PhD Thesis Summary

Ab Initio Insights into Molecular Magnetism: A Multireference Study of Transition Metal Complexes

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Introduction and Motivation

Transition metal complexes are central to chemical and biological processes. Magnetic properties of transition metal complexes are a result of their intricate electronic structure. They have open shells, near-degenerate states, and both strong/static and dynamic electron correlation effects. Multireference (MR) methods are required to accurately describe their electronic structure and properties.[1] The complete active space self-consistent field (CASSCF)[2] method is used to treat the static correlation, while the N-electron valence state perturbation theory (NEVPT2)[3] method is a popular choice to treat the dynamic correlation. The quasi-degenerate variant of NEVPT2 (QD-NEVPT2) is used to deal with systems with near-degenerate states.[4] Systems which require large active spaces, which are beyond the capabilities of conventional CASSCF, are treated with approximate full configuration interaction methods which include the density matrix renormalization group (DMRG)[5] and selected configuration interaction (selected CI) methods[6]. In the thesis, these methods were used to study the electronic structure and spectroscopic properties of several transition metal complexes across numerous projects, which are described in the objectives below. This is a brief summary of the work done in the thesis, where exchange coupling and EPR parameters were calculated from first principles.

Objectives

The work in the thesis was done under three projects:

1. The first project involved the study of exchange interactions in copper dimers using multireference methods and broken symmetry coupled cluster theory.[7]
2. The second project was a collaborative theoretical and experimental study of an ambiguous natured cobalt-oxo TAML intermediate.[8]
3. In the final project, a new methodology to evaluate spin-orbit coupling by combining QD-NEVPT2 with selected CI references for calculations of molecular g-tensors, was implemented and tested on benchmark transition metal complex systems.

Key Results and Findings

Magnetic Exchange Coupling in Copper Dimers

In this project, magnetic exchange coupling constants J were calculated for two antiferromagnetically coupled copper dimers shown in Figure 1.[7] Building on Roemelt et al.'s[9] work on Mn complexes, DMRG-SCF and DMRG-NEVPT2 methods were used to study the late transition metal complexes. Compared to Mn complexes, these methods failed to produce accurate results as the dynamic correlation in these Cu dimers required treatment beyond what is captured by second-order perturbations. Difference-dedicated CI (DDCI) methods[10] have shown promising results for Cu systems and were then subsequently

used to treat the dynamic correlation effects on top of a CASSCF calculation with the minimal active space of (2,2). The DDCI3 method, which treats excitations with 3 degrees of freedom, produced excellent results but came at a large computational cost as tight selection thresholds were required. Finally, a new method that combined the use of broken-symmetry with a local implementation of coupled cluster theory (BS-LPNO-CCSD) was also employed.[11] This method was shown to converge to accurate results for a smaller dimer system Cu_2Cl_6, at extremely tight thresholds, making it unsuitable for larger systems like the target Cu dimers.

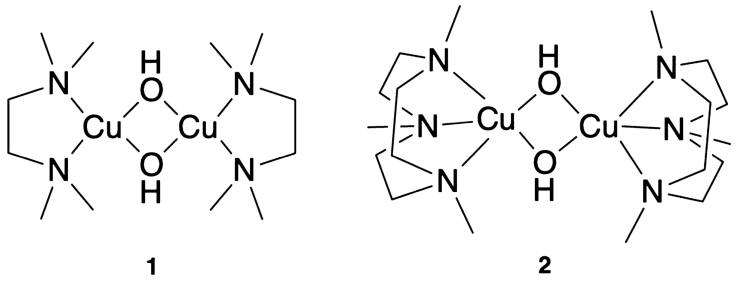

Figure 1: Antiferromagnetically coupled copper dimers.

Electronic Structures of Interconvertible Cobalt-Oxygen TAML Intermediates

Next, the electronic structure of an ambiguous cobalt-oxo TAML intermediate was studied in a collaborative theoretical and experimental study.[8] The theoretical results are presented in the thesis with a brief discussion of the experimental findings. Examples of well-characterized Co-oxo complexes are few, as such complexes are unstable in tetragonal symmetry, a result of the well-known oxo wall phenomenon.[12] Stable complexes of this sort require a non-tetragonal field or Lewis/Brønsted acids to provide a stabilizing interaction. The characterization of a cobalt-oxo TAML complex was open-ended, as some studies showed it had a rhombic g-tensor EPR spectra, while others showed it had an isotropic g-tensor.[8]

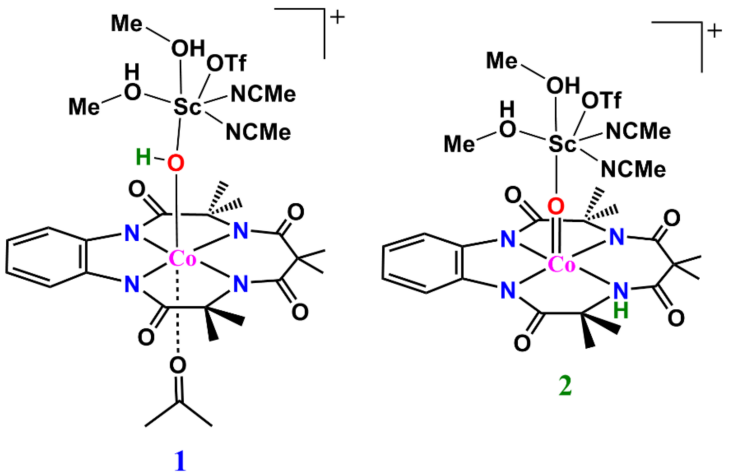

Figure 2: Interconvertible cobalt-oxygen TAML intermediates.

This ambiguity in previous studies was explained by the proposed two interconvertible temperature-dependent tautomers, shown in Figure 2. Through MR CASSCF and NEVPT2 calculations, the electronic structures of the two intermediates were determined,

which were found to be of multiconfigurational character. g-tensors were calculated and compared to the experimental EPR parameters to assess the quality of the calculations. The proposed intermediate **1**, obtained at a higher temperature, was characterized as a blue colored Co−OH specie dominated by configurations with Co(III) character and had a highly anisotropic g-tensor. This intermediate, upon cooling, converted to intermediate **2**, which was a green colored Co−O specie dominated by configurations with Co(III) and Co(IV) character, and had an isotropic g-tensor.

Molecular g-tensors with QD-NEVPT2 using Selected CI References

The last project involved the implementation of a new methodology to evaluate spin-orbit coupling for calculations of molecular g-tensors. To properly evaluate EPR parameters of transition metal complexes, which exhibit strong electron correlation effects and spin-orbit coupling, MR methods are required. Conventional MR methods are limited by accurate treatment of systems with near-degenerate states[13], as well as exponential scaling of cost with increase in the active space size[14].

To address this, a new methodology was implemented to evaluate spin-orbit coupling by combining QD-NEVPT2[4] with selected CI references based on Ugandi and Roemelt's spin-pure heatbath CI (HCI) solver[15]. The new methodology was tested on benchmark transition metal complex systems, shown in Figure 3. The results indicated the importance of the choice of active space, as well as the inclusion of ligand-based orbitals in the active space, requiring the use of the HCI-SCF method, to obtain accurate g-tensor results. Inclusion of dynamic correlation effects with QD-NEVPT2 was shown to be counter-productive as it decreased the numerical accuracy, indicating error cancellations.

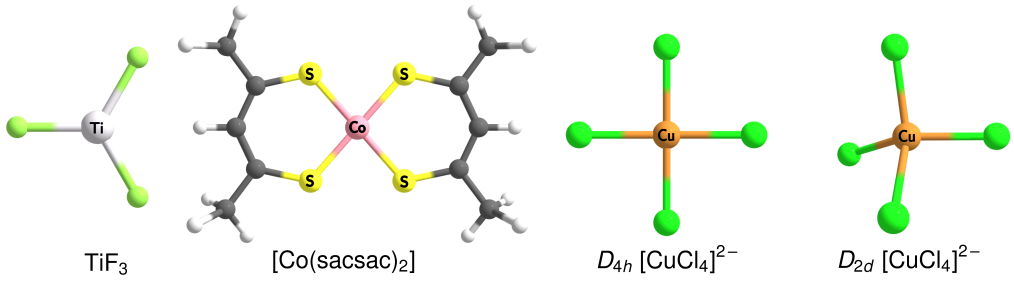

Figure 3: Transition metal complexes for which molecular g-tensors were evaluated using the new methodology.

Conclusions and Outlook

It was shown that to adequately describe the underlying physics of transition metal systems, MR methods are required. Advantages and limitations of different MR approaches were highlighted. In particular, the trade-off between accuracy and computational cost is an ever-present challenge for MR methods. The thesis provides new insights into the electronic structure and magnetic properties of these systems. Effective, albeit costly, methods presented in the work are an interesting avenue for future work.

References

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