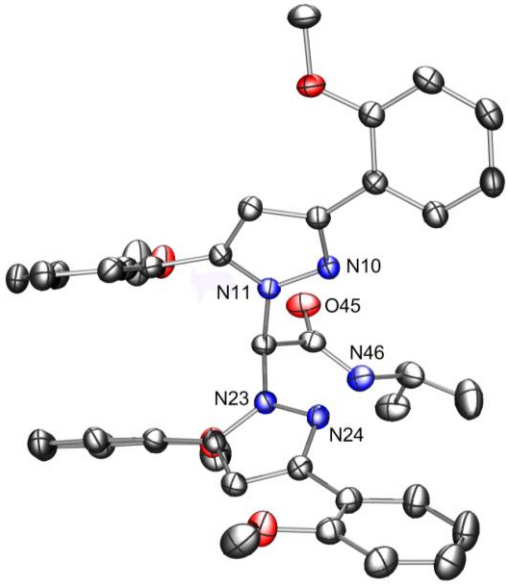


Figure S17. X-ray crystal structure of compound **27**. Thermal ellipsoids at 50% probability and hydrogen atoms and solvent molecules have been removed for clarity.

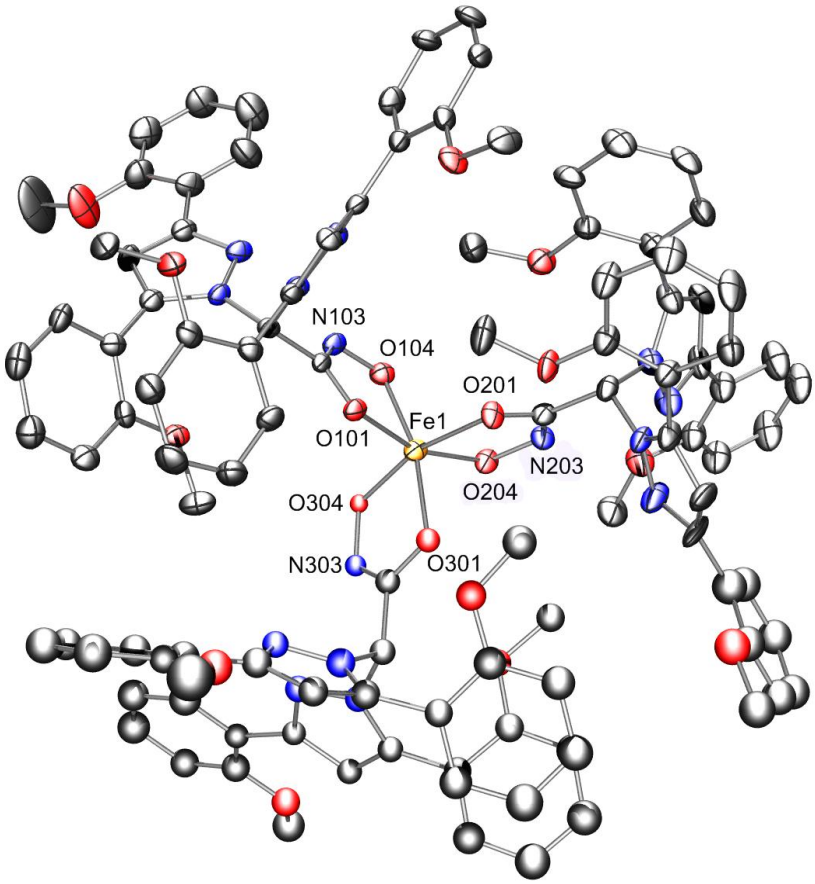


Figure S18. X-ray crystal structure of complex **32**. Thermal ellipsoids at 30% probability and the hydrogen atoms, solvent molecules and the minor component of disorder have been removed for clarity.