

1. Answer ALL parts a) — c)

A) Explain briefly why ligand exchange reactions of Cr(III) are typically very slow.

The Cr(III) aqua ion has three electrons in the  $t_{2g}$  orbital of the d-shell, leading to considerable LFSE (Ligand field stabilization energy), and so undergoes ligand substitution reactions very slowly.

B) Which of the two manganese complexes shown below will have the greatest value of  $\Delta_o$ ? Give an explanation for your conclusion.

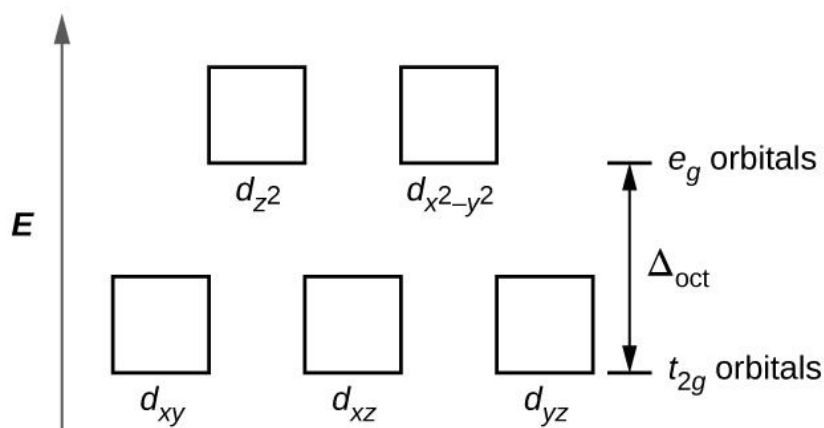


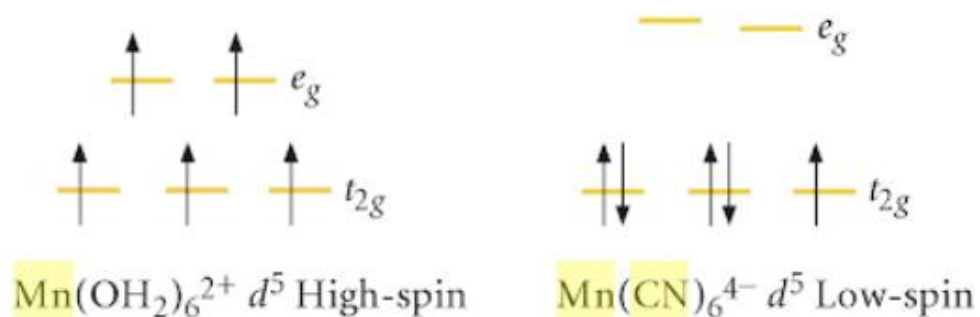
The complex  $[Mn(H_2O)_6]^{2+}$  has a magnetic moment 5.9, whereas the magnetic moment of  $[Mn(CN)_6]^{4-}$  is 2.2. Both have 5 d-electrons.

Using the relationship between magnetic moment and the number of unpaired electrons,  $\mu = [n(n + 2)]^{1/2}$ , we find that if  $n = 5$ , then  $\mu$  should be 5.92 for the aqua complex. Thus the  $[Mn(H_2O)_6]^{2+}$  complex is a high-spin  $d^5$  complex.

Using the same relationship, if  $n = 1$  (as it would be in the low-spin case), we expect  $\mu$  to be 1.73, which is close to the value observed in the cyano complex. Therefore, the  $[Mn(CN)_6]^{4-}$  complex must be a low-spin complex. This makes sense when we note that  $CN^-$  imparts a strong ligand field (high in the spectrochemical series) and  $H_2O$  imparts a weak ligand field. For  $CN^-$ , the magnitude of  $\Delta$  is large enough that the electrons prefer to be paired up in the  $t_{2g}$  orbitals rather than unpaired and occupying the higher energy  $e_g$  orbitals.

C) Draw d-orbital splitting diagrams for each electronic configuration for which both high- and low-spin possibilities exist for octahedral transition metal complexes. In such cases, which factors determine whether an octahedral metal complex adopts a high- or a low-spin d-electron configuration?





A complex is high spin or low spin depends on two main factors: the crystal field splitting energy and the pairing energy. The electrons will take the path of least resistance--the path that requires the least amount of energy. If the pairing energy is greater than  $\Delta$ , then electrons will move to a higher energy orbital because it takes less energy. If the pairing energy is less than  $\Delta$ , then the electrons will pair up rather than moving singly to a higher energy orbital. Below, tips and examples are given to help figure out whether a certain molecule is high spin or low spin.

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