**Proton-Assisted Reduction of CO2 by Cobalt Aminopyridine Macrocycles**

[Chapovetsky, A.; Do, T. H.; Haiges, R.; Takase, M. K.; Marinescu, S. C. *J. Am. Chem. Soc.* **2016**, *138*, 5765–5768.](https://pubs.acs.org/doi/full/10.1021/jacs.6b01980)

This literature discussion was written in Spring 2021 to celebrate Prof. Marinescu, the recipient of the ACS Harry Gray Award for Creative Work in Inorganic Chemistry by a Young Investigator.

**Learning Goals**

**Students should be able to**:

1. Determine the oxidation number of metal centers and count valence electrons in metal complexes
2. Deduce a likely mechanism for a ligand substitution reaction
3. Justify the observed colors of metal complexes containing different ligands
4. Perform a density calculation of a unit cell
5. Locate symmetry operations of a macrocycle
6. From the proposed catalytic cycle (Please see Figure 3 of the article) for the reduction of CO2 with cobalt complex **1**, [Co(L1)(acetone)2][BF4]2, identify the oxidation state of the metal, the number of d electrons, and the total number of electrons for each complex.
7. In order for CO2 to coordinate the cobalt center, an empty site must be generated by removing the coordinating solvent (complex **4** → **5**).
8. What is the likely mechanism (associative or dissociative) for the ligand substitution reaction for this step?
9. Write the necessary equation for each sub-reaction involved in the mechanism that you propose.
10. Munakata and co-workers report the ability of various solvents to coordinate to a metal center or the coordination power.1 Among the solvents employed in this article, pyridine exhibits the highest coordination power, followed by water, and acetonitrile, respectively. Please rank the rate of ligand substitution of the [Co(L1)(solvent)2]+ complexes **4**, when solvent = pyridine, water, and acetonitrile. Please provide a brief explanation to support your answer.
11. The cobalt complexes and intermediates from the proposed catalytic cycle exhibit different colors. For example, the Co complex **1** [Co(L1)(acetone)2][BF4] is orange, while the Co complex **4** [Co(L1)(pyridine)2][BF4] is amber in color. Please justify the observed colors of these two complexes. Also, please estimate the value of the ∆oct in cm–1for both complexes.
12. The authors indicate that the cobalt catalysts suffer deactivation due to the generated CO during the catalytic cycle. Please briefly explain how CO can deactivate the catalyst.
13. Please discuss the effect of the substituents of the pendant amine groups on the peak potentials observed from the CV experiments and on the turnover numbers. In addition, please discuss how the authors used this information to establish the proposed catalytic cycle (Figure 3).
14. The cobalt complex **1** (C26H28Cl2CoN8O10) crystallizes in a tetragonal unit cell (a = b ≠ c, and *α* = *β* = *γ* = 90°) with the density of 1.579 g/cm3. The unit cell has the cell edge lengths as follows: a = 11.4612 Å; b = 11.4612 Å; c = 23.7694 Å. Please perform a calculation to determine the number of cobalt complexes that are contained in one unit cell.
15. The azacalix[4](2,6)pyridine ligands adopt a saddle conformation with D2d symmetry. Please locate every symmetry operation of this ligand.

**Reference**

1. Munakata, M.; Kitagawa, S.; Miyazima, M. *Inorg. Chem.* **1985**, *24*, 1638–1643.

<https://doi.org/10.1021/ic00205a009>