Inorganic Chemistry

Midterm Examination   Apr. 27, 2011

1. Werner won the Nobel prize for chemistry in 1913. The citation is as follows: work on the linkage of atoms in molecules which has thrown new light on earlier investigations and opened up new fields of research especially in inorganic chemistry. Elaborate the statement and describe his coordination theory. (10%)

2. Give structures for the following (8%):
    (a) Bis(en)Co(III)-μ-amido-μ-hydroxobis(en)Co(III) ion
    (b) DiaquadiiododinitritoPd(IV), all isomers
    (c) Fe(dtc)$_3$, all isomers

    dtc =
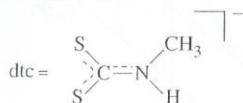
3. Give the d orbitals splitting (qualitatively) in the following crystal fields (8%):
    (a) octahedral (b) tetrahedral (c) square planar (d) trigonal planar

4. Draw the molecular orbitals diagram of octahedral ML$_6$ by considering sigma donor interaction only. Specify the Δo (10%)

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4{}^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2 + y^2 + z^2$
A_{2g}	1	1	−1	−1	1	1	−1	1	1	−1		
E_g	2	−1	0	0	2	2	0	−1	2	0		$(2z^2 - x^2 - y^2, x^2 - y^2)$
T_{1g}	3	0	−1	1	−1	3	1	0	−1	−1	(R_x, R_y, R_z)	
T_{2g}	3	0	1	−1	−1	3	−1	0	−1	1		(xy, xz, yz)
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1		
A_{2u}	1	1	−1	−1	1	−1	1	−1	−1	1		
E_u	2	−1	0	0	2	−2	0	1	−2	0		
T_{1u}	3	0	−1	1	−1	−3	−1	0	1	1	(x, y, z)	
T_{2u}	3	0	1	−1	−1	−3	1	0	1	−1		

5. How does the Pi-bonding effect on the Δo in octahedral ML$_6$ complex? Give the spectrochemical series of the ligands. (10%)

6. For each of the following configurations, construct a microstate table and reduce the table to its constituent free-ion terms. Identify the lowest-energy term for each.(10%)
    (a) p^3
    (b) $p^1 d^1$ (as in a $4p^1 3d^1$ configuration)

d^7

7. $[Co(NH_3)_6]^{2+}$ has absorption bands at 9000 and 21100 cm⁻¹. Calculate Δo and B for this ion. (Hints: The $^4T_{1g} \longrightarrow {}^4A_{2g}$ transition in this complex is too weak to be observed. The graph in Figure 1 may be used for d^7 as well as d^2 complexes) (10%)
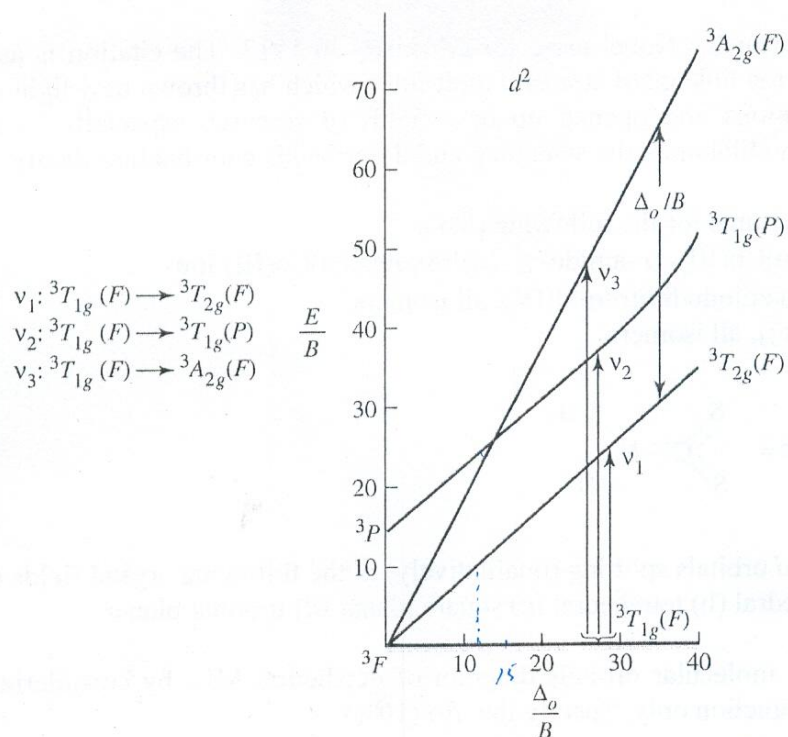

$\nu_1: {}^3T_{1g}(F) \longrightarrow {}^3T_{2g}(F)$
$\nu_2: {}^3T_{1g}(F) \longrightarrow {}^3T_{1g}(P)$
$\nu_3: {}^3T_{1g}(F) \longrightarrow {}^3A_{2g}(F)$

FIGURE 1 Spin-Allowed Transitions for d^2 Configuration

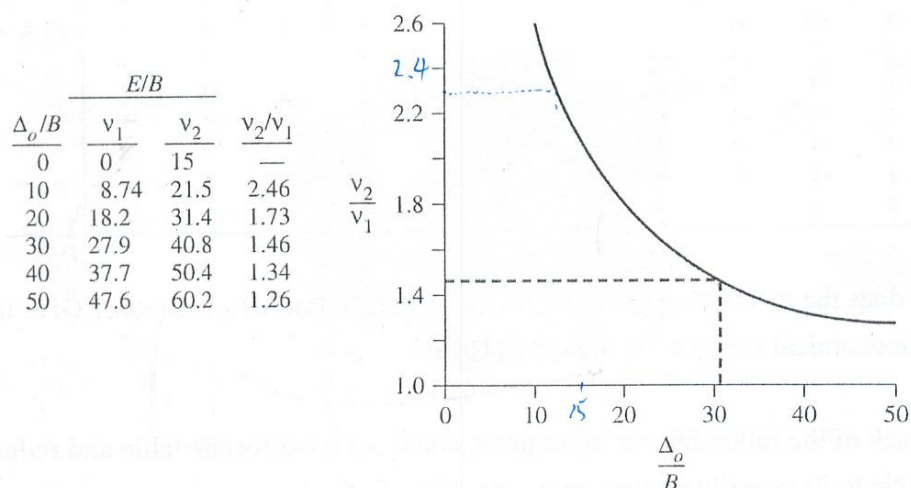| Δ_o/B | E/B | | |
	ν_1	ν_2	ν_2/ν_1
0	0	15	—
10	8.74	21.5	2.46
20	18.2	31.4	1.73
30	27.9	40.8	1.46
40	37.7	50.4	1.34
50	47.6	60.2	1.26

FIGURE 2 Value of ν_2/ν_1 Ratio for d^2 Configuration.

8. An aqueous solution of $Ni(NO_3)_2$ is green. Addition of aqueous NH_3 causes the color of the solution to change to blue. If ethylenediamine is added to the green solution, the color changes to violet. Account for the colors of these complexes. Are they consistent with the expected positions of these ligands in the spectrochemical series? (6%)

9. Match the following complex molecules with the proper ground state symbol:

   (a) $[Cr(NH_3)_6]^{3+}$ (1) $^6A_{1g}$

   (b) $[CoF_6]^{3-}$ (high spin)   (2) $^1A_{1g}$

   (c) $[Mn(H_2O)_6]^{2+}$ (high spin)   (3) $^3T_{1g}$

   (d) $[Ni(NH_3)_6]^{2+}$ (paramagnetic)   (4) $^4A_{2g}$

   (e) $[RhCl_6]^{3-}$ (diamagnetic)   (5) $^5T_{2g}$

   (f) $[Mn(CN)_6]^{3-}$ (low spin)   (6) $^3A_{2g}$

   (g) $[Ti(H_2O)_6]^{3+}$ (7) $^2T_{2g}$ (7%)

10. A 2.00×10^{-4} M solution of $Fe(S_2CNEt_2)_3$ (Et = C_2H_5) in $CHCl_3$ at 25 °C has absorption bands at 350 nm (A = 2.34), 514nm (A = 0.532), 590nm (A = 0.370), and 1540nm (A = 0.0016). (6%)

    (a) Calculate the molar absorptivity for this compound at each wavelength.

    (b) Are these bands more likely due to d-d transitions or charge-transfer transitions? Explain.

11. Predict whether these complexes would be labile or inert and explain your choices. The magnetic moment is given in Bohr magnetons (μ_B) after each complex.(4%)

    (a) Ammonium oxopentachlorochromate (V)   1.82

    (b) Potassium hexaiodomanganate(IV)   3.82

    (c) Potassium hexacyanoferrate(III)   2.40

    (d) Hexaammineiron(II) chloride   5.45

12. Consider the half-lives of substitution reactions of the pairs of complexes:

Half-Lives Shorter than 1 Minute	Half-Lives Longer than 1 Day
$[Cr(CN)_6]^{4-}$	$[Cr(CN)_6]^{3-}$
$[Fe(H_2O)_6]^{3+}$	$[Fe(CN)_6]^{4-}$
$[Co(H_2O)_6]^{2+}$	$[Co(NH_3)_5(H_2O)]^{3+}(H_2O$ exchange$)$

Interpret the differences in half-lives in terms of the electronic structures of each pair.(6%)

13. When the two isomers of $Pt(NH_3)_2Cl_2$ react with thiourea [tu $= S{=}C(NH_2)_2$], one product is $[Pt(tu)_4]^{2+}$ and the other is $[Pt(NH_3)_2(tu)_2]^{2+}$. Identify the initial isomers and explain the results. (4%)

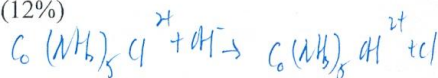14. Predict the products (equimolar mixtures of reactants) (3%):
    (a) $[Pt(CO)Cl_3]^-$ + NH_3 ⟶
    (b) $[Pt(NH_3)Br_3]^-$ + NH_3 ⟶
    (c) $[(C_2H_4)PtCl_3]^-$ + NH_3 ⟶
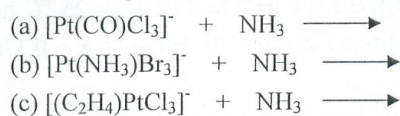
15. Exchange of an H_2O ligand on $[(CO)_3Mn(H_2O)_3]^+$ is much more rapid than on the analogous $[(CO)_3Re(H_2O)_3]^+$. The activation volume (change in volume on formation of the activated complex) is -4.5 ± 0.4 cm^3 mol^{-1}. The Mn complex has infrared bands at 2051 and 1944cm^{-1} that can be attributed to C-O stretching vibrations. (6%)
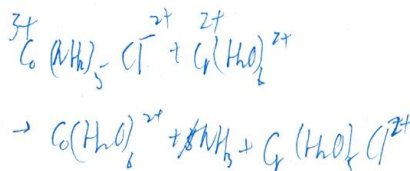   (a) Suggest why the Mn complex reacts more rapidly than the analogous Re complex.
    (b) Is the activation volume more consistent with an A (or Ia) or a D (or Id) mechanism? Explain.
    (c) On the basis of the IR spectrum, is the reactant more likely a fac or mer isomer?

16. Describe the following mechanisms and their evidences: (12%)
    (a) S_N1CB in base hydrolysis reaction.
    (b) Inner-sphere mechanism in electron transfer reaction.

~ The End ~