Literature discussion of “Proton-Induced Switching of Paramagnetism: Reversible Conversion Between a High and Los Spin CoIII Center Within a Heterobimetallic Core”

A.S. Borovik and co-workers, *J. Am. Chem. Soc.* **2025**, *147*, 3129-3139.

**Introduction:**

1. Look at the general structure of a heterobimetallic compound shown in Fig. 1. The [poat]3- ligand is shown bound to M in the figure. How many Lewis basic sites are present on the [poat]3- ligand? What is the depicted denticity of the ligand in the figure?
2. What is a plausible reason for the difference in ligand denticity and the total number of Lewis basic sites?

**Results:**

1. Scheme 1 shows the synthetic path converting the [CoII(OH)FeIIIpoat]+ to the oxidized [CoIII(OH)FeIIIpoat]2+ and finally to the [CoIII(O)FeIIIpoat]+. For the initial CoIIFeIII structure, give the *dn* and total electron count at each metal center.
2. Based on these electron counts, what might account for the relatively easy oxidation of CoII to CoIII by reaction with AgOTf?
3. Figure 3 shows the x-ray structures for both the [CoIII(OH)FeIIIpoat]2+ and [CoIII(O)FeIIIpoat]+. What are the relative geometries around each metal center? Do they change between structures?
4. Draw out and label the idealized crystal field splitting diagram for both FeIII and CoIII centers.
5. Given that the spin of an unpaired electron is ½, what would be the spin of a metal center with 2 unpaired electrons? Two paired electrons? How many unpaired electrons would be necessary for a metal with S = 2?
6. Based on the *S*Co values reported in Table 2, what spin state does CoIII adopt in both the hydroxo and oxo structures?
7. The *S*tot is the overall spin for both the FeIII and CoIII centers in the molecule. Looking at the reported values, why is *S*tot always less than or equal to *S*Fe? How did the authors confirm this?
8. Figure 6 shows the calculated d orbital energy levels for CoIII for both the bridging OH and O compounds. Describe what occurs to the d orbitals when the bridging OH is deprotonated. What about this change enables the CoIII to switch from a low- to high-spin state in the molecule? Why does this occur?