2   Molecular 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 $2400\,\mathrm{cm}^{-1}$ and $2330\,\mathrm{cm}^{-1}$.

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

Answer. $\boxed{\text{One}}$ complex. The two bands correspond to a symmetric and an asymmetric bending mode[1] of the same compound. □

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

Answer. Let

$$\nu_{1,H} = 2400\,\mathrm{cm}^{-1} \qquad\qquad \nu_{2,H} = 2330\,\mathrm{cm}^{-1}$$

We have that

$$\mu_{NH} = \frac{m_N m_H}{m_N + m_H} = \frac{14 \cdot 1}{14 + 1} = 0.933 \qquad\qquad \mu_{ND} = \frac{m_N m_D}{m_N + m_D} = \frac{14 \cdot 2}{14 + 2} = 1.75$$

Thus,

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

Plugging in numbers, we learn that

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

□

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 $M_I = -3, -2, \ldots, 3$ (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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[1]Not a stretch according to Dr. Anderson.

3. The intensities and frequencies (vs. H_3PO_4) of resonances in the $121.4\,\text{MHz}$ $^{31}P\{^1H\}$ 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	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. To convert to chemical shift (ppm), use the formula

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

where ν_1 is the measured frequency for a given nucleus, $\nu_{\text{ref}} = 0$ in this case, and $\nu_0 = 121.4\,\text{MHz}$ 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 $-27.62\,\text{ppm}$ is

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

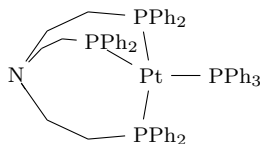and the coupling constant for the peak centered around $-5.877\,\text{ppm}$ is

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

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

$J_1 = 0.66$	$J_2 = 0.66$	$J_3 = 0.658$	$J_4 = 0.659$	$J_5 = 0.660$	$J_6 = 0.660$

where all quantities are in units of ppm.

Lastly, the structure is as follows.

4. Predict the spin state, μ_{eff}, and χT 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 $\boxed{\text{high spin.}}$ It follows that as a d^5 metal center, Mn(II) will have 5 unpaired electrons. Thus,

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

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

   (b) Octahedral Ir(III).

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

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

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

   (c) Octahedral Ru(III).

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

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

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

   (d) Square planar Co(I).

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

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

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

(e) Square planar Pt(II).

Answer. As a third-row transition metal, Pt(II) will be $\boxed{\text{low spin.}}$ It follows that as a d^8 metal center with D_{4h} geometry, Pt(II) will have 0 unpaired electron. Thus,

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

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

$\square$

(f) Octahedral Ni(II).

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

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

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

$\square$

(g) Tetrahedral Cr(0).

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

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

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

$\square$

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. $\square$

(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,

$$\boxed{g < 2}$$

$\square$

(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,

$$\boxed{g \approx 2}$$

□

(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,

$$\boxed{g \approx 2}$$

□

(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,

$$\boxed{g > 2}$$

□

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 γ ray would not need to be as high intensity to pierce through the surrounding electron cloud, meaning that the the isomer shift will be lower for ferrocenium.   □

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 $\boxed{\text{number}}$ of adjacent scatterers (including phosphine ligands), some information on the $\boxed{\text{type}}$ of scatterers that may help determine what they are, and the $\boxed{\text{distance}}$ of scatters, i.e., the bond length.   □

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

Answer. You could have two different isomers, one square pyramidal and one trigonal bipyramidal.

□

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.

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.
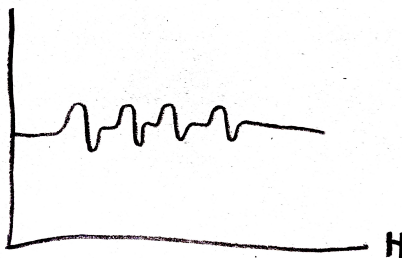
9. The EPR spectrum of an axially symmetric Cu^{2+} complex in a frozen solution that is 100% ^{63}Cu consists of three well-resolved low field g-parallel components, a fourth component of the multiplet that overlaps the g-perpendicular signal, and some higher field lines. The minima between the four 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 $g_{\parallel}$;

   Answer. As stated in the question, the $g_{\parallel}$ component of the EPR spectrum appears in a quartet with center minimum at $2810\,G$. Thus,

   $$g = \frac{h\nu}{\beta H_r}$$
   $$= \frac{(6.626 \times 10^{-34}\,J\,s)(9.12 \times 10^9\,s^{-1})}{(9.3 \times 10^{-24}\,J\,T^{-1})(0.281\,T)}$$
   $$\boxed{g = 2.32}$$
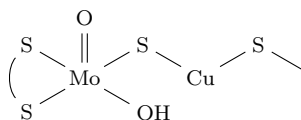
   (b) Compute the hyperfine coupling constant.

   Answer. We have that

   $$a = g\beta A$$
   $$= (2.32)(9.3 \times 10^{-24}\,J\,T^{-1})(0.009\,T)$$
   $$= 1\,J$$

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

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

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

Answer.   □

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

Answer.   □

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

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.   □