Chapter 5

FINISHING REMARKS

Chapters 2, 3 and 4 cover my exploration of hypoelectronic dodecaborate clusters. In Chapter 5, I provide a brief discussion of the results presented in this thesis along with a few words on the current state of dodecaborate research and my concluding thoughts.

Research into hypoelectronic dodecaborates have accelerated rapidly over the past decade. A range of promising applications are being explored, utilizing the strong visible absorption, noncoordinating properties and highly reversible redox behavior of these clusters. In this thesis I have presented an initial experimental foray into the electronic structure of hypoelectronic $[B_{12}(OR)_{12}]$ *clusters. Additionally, I have provided evidence indicating that a previously unknown super-oxidized* $[B_{12}(OR)_{12}]^{1+}$ *species can be isolated. My findings will be briefly discussed below, along with a quick outlook on where to go from here.*

5.1 Current State of Affairs

Over the past decade, there has been a marked increase in the interest for hypoelectronic dodecaborate clusters. Although icosahedral dodecaborate clusters were first isolated about 70 years ago, [1] no hypoelectronic analogues were reported until the late 1990s when the Hawthorne lab first isolated *hypocloso*-$[B_{12}Me_{12}]^{1-}$ (Me = CH_3),[2] *hypocloso*-$[B_{12}(OBz)_{12}]^{1-}$ and *hypercloso*-$B_{12}(OBz)_{12}$ (Bz = $CH_2C_6H_5$).[3] Developments in the years following these initial reports were limited to chemical isolation and electrochemical observation of additional hypoelectronic analogues, including a range of $[B_{12}(OR)_{12}]$ clusters[4] and the perhalogenated *hypocloso*-$[B_{12}X_{12}]^{1-}$ (X = F, Cl, Br, I) analogues.[5,6] A major breakthrough came when the Spokoyny lab published a more convenient route for microwave-assisted synthesis of *hypercloso*-$B_{12}(OR)_{12}$,[7] which was rapidly followed by publications outlining multiple interesting applications. Most notably, *hypercloso*-$B_{12}(OR)_{12}$ carrying fluoroaryl-substituents can act as powerful photoinitiators, capable of activating styrenes, as well as recalcitrant substrates like isobutylene.[8] Later work (see Appendix A) has shown that the anionic *hypocloso*-$[B_{12}(OR)_{12}]^{1-}$ species obtained after monomer photooxidation acts as weakly coordinating anions.[9] The reversible redox behavior and noncoordinating nature of $[B_{12}(OR)_{12}]$ has also led to promising application in charge-storage devices[10] and as dopants in conducting polymers.[11]

Systematic explorations of $[B_{12}(OR)_{12}]$ applications are complicated by the complex in-solution behaviors observed for the hypoelectronic clusters under many conditions. Chapter 2 gives some examples of the issues facing researchers exploring the properties and reactivity of these species. It took us about two years to get a good handle on the clusters, in the specific settings that we were interested in. Other researchers exploring the clusters under different conditions would likely have to go through similar iterative processes to find conditions that work for their needs.

5.2 Electronic Structure and Super-oxidized Clusters

In Chapters 3 and 4 we presented our work toward understanding the electronic structure of $[B_{12}(OR)_{12}]$ clusters, including the super-oxidized $[B_{12}(OR)_{12}]^{1+}$ species. Our observations lead to a few key conclusions:

1) the frontier orbitals of hypoelectronic $[B_{12}]$ clusters are confined to the cluster core and made up primarily by boron 2p orbitals, with some contributions from oxygen 2p orbitals

2) the spin density of both $[B_{12}]^{1-}$ and $[B_{12}]^{1+}$ is highly delocalized across the B_{12} pseudo-icosahedron

3) higher oxidation states lead to increased distortion, which is demonstrated by the added anisotropy and the appearance of an additional weak $^{10/11}B$ hyperfine coupling in the $[B_{12}]^{1+}$ EPR data

4) the visible and NIR electronic transitions most likely occur between orbitals largely confined to the cluster core, based on that the excitation energies are relatively independent of the R-groups.

Before moving on, I want to spend a few words explaining the EPR observations. Based on the $[B_{12}]^{1-}$ and $[B_{12}]^{1+}$ pulsed EPR data, it is clear that the HOMO(a_{1u}) and LUMO(a_{2u}) of B_{12}^{0} are located on the cluster core, not stretching beyond the oxygen atoms. In particular, the very weak ^{19}F hyperfine interactions observed for the fluoroaryl derivatives show that no spin density is located on the aryl rings. That we only observe a single class of $^{10/11}B$ and ^{1}H hyperfine interactions in the $[B_{12}]^{1-}$ clusters strongly suggest that the a_{1u} symmetry orbital is evenly delocalized across the cluster core. Given that the $[B_{12}]^{1+}$ ENDOR spectra and the magnitude of the strong $^{10/11}B$ hyperfine tensor is highly reminiscent of $[B_{12}]^{1-}$, we feel confident also viewing the a_{2u} symmetry orbital as highly delocalized. However, we suggest that oxidation to $[B_{12}]^{1+}$ leads to significant distortion along the z-axis, which results in a SOMO(a_{2u}) where the spin density is concentrated in 2p orbitals from the equatorial boron atoms. The strong $^{10/11}B$ hyperfine interaction would then correspond to spin density evenly distributed across the equatorial boron atoms, while the weak coupling would stem from the boron atoms at the far edges in the z-direction.

It is interesting to think about why hypoelectronic $[B_{12}(OR)_{12}]$ clusters are stable, given that $[B_{12}H_{12}]^{2-}$ immediately decomposes upon oxidation. Symmetry lowering has been invoked by many authors, as raising the depopulated orbital and lowering the fully populated orbitals should lead to lowering of the overall cluster energy. The EPR results for $[B_{12}]^{1+}$, discussed above, substantiate this. Electron donation from the OR substituent has also been suggested as a key contributor to the stability. [3,12,13] Given that the redox potential of the clusters is highly dependent on the R-group identity, this seems reasonable.[4,7] It is interesting, however, that the B-B bonding frontier orbitals appear to have very little density on the R-groups. Our interpretation is that the electron donation into the B_{12} core primarily involves oxygen lone pairs, and that the role of the R-groups is primarily to modulate how tightly the oxygen holds on to its electrons.

5.3 Future Directions

Hypoelectronic dodecaborate clusters are interesting for a range of applications, as demonstrated in recent publications.[8–11] However, many question marks still remain. Following work will need to establish how the clusters act under various conditions, and develop systematic understand of their reactivity, photophysics and electrochemical properties. Once the field has matured, we believe a rich array of powerful applications will emerge.

The ability of alkyloxy-perfunctionalized clusters to maintain super-oxidized $[B_{12}]^{1+}$ states opens up to questions regarding what the true oxidation limits of dodecaborate clusters are. Cyclic voltammograms in dichloromethane do suggest a 4th oxidation for $[B_{12}(OEt)_{12}]$, which may indicate that $[B_{12}]^{2+}$ could be generated in sufficiently inert solvents. Electrochemical experiments in liquid SO_2 might shed light on whether the 4th wave corresponds to formation of $[B_{12}]^{2+}$, and to what extent such species are stable. It appears unlikely that further oxidation to $[B_{12}]^{3+}$ (and beyond) could be achieved without compromising the integrity of the B_{12} pseudo-icosahedron. Depopulation of the e_g set would weaken the effects of stabilization by symmetry lowering, which ought to result in immediate cluster decomposition. That said, we have now learned that $[B_{12}]^{1+}$ cores can be stable, which many would have argued against using similar reasoning. I look forward to seeing how this line of research develops.

Although the work presented in this thesis provides important insights into the electronic structure of hypoelectronic dodecaborates, many questions remain. I will mention a few crucial areas that need further exploration. Obtaining NIR spectra of $[B_{12}]^{1+}$ could provide the final piece required to definitively assign the electronic transitions discussed in Chapter 4. Furthermore, it is possible that multiple NIR bands would be observed, which would strongly support that hypoelectronic clusters display D_{3d} symmetry in solution (at least in the $[B_{12}]^{1+}$ state). More complex interpretation of the EPR data, involving modeling of the 2p orbital orientations or computational work, will be needed to quantitatively calculate the spin densities in orbitals of 2p parentage. Additionally, data collected for alkyloxy-perfunctionalized clusters in both their

$[B_{12}]^{1+}$ and $[B_{12}]^{1-}$ states is required for proper apples-to-apples comparisons. Finally, it would be very interesting to investigate the highest energy occupied molecular orbitals in all oxidation states using photoelectron spectroscopy, which has to our knowledge only been done for *closo*-$[B_{12}X_{12}]^{2-}$ clusters.[14]

The work presented in this thesis represents early attempts at describing the electronic structure and transitions of hypoelectronic dodecaborate clusters. I hope our observations will guide coming researchers wishing to perform more in-depth studies of the areas discussed here. I will be excited to learn what they find and whether our interpretations hold up to the test of time.

I wish the best of luck to any and all who choose to pursue these topics!

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