Literature discussion of “Macrocyclic Cu(II) Complexes as Catalysts for Electrochemically Mediated Atom Transfer”

P.V. Bernhardt and co-workers, *Inorg. Chem.* **2024**, *63*, 6453-6464.

*Prior to class, please read through the first 5 ½ pages (stop at Electron Paramagnetic Resonance Spectroscopy) and answer the first question below.*

**Introduction:**

1. Look at **Chart 1** showing six known tetradentate N-based ligands. Based on how each ligand is depicted, predict whether the ligand will bind in planar or non-planar manner to a metal center.

**Results and Discussion**

*Structural Characterization*

1. Crystal structures for the copper compounds of Me4cyclen, Me4cyclam, and Me2py2clen are shown in **Fig. 1-3**. What are the geometries of these ligands around the Cu center? How does this binding mode compare with your predictions in the question above?
2. What factors likely drive the binding geometry of these ligands to Cu? Refer to the 3D models in the CCDC that is linked at the end of the Experimental section in order to manipulate the structures.

*UV-Vis Spectrophotometric Titrations*

1. **Fig. 4** shows the UV-Vis titration of [Cu(Me2py2clen)(NCCH3)2]2+ with Cl- and Br- ions. How does the max shift in the UV-Vis spectra when a single solvent ligand is replaced by a halide? When both solvent ligands are replaced?
2. Think about the relative position of CH3CN vs halides in the spectrochemical series: where is each ligand located? How might this difference result in the change in lmax?
3. Looking at the titration data in **Fig. 4**, how many equivalents of Cl- are added to fully generate the dichloro copper compound? How many for the dibromo? Drawing on what you know about periodic properties, what might be the cause(s) of the different binding constants of these two halides?