

# CHEM 30200 (Synthesis and Physical Methods in Inorganic Chemistry) Problem Sets

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## 1 Materials Spectroscopy

- 1/31: 1. Does the wavelength of the characteristic radiation caused by bombarding of the anode material with electrons depend on voltage? Please, explain.

*Answer.* No it does not.

Characteristic radiation is generated when an incident electron knocks an orbital electron out of the inner shell of an atom in the anode, and then an outer shell electron loses energy (in the form of characteristic radiation) to fall down and fill the core hole. Thus, the wavelength of characteristic radiation is determined by the energy level gaps in the anode material, not the voltage of the incident electrons. Indeed, the only way that voltage affects characteristic radiation is by turning it on and off: We just need it to be high enough so that the incident electrons *can* kick out an inner shell electron.  $\square$

2. Please, explain which effects take place in the X-ray tube upon increasing the current and voltage.

*Answer.* We address the effects one at a time.

Increasing the current: The intensity of both bremsstrahlung and characteristic radiation increases. This is because higher current means that more electrons are emitted, which means that more electrons deflect and/or are knocked out.

Increasing the voltage: The intensity of both bremsstrahlung and characteristic radiation increases. The frequency of the characteristic radiation will not change (see Q1), but both the maximum frequency and general distribution of the bremsstrahlung radiation will shift higher. This is because the bremsstrahlung radiation that an electron can emit is capped by its translational kinetic energy as an incoming particle, and increasing the voltage increases the translational kinetic energy of the incoming electrons.  $\square$

3. Determine the maximum wavelength of the X-ray emission caused by electrons traveling with 35 keV of energy.

*Answer.* From the Duane-Hunt law, we know that the frequency  $f$  at which the most X-rays are emitted is given by  $f = Ve/h$ . Additionally, we know that  $c = \lambda f$ . Therefore,

$$\begin{aligned}\lambda &= \frac{c}{f} \\ &= \frac{ch}{Ve} \\ &= \frac{(2.998 \times 10^8 \text{ m s}^{-1})(6.626 \times 10^{-34} \text{ J s})}{(3.5 \times 10^4 \text{ eV})(1.602 \times 10^{-19} \text{ C})}\end{aligned}$$

$\lambda = 35 \text{ pm}$

meaning that these are hard X-rays.  $\square$

4. Which material will work better for X-ray absorption: Fe or Pb? Note: Fe has atomic number and atomic weight equal to 26 and 55.8, respectively; Pb has atomic number and atomic weight equal to 82 and 207.2, respectively. Please, explain.

*Answer.* Pb will work better for X-ray absorption.

Absorption depends on *contact*, a quantity proportional to the atomic number  $Z$  of the target element. Thus, elements with higher  $Z$ -numbers will have greater contact and hence greater absorption. It follows since  $Z(\text{Pb}) > Z(\text{Fe})$  that Pb has greater X-ray absorption.  $\square$

5. List three types of interactions of X-rays with matter.

*Answer.* Three ways X-rays can interact with matter are...

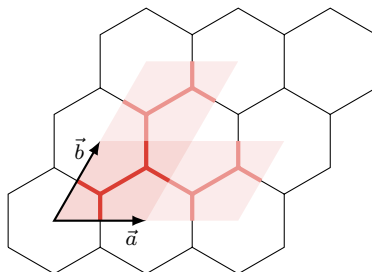
Absorption/fluorescence, elastic scattering, and inelastic scattering.

□

6. Define the Bravais lattice for graphene.

*Answer.* Graphene has a hexagonal 2D Bravais lattice.

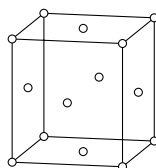
It is a honeycomb, and hence has a nonobvious rhombus-shaped unit cell, as pictured below.



□

7. Pt has a structure where Pt atoms occupy the positions at the vertices of the cube and in the middle of the facets. Please, draw the Bravais lattice for Pt. How many atoms are in the basis for the lattice? If the Pt atoms at the facets of the cube will be replaced with something else (e.g., Au), will it affect the Bravais lattice?

*Answer.* The Bravais lattice for Pt is face-centered cubic, as depicted below.



There is 1 atom in the basis.

Effects on the Bravais lattice: We have a new simplest repeating unit. Indeed, instead of repeating one Pt atom, we repeat one Pt atom and three Au atoms as follows. Consider any of the corner Pt atoms in the above unit cell (for example, the one in the front, bottom, right). Choose the three Au atoms closest to it in the above unit cell (continuing with our example, this would be the ones in the front, bottom, and right faces). This little tetrahedron of one Pt and three Au atoms forms the full crystal by replicating along the preexisting crystal axes. Thus, this  $\text{PtAu}_3$  unit is our basis, and the new Bravais lattice is primitive cubic. □

8. What are the types of Bravais lattices?

*Answer.* There are four types:

Primitive, body-centered, base-centered, and face-centered.

□

9. Pt was alloyed with Co and a PtCo alloy was formed. Please, analyze the peak positions measured for the Pt and PtCo alloy, and make a conclusion about the trend of peak positions in the XRD diffractogram of  $\text{CoPt}_3$  if it has the same lattice.

	Pt	PtCo	$\text{CoPt}_3$
(111)	39.036	40.252	39.645
(200)	45.876	46.425	46.151
(220)	66.905	68.117	67.511
(311)	80.624	81.662	81.143

*Answer.* Per Vegard's law, there is an approximately linear relationship between the lattice constants of an alloy and its composition. The left metal above is 100% platinum, the middle alloy is 50% platinum, and the right alloy is 75% platinum: Thus, the values in the right column should be averages of the respective values in the left two columns, as 75% is an average of 100% and 50%: See above.  $\square$

10. The shell of an unknown material was grown around Pt nanoparticles. As a result, the peak positions of Pt were shifted by  $\sim 1.5\%$  toward the higher  $2\theta$ . Please, calculate the strain.

*Answer.* The strain  $\varepsilon$  will depend on  $\theta$  via the following relationship.

$$n\lambda = 2(d - \varepsilon d) \sin(1.015\theta)$$

$$2d \sin(\theta) = 2d \sin(1.015\theta) - \varepsilon \cdot 2d \sin(1.015\theta)$$

$$\varepsilon = \frac{\sin(1.015\theta) - \sin(\theta)}{\sin(1.015\theta)}$$

Plugging in  $2\theta = 39.036$  from Q9, for example, we get

$$\varepsilon = 0.014$$

$\square$

11. Please, think about your project and come up with an experiment that involves X-ray diffraction. If this method is not relevant to the scope of your research, explain your reasoning.

*Answer.* We actually use PXRD all the time in our research! Most recently, we investigated the catalytic potential of a photosensitizing covalent organic framework<sup>1</sup>. The COF's theoretical photosensitizing ability comes from its crystalline, completely  $\pi$ -conjugated chromaphores, so to confirm that it was absorbing light as per our mechanistic prediction, we needed to confirm that it was crystalline. To do so, we ran a PXRD and compared it to the simulated profile via a Rietveld refinement.  $\square$

## 2 Molecular 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.* 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

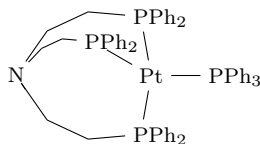
$$\begin{aligned} J_3 &= \frac{[(-4.890 \text{ ppm}) - (-5.547 \text{ ppm})] + [(-5.547 \text{ ppm}) - (-6.207 \text{ ppm})] + [(-6.207 \text{ ppm}) - (-6.864 \text{ ppm})]}{3} \\ &= \frac{(-4.890 \text{ ppm}) - (-6.864 \text{ ppm})}{3} \\ &= 0.658 \text{ ppm} \end{aligned}$$

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,

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

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

□

(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,

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

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

□

(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,

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

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

□

(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,

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

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

□



(e) Square planar Pt(II).

*Answer.* As a third-row transition metal, 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  $\gamma$  ray would not need to be as high intensity to pierce through the surrounding electron cloud, meaning that 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.

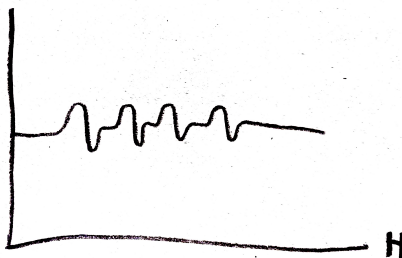
*Answer.* You can obtain the number of adjacent scatterers (including phosphine ligands), some information on the type of scatterers that may help determine what they are, and the distance of scatters, i.e., the bond length. □

- (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.* 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  $^{63}\text{Cu}^{2+}$  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.* As stated in the question, the  $g_{\parallel}$  component of the EPR spectrum appears in a quartet with center minimum at 2810 G. Thus,

$$\begin{aligned}
 g &= \frac{h\nu}{\beta H_r} \\
 &= \frac{(6.626 \times 10^{-34} \text{ J s})(9.12 \times 10^9 \text{ s}^{-1})}{(9.3 \times 10^{-24} \text{ J T}^{-1})(0.281 \text{ T})} \\
 \boxed{g = 2.32}
 \end{aligned}$$

□

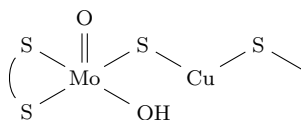
- (b) Compute the hyperfine coupling constant.

*Answer.* We have that

$$\begin{aligned}
 a &= g\beta A \\
 &= (2.32)(9.3 \times 10^{-24} \text{ J T}^{-1})(0.009 \text{ T}) \\
 &= 1 \text{ J}
 \end{aligned}$$

□

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<sub>2</sub>) 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. □

## References

- (1) Fan, Y.; Kang, D. W.; Labalme, S.; Li, J.; Lin, W. *Angewandte Chemie* **2023**, DOI: 10.1002/anie.202218908.