

Template Synthesis of Ligands for Highly Charged Metal Cations

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Macrocyclic and macrobicyclic ligands may enhance the stability of their metal complexes due to the inherent entropic and kinetic properties of a ligand ring or cage-type structure. In general, as the binding site becomes more encapsulated or preformed the reorganization entropy decreases, leading to a relatively higher formation constant for metal binding. Thus it would be expected that the formation constants be greatest for the series macrobicyclic > macrocyclic > exocyclic (Figure 1).

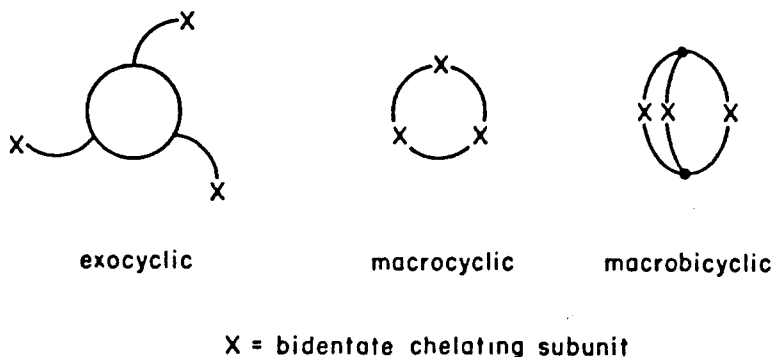


Fig. 1. Possible topologies for macrocyclic ligands.

For synthetic purposes, the idealized macrobicyclic structure in Figure 1 can be viewed as a 'capped' tripod. We have explored a new binding subunit for this work, 2,3-dihydroxyterephthalamide. A highly successful example of this approach is shown in Figure 2, where an essentially one-step synthesis gives a 50% isolated yield of the macrocycle formed from six amide linkages.

In the quite different chemistry of the lanthanides we have used a conceptually similar approach to prepare cage complexes of the lanthanides from which the metal ion cannot escape without breaking a C—C or C—N bond. The proposed structure for such a ytterbium complex is shown in Figure 3. This complex is relatively hydrolytically stable. In contrast, the intermediate compounds with 1 or 2 methylene bridges are readily hydrolyzed since they allow ready exit of the metal ion. The structures of several of these intermediates have been determined.

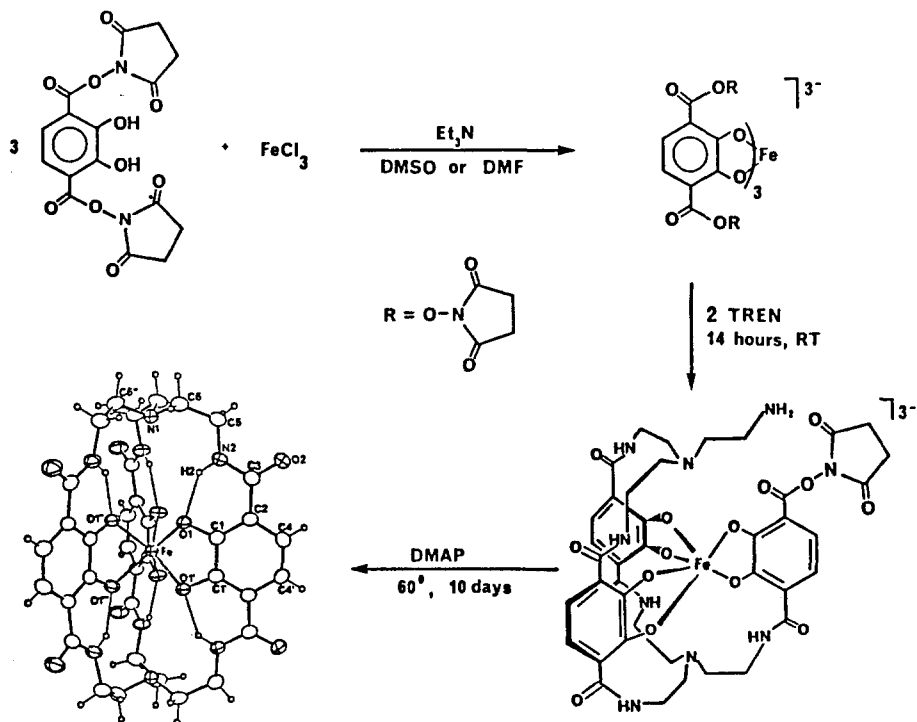


Fig. 2. Template synthesis of ferric (bicapped TREN)CAM.

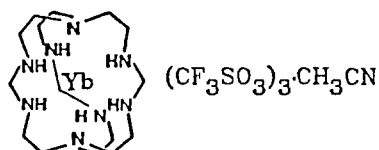
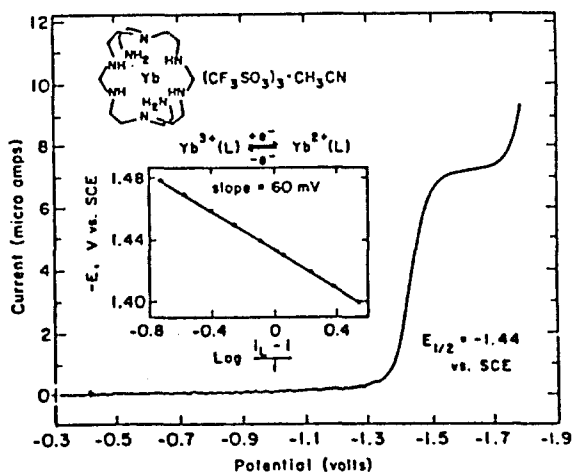


Fig. 3. A schematic drawing of the proposed structure of the completely encapsulated ytterbium complex.

Fig. 4. Normal pulse polarogram of $\text{Yb}^{3+}(\text{L})$ in 0.3 M sodium triflate acetonitrile solution. Negative potentials (V vs SCE) are plotted to the right and reduction currents are plotted upward. The inset shows a plot of $-E$ vs $\log(i_L - i/i)$ for the normal pulse polarogram.

The electrochemistry for the Yb complex shown in Figure 4 (along with the electrochemical behavior) shows the +3 complex is stabilized by 10^{14} relative to the +2 complex.

Acknowledgement

I thank my coworkers, whose names appear in the publications listed below, whose efforts are summarized in my presentation.

References

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