

## 2 Magnetism and More Spectroscopy

- 3/3: 1. You propose that you have made a terminal amide ( $\text{NH}_2$ ) complex. You observe two stretching frequencies in the IR spectrum at  $2400\text{ cm}^{-1}$  and  $2330\text{ cm}^{-1}$ .

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

*Answer.* One complex. The two bands correspond to a symmetric and an asymmetric bending mode<sup>[1]</sup> of the same compound. □

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

*Answer.* Let

$$\nu_{1,\text{H}} = 2400\text{ cm}^{-1}$$

$$\nu_{2,\text{H}} = 2330\text{ cm}^{-1}$$

We have that

$$\mu_{\text{NH}} = \frac{m_{\text{N}}m_{\text{H}}}{m_{\text{N}} + m_{\text{H}}} = \frac{14 \cdot 1}{14 + 1} = 0.933 \qquad \mu_{\text{ND}} = \frac{m_{\text{N}}m_{\text{D}}}{m_{\text{N}} + m_{\text{D}}} = \frac{14 \cdot 2}{14 + 2} = 1.75$$

Thus,

$$\nu_{1,\text{D}} = \frac{\sqrt{\mu_{\text{NH}}}}{\sqrt{\mu_{\text{ND}}}} \cdot \nu_{1,\text{H}} \qquad \nu_{2,\text{D}} = \frac{\sqrt{\mu_{\text{NH}}}}{\sqrt{\mu_{\text{ND}}}} \cdot \nu_{2,\text{H}}$$

Plugging in numbers, we learn that

$\nu_{1,\text{D}} = 1750\text{ cm}^{-1} \qquad \nu_{2,\text{D}} = 1700\text{ cm}^{-1}$

□

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.

*Answer.* Since there are  $n = 2$  copper atoms each with nuclear spin  $I = 3/2$ , then  $2nI + 1$  rule predicts that there will be

$$2 \cdot 2 \cdot \frac{3}{2} + 1 = 7$$

lines in the spectrum. As to the relative intensities, since the  $M_I$  contributions from all relevant nuclei sum, we know that overall,  $I = 3/2$  and  $M_I = -3, -2, \dots, 3$  (i.e., can take on *seven* values, again as predicted by the  $2nI + 1$  rule). Additionally, we can identify the number of microstates that can yield each value of  $M_I$ . For instance,  $-3$  must be the sum of  $(-3/2) + (-3/2)$ . However,

$$-2 = (-3/2) + (-1/2) = (-1/2) + (-3/2)$$

so there are *two* microstates that correspond to it. Continuing on, we can determine that the quantum number  $M_I$  corresponds to  $M_I + 4$  microstates. Additionally, the transition energies will grow as  $M_I$  increases (according to the relevant triplet hyperfine splitting diagram), meaning that the peak splitting pattern

$$1 : 2 : 3 : 4 : 3 : 2 : 1$$

will indeed be realized as quantum number (and hence energy) varies from lesser to greater. □

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<sup>1</sup>Not a stretch according to Dr. Anderson.

3. The intensities and frequencies (vs.  $\text{H}_3\text{PO}_4$ ) of resonances in the 121.4 MHz  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $\text{Pt}(\text{PPh}_3)\{\eta^3\text{-N}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3\}$  are listed below. Determine the chemical shifts (i.e.,  $\delta$  values) and coupling constants, and draw the structure.

Frequency	Intensity	Chemical shift
-3393.4	7.8	-27.95
-3313.5	7.7	-27.29
-1484.8	31.1	-12.23
-1404.9	31.3	-11.57
-833.3	0.7	-6.864
-753.5	1.9	-6.207
-673.4	2.0	-5.547
-593.6	0.6	-4.890
263.7	7.9	2.172
343.7	7.7	2.831
1385.5	2.6	11.41
1465.6	7.8	12.07
1545.8	7.6	12.73
1625.6	2.7	13.39
3604.5	0.7	29.69
3684.6	1.9	30.35
3764.4	1.9	31.01
3844.7	0.6	31.67

*Answer.* Confirm chemical shift formula: Times  $10^6$ , not divided by??

Coupling constant: So for adjacent nuclei, subtract the frequencies and then convert to chemical shift??

To convert to chemical shift (ppm), use the formula

$$\frac{\nu_1 - \nu_{\text{ref}}}{\nu_0} \times 10^6$$

where  $\nu_1$  is the measured frequency for a given nucleus,  $\nu_{\text{ref}} = 0$  in this case, and  $\nu_0 = 121.4$  MHz is the spectrometer frequency. An example calculation for the first row in the given table is shown below.

$$\frac{-3393.4 \text{ Hz} - 0 \text{ Hz}}{121.4 \text{ MHz}} \times 10^6 = \frac{-3393.4 \text{ Hz}}{121.4 \text{ Hz}} = -27.95 \text{ ppm}$$

The rest of the results are tabulated above in blue. There are six peaks present in the spectrum. The coupling constant of each peak is either equal to the peak splitting, or the average of the three peak splittings in the case of the three quartets present. For example, the coupling constant for the peak centered around -27.62 ppm is

$$J_1 = (-27.29 \text{ ppm}) - (-27.95 \text{ ppm}) = 0.66 \text{ ppm}$$

and the coupling constant for the peak centered around -5.877 ppm is

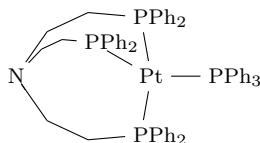
$$\begin{aligned} J_3 &= \frac{[(-4.890 \text{ ppm}) - (-5.547 \text{ ppm})] + [(-5.547 \text{ ppm}) - (-6.207 \text{ ppm})] + [(-6.207 \text{ ppm}) - (-6.864 \text{ ppm})]}{3} \\ &= \frac{(-4.890 \text{ ppm}) - (-6.864 \text{ ppm})}{3} \\ &= 0.658 \text{ ppm} \end{aligned}$$

Altogether, the coupling constants from lowest ppm to highest ppm are given by

$J_1 = 0.66$	$J_2 = 0.66$	$J_3 = 0.658$	$J_4 = 0.659$	$J_5 = 0.660$	$J_6 = 0.660$
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where all quantities are in units of ppm.

Lastly, the structure is as follows.



□

4. Predict the spin state,  $\mu_{\text{eff}}$ , and  $\chi T$  values for the following ions in the indicated geometry.

(a) Tetrahedral Mn(II).

*Answer.* As a first-row transition metal with  $T_d$  geometry, Mn(II) will be high spin. It follows that as a  $d^5$  metal center, Mn(II) will have 5 unpaired electrons. Thus,

$$\mu_{\text{eff}} = \sqrt{4 \left( \frac{5}{2} \left( \frac{5}{2} + 1 \right) \right)} \qquad \chi T = \frac{1}{2} \left( \frac{5}{2} \left( \frac{5}{2} + 1 \right) \right)$$

$\mu_{\text{eff}} = 5.92$ 
 $\chi T = 4.375$

□

(b) Octahedral Ir(III).

*Answer.* As a third-row transition metal, Ir(III) will be low spin. It follows that as a  $d^6$  metal center, Ir(III) will have 0 unpaired electrons. Thus,

$$\mu_{\text{eff}} = \sqrt{4 \left( \frac{0}{2} \left( \frac{0}{2} + 1 \right) \right)} \qquad \chi T = \frac{1}{2} \left( \frac{0}{2} \left( \frac{0}{2} + 1 \right) \right)$$

$\mu_{\text{eff}} = 0$ 
 $\chi T = 0$

□

(c) Octahedral Ru(III).

*Answer.* As a second-row transition metal, Ru(III) will be low spin. It follows that as a  $d^5$  metal center with  $O_h$  geometry, Ru(III) will have 1 unpaired electron. Thus,

$$\mu_{\text{eff}} = \sqrt{4 \left( \frac{1}{2} \left( \frac{1}{2} + 1 \right) \right)} \qquad \chi T = \frac{1}{2} \left( \frac{1}{2} \left( \frac{1}{2} + 1 \right) \right)$$

$\mu_{\text{eff}} = 1.73$ 
 $\chi T = 0.375$

□

(d) Square planar Co(I).

*Answer.* As a square planar complex, Co(I) will be low spin. It follows that as a  $d^8$  metal center with  $D_{4h}$  geometry, Co(I) will have 0 unpaired electron. Thus,

$$\mu_{\text{eff}} = \sqrt{4 \left( \frac{0}{2} \left( \frac{0}{2} + 1 \right) \right)} \qquad \chi T = \frac{1}{2} \left( \frac{0}{2} \left( \frac{0}{2} + 1 \right) \right)$$

$\mu_{\text{eff}} = 0$ 
 $\chi T = 0$

□

(e) Square planar Pt(II).

*Answer.* As a square planar complex, Pt(II) will be low spin. It follows that as a  $d^8$  metal center with  $D_{4h}$  geometry, Pt(II) will have 0 unpaired electron. Thus,

$$\mu_{\text{eff}} = \sqrt{4 \left( \frac{0}{2} \left( \frac{0}{2} + 1 \right) \right)} \quad \chi T = \frac{1}{2} \left( \frac{0}{2} \left( \frac{0}{2} + 1 \right) \right)$$

$\mu_{\text{eff}} = 0$ 
 $\chi T = 0$

□

(f) Octahedral Ni(II).

*Answer.* As a first-row transition metal with  $O_h$  geometry, Ni(II) will be low spin. It follows that as a  $d^8$  metal center, Ni(II) will have 2 unpaired electrons. Thus,

$$\mu_{\text{eff}} = \sqrt{4 \left( \frac{2}{2} \left( \frac{2}{2} + 1 \right) \right)} \quad \chi T = \frac{1}{2} \left( \frac{2}{2} \left( \frac{2}{2} + 1 \right) \right)$$

$\mu_{\text{eff}} = 2.82$ 
 $\chi T = 1$

□

(g) Tetrahedral Cr(0).

*Answer.* High spin. As a first-row transition metal with  $T_d$  geometry, Cr(0) will be high spin. It follows that as a  $d^6$  metal center, Cr(0) will have 4 unpaired electrons. Thus,

$$\mu_{\text{eff}} = \sqrt{4 \left( \frac{4}{2} \left( \frac{4}{2} + 1 \right) \right)} \quad \chi T = \frac{1}{2} \left( \frac{4}{2} \left( \frac{4}{2} + 1 \right) \right)$$

$\mu_{\text{eff}} = 4.90$ 
 $\chi T = 3$

□

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).

*Answer.* Cu(II) has a  $d^9$  configuration, i.e., its  $d$ -shell is more than half filled. Thus, by the rule discussed in class,

$$\boxed{g > 2}$$

The intuitive (but not quantum mechanically accurate) reason for this is that in a  $d^9$  configuration, one *hole* hops around producing a ring current that *reinforces* the magnetic field, which means that we don't need  $H_r$  to be as high in  $g = h\nu/\beta H_r$  to achieve the transition. With  $H_r$  lower,  $g$  is higher. □

(b) Cr(V).

*Answer.* Cr(V) has a  $d^1$  configuration, i.e., its  $d$ -shell is less than half filled. Thus, by the rule discussed in class,

$$\boxed{g < 2}$$

□

(c) Mn(II).

*Answer.* Mn(II) has a  $d^5$  configuration, i.e., its  $d$ -shell is exactly half filled. Thus, by the rule discussed in class,

$$g \approx 2$$

□

(d) Fe(III).

*Answer.* Fe(III) has a  $d^5$  configuration, i.e., its  $d$ -shell is exactly half filled. Thus, by the rule discussed in class,

$$g \approx 2$$

□

(e) Co(II).

*Answer.* Co(II) has a  $d^7$  configuration, i.e., its  $d$ -shell is more than half filled. Thus, by the rule discussed in class,

$$g > 2$$

□

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?

*Answer.* In XAS, varying oxidation states shift the  $K$ -edge. In particular, since ferrocenium has a more highly oxidized iron atom, Fe will hold onto its electrons more tightly, shifting its  $K$ -edge higher. In Mossbauer, a higher oxidation states mean less electron density at the nucleus. Thus, the isomer shift will be affected in a predictable way. □

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.

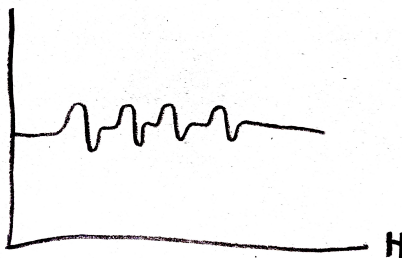
*Answer.* You can obtain the number of adjacent scatterers (including phosphine ligands), some information on the type of scatterers that may help determine what they are, and the distance of scatters, i.e., the bond length. □

- (b) A Mossbauer spectrum of an  $\text{FeL}_5$  complex shows two signals with differing isomer shifts and quadrupole splittings. Offer an explanation for this.

*Answer.* Differences in isomer shifts for iron compounds usually correlate with with differing oxidation states. Additionally, spin state and anisotropy in the  $d$ -orbital splitting diagram usually correlate with quadrupole splitting. Thus, it is possible that there are certain instance of the complex with different electronic structures. Alternatively, there may be some splitting occurring due to an applied magnetic field. □

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

*Answer.* Since the  $d^9$  (one electron unpaired) ion is in solution (not frozen), the  $g$ -values will be isotropic. Additionally,  $I = 3/2$  and the relevant selection rules ( $\Delta M_S = \pm 1$  and  $\Delta M_I = 0$ ) means that the hyperfine splitting splits the peak into a quartet of peaks with the same height. Thus, the EPR spectrum should resemble the following.



□

9. The EPR spectrum of an axially symmetric  $\text{Cu}^{2+}$  complex in a frozen solution that is 100%  $^{63}\text{Cu}$  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...

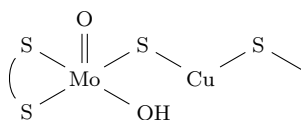
- (a) Compute the value of  $g_{\parallel}$ ;

*Answer.* We know that  $g = h\nu/\beta H_r$ . Do we just plug in  $\nu$  as the spectrometer frequency and  $H_r$  as the magnetic field?? Do we average somehow? □

- (b) Compute the hyperfine coupling constant.

*Answer.* How do you calculate the hyperfine coupling constant  $a$ ?? Perhaps use  $a = g\beta A$  where  $A$  is one of the peak splittings? □

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.

*Answer.* The heavy atoms can be identified by the  $K$ -edge energy. The oxidation state can technically be identified by the  $K$ -edge shift from the standard, although XAS is typically more useful for measuring relative oxidation states than “absolute” ones. The coordination environment can be determined by fitting the EXAFS data to the EXAFS equation. □

- (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  $\text{OH}_2$ ) with ENDOR spectroscopy?

*Answer.* ENDOR turns on extra transitions. Protonation should correlate with the oxidation state, affecting splitting. Since ENDOR allows us to resolve extra transitions and learn more about electron transitions that are coupled to local nuclear transitions, that could also be of use. □

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

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

*Answer.* We take the pythagorean average of the two?? See Lecture 6.2. □

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

*Answer.* □

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

*Answer.* □

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

*Answer.* □

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.

*Answer.* Ti(III) is  $d^1$  and Cu(II) is  $d^9$ . Thus, each metal center has one unpaired electron, and they are likely to couple parallel, or ferromagnetically. However, when Fe(III) is present, we have more of a situation of one hole moving around, and thus antiferromagnetic exchange is more active. □