

## Inorganic Chemistry Cumulative Exam

March 3<sup>rd</sup>, 2016

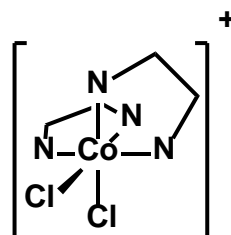
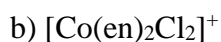
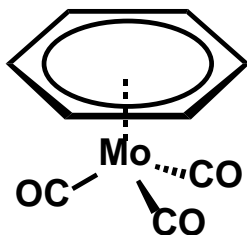
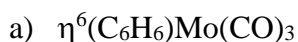
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A few rules:

- There is no need for a calculator to complete this exam.
- Please read the questions carefully.
- One of the critical aspects of a successful scientific article is conciseness. This is your opportunity to prepare. Please explain your answers *adequately, but concisely*.
- Last but not least, please **print legibly!**

The questions amount to 150 points. The point value of each question can be found in brackets. The pass line is at 85 points.

- 1) (20)  $[\text{Cr}_2\text{O}_7]^{2-}$  ions are carcinogenic pollutants in drinking water generated traditionally from applications such as prevention of corrosion. They became prominent in popular culture thanks to Erin Brokovich (or perhaps we should say Julia Roberts?). These ions present Cr in its highest possible oxidation state. Using the electronic configuration of Cr, **rationalize** why higher oxidation states are not reachable in realistic chemical conditions.
- 2) (10) For the following coordination complexes, **give** the (i) metal oxidation state, (ii) metal *d* electron count, and (iii) total valence electron count of the metal (usually, values close to or exactly 18 electrons). Just so you know, undergraduates did well on this very question in the Fall 2015 semester.



- 3) (20) In a classical paper from 1959 (*J. Chem. Soc.*, **1959**, 4033), Blackie and Gold report that addition of KCN to an aqueous solution of  $[\text{Ni}(\text{NH}_3)_6]^{2+}$  leads to the formation of  $[\text{Ni}(\text{CN})_4]^{2-}$ . Specifically, they state that “when the ratio CN/Ni is 4 [...] the solution contains only diamagnetic species in significant amounts”, as opposed to the paramagnetic character of the initial compound. Using crystal field theory arguments and schematic diagrams of *d* orbitals, **explain** why  $[\text{Ni}(\text{NH}_3)_6]^{2+}$  is paramagnetic whereas  $[\text{Ni}(\text{CN})_4]^{2-}$  is diamagnetic.

- 4) (20) In a paper from 2012 (*Inorg. Chem.*, **2012**, 51, 7851), Mack *et al.* report the effect of bite angle in tridentate pyridine-derived ligands on the Jahn-Teller distortions of Cu(II) complexes of the type  $[\text{Cu}(\text{tpy})_2]^{2+}$  (tpy=tridentate pyridine ligand). **Explain** the Jahn-Teller effect. You will need to use crystal field theory arguments and schematic diagrams of *d* orbitals.
- 5) (10) **Name** two other ions that can show the Jahn-Teller effect.
- 6) (20)  $\text{TiO}_2$  and  $\text{ZnO}$  are white solids often used in white paints, sunscreen or diaper rash creams due to their very low toxicity. The Ti coordination in  $\text{TiO}_2$  is octahedral. The Zn coordination in  $\text{ZnO}$  is tetrahedral. As such, they can be treated with simple molecular theories. Using crystal field theory arguments and schematic diagrams of *d* orbitals, **explain** why these two solids are white.
- 7) (20)  $\text{LiCoO}_2$  is one of the classical Li-ion battery electrodes, as it was employed in the first device commercialized in the early 1990s by SONY. This compound is diamagnetic, where Co is in an octahedral coordination. Using crystal field theory arguments and schematic diagrams of *d* orbitals, **explain** why.
- 8) (10) Oxides crystallizing in a spinel structure are popular materials in magnetic memories and battery electrodes. Their chemical formulas are summarized as  $\text{AB}_2\text{O}_4$ , where A and B can be a variety of cations. The normal spinel structure can be described as a face centered cubic (*fcc*) array of  $\text{O}^{2-}$  with A occupying a fraction of the tetrahedral holes and B occupying a fraction of the octahedral holes. How many **total** tetrahedral and octahedral holes, respectively, exist per  $\text{O}^{2-}$  ion in an *fcc* array?

### Bonus Questions

- 9) (5) Which phone number should you dial in case of a fire in the lab?
- 10) (5) What is the minimum personal protective equipment that **must** be worn when stepping into the lab?
- 11) (5) Name a class of compounds that should never be mixed into waste streams that have a pH below 3.
- 12) (5) Name a speaker in the series of Department of Chemistry Seminars presenting research in Inorganic Chemistry.