**Low-Coordinate Transition-Metal Complexes of a**

**Carbon-Substituted Hemiporphyrazine**

Please complete these guiding questions to *Inorganic Chemistry* **2007**, *46*(16), 6239-6241. <https://doi.org/10.1021/ic7011099>

1. Explain why the authors state in the first sentence of the article that “Transition-metal complexes with low coordination numbers continue to be challenging synthetic goals for chemists.”

Transition metals with low coordination numbers tends to be unstable due to lower total valence electron counts. For example, they tend to be water-sensitive due to their high Lewis acidity. The low coordination number also reduces the amount of steric bulk around the metal center, often making the center available for further interactions with other ligands. In addition, the presence of ligands can also affected the redox behavior of some metals.

2. a) Compare the structure of porphine, the simplest porphyrin, to the N-confused porphyrin analog shown in Figure 1 and the H2dchp ligand in Scheme 1. Draw the structures of the latter two ligands in the table.

For the N-confused porphyrin, circle the part of the molecule that differs from porphine. For all 3 ligands, identify the denticity of the ligand assuming only nitrogen is involved in metal-ligand interactions.

|  |  |  |
| --- | --- | --- |
|   |   |  |
|  |  |  |

b) Why are porphine and N-confused porphyrin distinct compounds and not conformational isomers of the same compound?

c) When the metal interacts with the H2dchp ligand, why are the 4 imine nitrogens unable to act as a donor atom to the metal?

3. The reaction conditions for synthesizing the Fe, Mn, and Co complexes in Scheme 1 require refluxing pyridine. Using an appropriate resource, report the temperature that would correspond to these conditions. Cite your source.

4. Use the CBC method to determine the following for the Mn complex in Scheme 1, *ignoring* the metal C-H interactions for the moment.

a) [ML*l*X*x*Z*z*]Q± designation and equivalent neutral class, if appropriate

b) Valence number, *d*-electron count, ligand bond number

c) "Formal" oxidation state; note if this is different from the valence number

d) Valence electron count for each metal in the complex

5. Use the CBC method to determine the following for the Mn complex in Scheme 1, taking into consideration the metal C-H interactions.

a) [ML*l*X*x*Z*z*]Q± designation and equivalent neutral class, if appropriate

b) Valence number, *d*-electron count, ligand bond number

c) "Formal" oxidation state; note if this is different from the valence number

d) Valence electron count for each metal in the complex

6. Consult the plots on the Parkin group website (<http://www.columbia.edu/cu/chemistry/groups/parkin/mlxz.htm>) to answer the following questions.

a) What percentage of Mn compounds have the [ML*l*X*x*Z*z*]Q± designation from question 4? From question 5?

b) Comparing total electron counts from question 4 and question 5, which is more common for Mn?

c) How common is/are the valence number(s) from questions 4 & 5?

d) How common is/are the ligand bond number(s) from questions 4 & 5?

7. Why did the authors cite the references in reference (3)?