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This literature discussion on the Hot Paper communication in Chemistry, A European Journal, highlights the first examples of borepinium and borfluorenium cations whose optical properties can be tuned and also the very first reported example of thermochromism in these cationic species. R. J. Gilliard, Chem. Eur. J. 2019, 25, 12512. <https://doi.org/10.1002/chem.201903348>

This assignment provides a demonstration of structure-function relationships in the context of a main group system. Students critically read and analyze a short communication paper and relate a challenging research report to fundamental chemistry principles.

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Questions

General Literature

1. This paper was published as a communication. How does this differ from a journal article?
2. What is one of the main highlights of this paper?
3. What does thermochromism mean?
4. What are some possible practical applications of the research presented in this paper?

Acid/Base Chemistry

5. Define a Lewis acid and base. What species are functioning as the Lewis acids and bases in compounds 5 and 11?
6. Tetrahydrofuran is an example of a coordinating solvent. Draw the chemical structure of THF and identify the coordinating atom.
7. Draw the structures of benzene and dichloromethane (DCM). Why are benzene and DCM considered as non-coordinating solvents?

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Coordination Chemistry

8. Draw a borafluorene molecule.
9. Despite being named borafluorene, these molecules do not contain the element fluorine. Why are fluorenes named like that? You will need to look beyond this paper for the answer (some reliable sites on the internet may be helpful.)
10. Why is carbene classified as an L-type ligand? What is represented by the arrow pointing at the boron from the ligand in compounds 5, 6, 10, and 11?

Molecular Geometry

11. Figure 2 shows crystal structures of 5, 6, 10, and 11. What is the coordination geometry around B1?
12. Define the geometry of tricoordinate and tetracoordinate boron. Identify an example of each in the journal article. What is the hybridization of the boron in these complexes?

Electronic Structure

13. What is the electronic configuration of ground state boron?
14. Why does boron tend to form three bonds? How does this relate to its electron configuration?
15. Calculate the formal charge of boron in compounds 7 and 10. Show your work.

Organometallics

16. The compounds 5, 6, 10, and 11 are said to be air and moisture sensitive. How does that affect their reactivity?

Instrumentation

17. What characterization methods were used in this study? Explain what type of information each method provides.
18. What do the DFT results suggest about the spontaneity and reversibility of the addition of THF? (Hint: what is the ΔG value for this reaction?)
19. Using ^{11}B NMR, how would one differentiate tricoordinate and tetracoordinate boron compounds?

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Photoelectronic Properties

20. UV-Vis absorption spectroscopy results in Figure 4b show a blue shift for compound 11 compared to 10. Explain why.
21. Identify the wavelength of maximum absorption of compounds 4 and 5 in Figure 4b. Consider the spectrum in Figure 4c, why does the absorbance differ after the addition of THF?
22. Why do you think the researchers made 2-methoxy-9-borofluorenum cation (compound 14)? What were they hoping to explore with this compound?
23. Look at compound 14 and the discussion of its reactivity. What is the effect of temperature on the B-O bond? What evidence do the authors provide to prove this phenomenon?