# 2   Magnetism and More Spectroscopy

3/3:

1. You propose that you have made a terminal amide (NH_2) complex. You observe two stretching frequencies in the IR spectrum at $2400\,cm^{-1}$ and $2330\,cm^{-1}$.

    (a) Do you have one or two complexes? Rationalize this based on symmetry.

    (b) If you deuterate this complex, where should the N–D stretches come?

2. Copper (II) acetate is a dimer and the two Cu atoms strongly interact. The EPR spectrum consists of seven lines with intensities of $1 : 2 : 3 : 4 : 3 : 2 : 1$. Copper nuclei have $I = 3/2$, and copper acetate consists of a ground state singlet with an accessible triplet excited state. Explain the number and relative intensity of the observed signals.

3. The intensities and frequencies (vs. H_3PO_4) of resonances in the $121.4\,MHz$ $^{31}P\{^1H\}$ NMR spectrum of $Pt(PPh_3)\{\eta^3\text{-}N(CH_2CH_2PPh_2)_3\}$ are listed below. Determine the chemical shifts (i.e., δ values) and coupling constants, and draw the structure.

Frequency	Intensity
−3393.4	7.8
−3313.5	7.7
−1484.8	31.1
−1404.9	31.3
−833.3	0.7
−753.5	1.9
−673.4	2.0
−593.6	0.6
263.7	7.9
343.7	7.7
1385.5	2.6
1465.6	7.8
1545.8	7.6
1625.6	2.7
3604.5	0.7
3684.6	1.9
3764.4	1.9
3844.7	0.6

4. Predict the spin state, μ_{eff}, and χT values for the following ions in the indicated geometry.

    (a) Tetrahedral Mn(II).

    (b) Octahedral Ir(III).

    (c) Octahedral Ru(III).

    (d) Square planar Co(I).

    (e) Square planar Pt(II).

    (f) Octahedral Ni(II).

    (g) Tetrahedral Cr(0).

5. Predict whether the following high-spin ions should have an isotropic EPR g-value greater than, equal, or less than 2.

    (a) Cu(II).

    (b) Cr(V).

(c) Mn(II).

(d) Fe(III).

(e) Co(II).

6. If you were handed two vials, one with ferrocene and one with ferrocenium, how could you use XAS and Mossbauer to determine which was which?

7. (a) Name 3 pieces of structural information you can get from a K-edge EXAFS spectrum on an unknown TM complex with at least one phosphine ligand.

   (b) A Mossbauer spectrum of an FeL_5 complex shows two signals with differing isomer shifts and quadrupole splittings. Offer an explanation for this.

8. Draw a clearly labeled diagram representing the expected EPR spectrum of an aqueous $^{63}Cu^{2+}$ ion ($I = 3/2$) at room temperature. Clearly indicate the position of the isotropic g-value.

9. The EPR spectrum of an axially symmetric Cu^{2+} complex in a frozen solution that is 100% ^{63}Cu consists of three well-resolved low field g-parallel components, a fourth component of the multiplet that overlaps the g-perpendicular signal, and some higher field lines. The minima between the four largely resolved components appear at $2720\,G$, $2810\,G$, and $2900\,G$. Given this information and a spectrometer frequency of $9.12\,GHz$. . .

   (a) Compute the value of $g_\parallel$;

   (b) Compute the hyperfine coupling constant.

10. The structure of the active site of carbon monoxide dehydrogenase was determined from XAS data to be
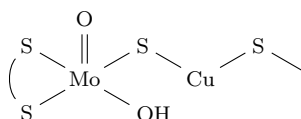
    (a) Indicate how you could identify the heavy atoms with XANES or EXAFS data, the oxidation state of these atoms, and the coordination environment.

    (b) Your results tell you that the oxidation states of Mo and Cu are 6+ and 1+, respectively. How could you determine the protonation state of the hydroxide (OH or OH_2) with ENDOR spectroscopy?

11. For the following fragments, predict the χT and μ_{eff} values for anti-ferromagnetic, ferromagnetic, and uncoupled scenarios. Using the indicated room temperature χT or μ_{eff} values, predict the coupling in these fragments. Assume no contributions from spin-orbit coupling.

    (a) $Cu^{II}-X-Cu^{II}$, $\chi T = 0.4\,cm^3\,K\,mol^{-1}$.

    (b) $Ni^{II}-X-Cr^{II}$, $\chi T = 4.4\,cm^3\,K\,mol^{-1}$.

    (c) $Fe^{III}-X-Fe^{III}$, $\mu_{eff} = 8.4\,\mu_B$.

    (d) $Fe^{II}-X-Fe^{III}$, $\chi T = 11\,cm^3\,K\,mol^{-1}$.

12. You synthesize a series of new metal oxides with each metal center in an O_h coordination environment. The two metals alternate in an edge-sharing AB. You note that when A = Ti(III) and B = Cu(II), the material exhibits strong ferromagnetic exchange. However, when A = Fe(III), a strong antiferromagnetic exchange is observed. Rationalize these two observations.