

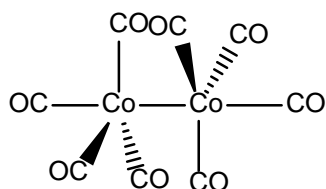
1. (20 pts) For transition metal ions that can be either high spin or low spin, the ionic radius of the high spin state is always larger than for the low spin state. Some examples, for coordination number 6: $\text{Mn}^{3+}(\text{ls}) r_+ = 72 \text{ pm}$ and $\text{Mn}^{3+}(\text{hs}) r_+ = 78.5 \text{ pm}$; $\text{Co}^{3+}(\text{ls}) r_+ = 68.5 \text{ pm}$ and $\text{Co}^{3+}(\text{hs}) r_+ = 75 \text{ pm}$; $\text{Ni}^{3+}(\text{ls}) r_+ = 70 \text{ pm}$ and $\text{Ni}^{3+}(\text{hs}) r_+ = 74 \text{ pm}$. Explain why the high spin state has the larger radius. For the three ions given, the trend across the Periodic Table is different. Explain.

High spin ions have electrons occupying e_g orbitals. From an ionic point of view, this means that higher energy orbitals are filled, which are larger and increase the size of the ion. From a covalent point of view, the e_g orbitals are antibonding, which increases the bond length to any ligand bound to it. As one goes across the Periodic Table for the high spin state the radius decreases from Mn^{3+} to Co^{3+} to Ni^{3+} , in agreement with the increasing Z^* . However, for the low spin state the trend is not monotonic – there is a decrease from Mn^{3+} to Co^{3+} but then an increase for Ni^{3+} . The Co^{3+} is a filled subshell, allowing for a small contraction, while Ni^{3+} must fill the e_g orbital, slightly enlarging the radius. For either spin state, the changes across the Periodic Table are very small.

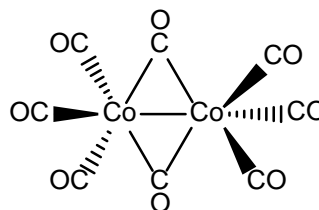
2. (20 pts) TiO_2 is a high melting, hard ceramic while TiCl_4 is a liquid at room temperature. Should Ti^{4+} be treated using ionic models or covalent models? Explain.

The +4 state in transition metal ions is a boundary between effective use of ionic models (nearly always good for +2 or +3 states) vs covalent models (nearly always good for +5, +6, or +7 states). In the case of Ti^{4+} , the ligand determines the better model. The more anionic but not polarizable O^{2-} ligand leads to an ionic model, consistent with the high melting point. In contrast, the lower charge Cl^- and somewhat more polarizable ligand gives sufficient overlap with the Ti^{4+} ion to lead to substantial covalency, as indicated by the lower melting point.

3. (20 pts) In class I provided the wrong structure for $\text{Mn}_2(\text{CO})_{10}$ – there are no bridging CO groups in this compound. However, the similar cobalt dimer, $\text{Co}_2(\text{CO})_8$ has two isomers, one of which does include bridging CO groups. Predict the structure of the two isomers and show how they are consistent with the EAN rule. Hint: bridging CO groups are considered to contribute 1 electron to each metal it bridges.



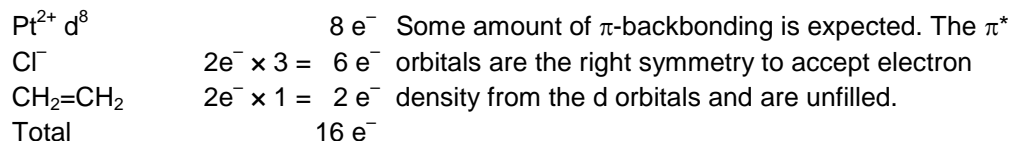
Per Co d^9		$9 e^-$
CO terminal	$2e^- \times 4 =$	$8 e^-$
Co-Co bond		$1 e^-$
Total		$18 e^-$



Per Co d^9		$9 e^-$
CO terminal	$2e^- \times 3 =$	$6 e^-$
CO bridging	$1e^- \times 2 =$	$2 e^-$
Co-Co bond		$1 e^-$
Total		$18 e^-$

CHM 501
Exam 3
April 27, 2016

4. (20 pts) Show that the ion $[\text{PtCl}_3(\text{CH}_2=\text{CH}_2)]^-$ is stable by the effective atomic number rule. Ethylene binds to the Pt through the pi bond, side on. Would you expect π -backbonding to the ethylene? Why or why not?



5. (20 pts) $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{Co}(\text{en})_3]^{3+}$, and $[\text{Co}(\text{NO}_2)_6]^{3-}$ are all yellow-orange while $[\text{CoF}_6]^{3-}$ and $[\text{Co}(\text{H}_2\text{O})_3\text{F}_3]$ are blue. Qualitatively explain the difference in these observations. Predict the number of unpaired spins in each of the five complexes.

All five of the complexes are Co^{3+} , so the color differences are due to the changes in the ligand field strength. The yellow complexes absorb blue light, relatively high energy, indicating that $10Dq$ is relatively large while the blue complexes absorb red light, low energy, telling us that $10Dq$ is relatively small. Thus, $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{Co}(\text{en})_3]^{3+}$, and $[\text{Co}(\text{NO}_2)_6]^{3-}$ are all low spin with 0 unpaired spins and $[\text{CoF}_6]^{3-}$ and $[\text{Co}(\text{H}_2\text{O})_3\text{F}_3]$ are both high spin with 4 unpaired spins. This is consistent with the spectrochemical series where NH_3 , en, and NO_2^- are strong ligands and H_2O and F^- are weak ligands.