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The electronic structure of two interconvertible Co (TAML) complexes: "A tour de force in bioinorganic spectroscopy"

Recently, my group contributed to a study that nicely demonstrates the fruitful interplay between spectroscopy and molecular electronic structure theory. In the course of the collaborative work between the eight (!) involved research groups an intense exchange of results and ideas took place until eventually a coherent picture could be obtained. Unfortunately, the fascinating process of how the final picture evolved in view of new results and discussions is beyond the scope of this article and the original published work [1]. On account of the sheer wealth of methods and techniques utilized in this study an anonymous reviewer referred to it as "a tour de force in bioinorganic spectroscopy".

Recent studies suggest that high-valent Co-oxo and -hydroxo species are key intermediates in artificial water oxidation reactions [2] which have a high scientific, societal and economic relevance. However, detailed characterizations of these intermediates under catalytic turnover conditions are difficult to achieve. Alternatively, one may extract information about electronic properties and chemical reactivities from molecular analogues. Yet, high valent, tetragonal metal complexes with a metal oxo double or triple bond involving late transition metals (including Co) are inherently instable, a phenomenon referred to as "oxo-wall" [3]. In a similar way, high-valent Co-hydroxide complexes tend to transform to oxo-bridged clusters. Recently, our experimental collaborators successfully synthesized a Co(TAML)=tetraamido macrocyclic tetraanionic ligand) oxo complex which has a formal Co^{IV} center, thus seemingly violating the "oxo-wall"-concept. Interestingly, the initially blue colored solution of the complex reversibly changes its color to a bright green when cooled down from 253 K to 193 K, indicating a change of the local chemical and electronic structure at the Co center. In light of a series of spectroscopic observations and our computational results, it was hypothesized that the two species involved in the aforementioned equilibrium are in fact [(TAML)Co-OH(LA)] (**1**) and [H(TAML)Co=O(LA)] (**2**) which are shown in Figure 1. Structurally, the two isomers differ in

the protonation site: While **1** is protonated at the oxo ligand, thereby creating a hydroxo moiety, **2** carries the proton at one of its amido groups of the TAML ligand.

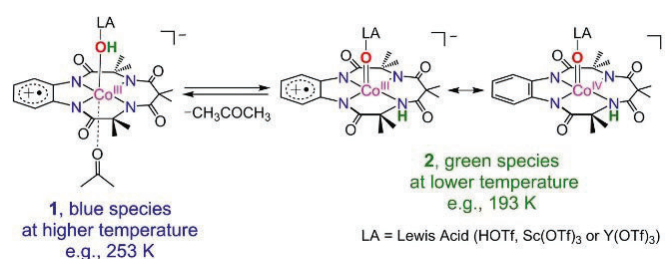


Fig. 1: Proposed structures of complexes **1** and **2** and their equilibrium depending on reaction temperatures. Reprinted with permission from reference [1]. Copyright 2025 American Chemical Society.

The two species **1** and **2** were thoroughly spectroscopically characterized by means of EPR, XANES, EXAFS, MCD, UV/Vis, rRaman and CSI-MS techniques. The spectroscopic data were complemented by reactivity measurements with respect to oxygen transfer (OAT) and hydrogen atom transfer reactions (HAT) as well as quantum chemical calculations conducted by us. For obvious reasons, not all experimental results can be discussed here but only the most intriguing findings will be briefly summarized. The X-band EPR spectrum of **1** yielded a rhombic g -tensor with principal g -values of $g_1 = 2.6011$, $g_2 = 2.1095$ and $g_3 = 2.0268$ which indicates unquenched angular momentum along the molecular z -axis, which roughly coincides with the Co-O bond axis. Previous studies show that such a rhombic g -tensor is observed when the electronic ground state features 'in-state' spin-orbit coupling due to a single hole in the near-degenerate (d_{xz} , d_{yz})-shell [4]. In contrast, however, the MCD spectrum of **1** provides strong evidence for the existence of two degenerate holes in the (d_{xz} , d_{yz}) shell. Obviously, the two experimental observations seem to contradict each other. In case of **2**, evidence from EXAFS and EPR spectroscopy hint towards the existence of a low-spin-Co^{III}=O center with a TAML based radical. Yet, the measured OAT reactivity of **2** strongly indicates that it features significant Co^{IV}=O character. Thus, the experimental evidence is again not entirely coherent calling for a sophisticated theoretical investigation to solve the apparent contradictions.

In agreement with results from EXAFS, our geometry optimizations at the DFT level of theory predict an increase of the average Co-N distance by 0.08 Å and a decrease of the Co-O distance from 2.11 Å to 1.85 Å upon going from **1** to **2**. It should

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be noted that the TAML aliphatic amido nitrogen is the most basic as protonation of that nitrogen is $\approx 19.5 \text{ kcal mol}^{-1}$ more favorable than the protonation of other basic sites.

Despite the relatively flat PES along the axial Co-O bond for both **1** and **2**, the axial ligand critically influences the local electronic structure at the Co center. As illustrated in Figure 2, the square pyramidal ligand field splits the Co d-orbitals according to (d_{xy}) , (d_{xz}, d_{yz}) , (d_z^2) , and $(d_{x^2-y^2})$. Obviously, the identity of the axial ligand, its geometric arrangement and the nature of metal ligand bonding determines the energetic ordering of the orbitals and hence the electronic ground state composition. Furthermore, owing to the redox-active nature of the TAML ligand, **1** and **2** have access to an additional set of low-lying electronic configurations with the Co center in different oxidation states. This assessment agrees with a recent study by Meeus *et al.* in which the electronic ground state of a structurally related Co compound is reported to be highly multiconfigurational [5].

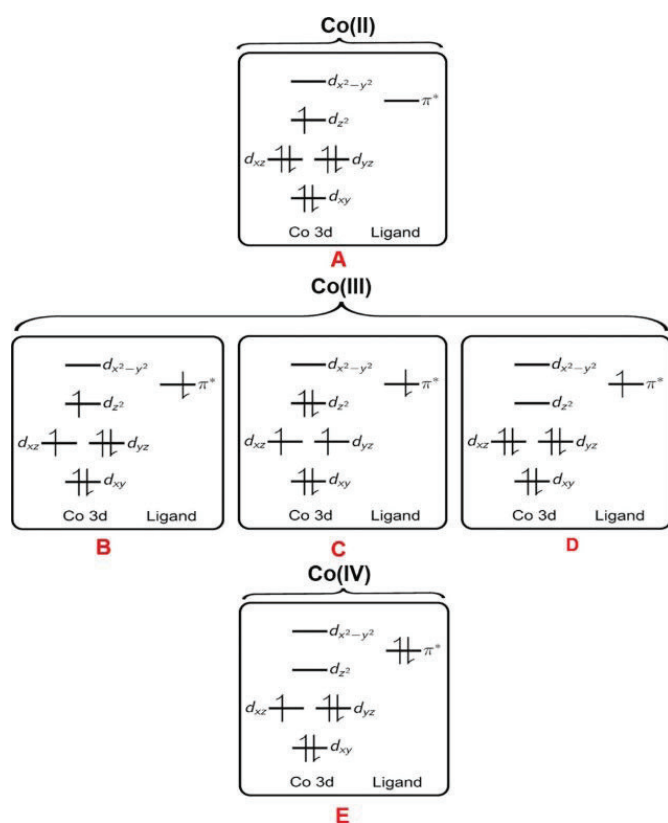


Fig. 2: Important configurations for the discussion of the electronic ground states of **1** and **2**. Reprinted with permission from reference [1]. Copyright 2025 American Chemical Society.

Figure 2 depicts a set of configurations that we found to be important to fully describe the electronic structures of **1** and **2** on the CASSCF+NEVPT2 level of theory. In case of **1**, the electronic ground state has significant contributions from configurations **A** through **C**. The actual composition depends on the axial Co-O bond length. Importantly, while configuration **B** gives rise to computed g -values close to the experimental ones, configuration **C** exhibits the two degenerate holes in the (d_{xz}, d_{yz}) shell that explain the observed MCD signals. Thus, the multiconfigurational character of the electronic ground state as predicted by our calculations allows to conclusively explain all spectro-

scopic data for **1**. In a similar way, our results indicate that the electronic ground state of **2** is dominated by low-spin $\text{Co}^{\text{III}}=\text{O}$ configuration **D** while still having significant contributions from Co^{IV} configuration **E**. For a more detailed description of the multifaceted results of our investigation we refer to the original article [1] and its Supporting Information. In summary, only our combined experimental and theoretical efforts could reveal the intricacies of the complicated electronic structures of **1** and **2** which lead to distinct physical and chemical properties.

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