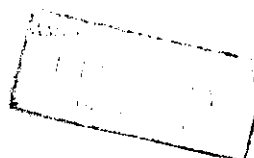
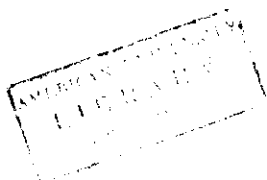


Name:	Student #:	Seat #:
Signature:		

American University of Beirut      Department of Chemistry  
Coordination Chemistry 229 Final Exam  
Monday July 01 1996 8-9:30pm



**Answer *all* questions.**

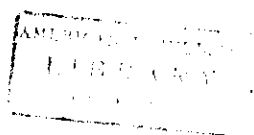
**Anyone caught, or judged to be cheating, will get a zero grade.**

**Any attempt to talk will deny that person a push-up (if one were to be given).**

**DATA:**

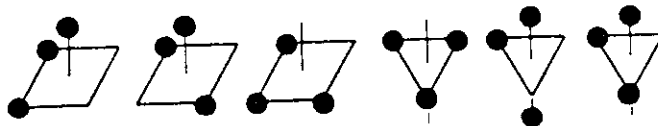
**Atomic numbers:**

**V = 23; Cr = 24;      Mn = 25;      Co = 27**

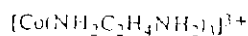
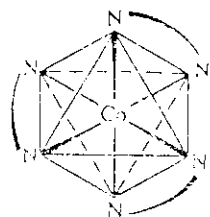


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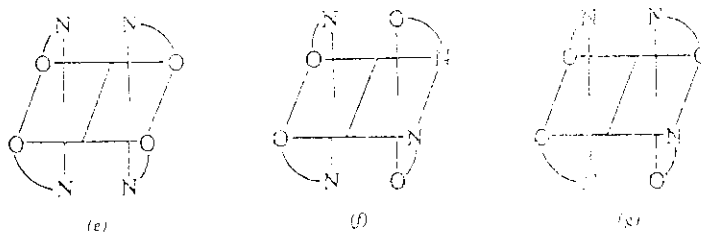
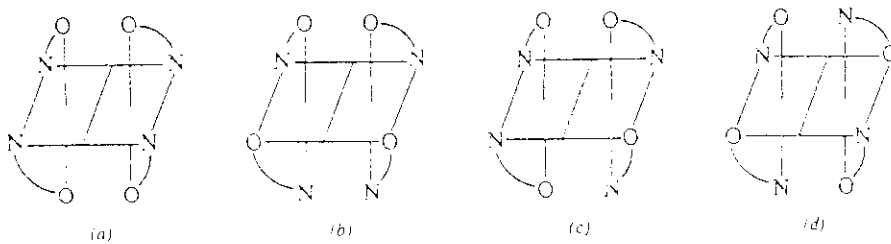
- Q1** The compound  $\text{Fe}(\text{CO})_3(\text{P}\phi_3)_2$ , where  $\phi$  = phenyl, exhibits two Raman bands. Six plausible structures for these compounds are shown below, in which CO ligands are indicated by dark circles.
- (a) Give the point group for *each* structure (put them under each structure).
- (b) With which structure is the Raman data consistent? (Circle your choice).



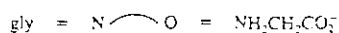
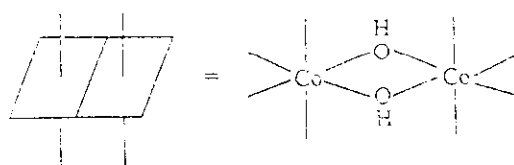
- Q2**
- (a) Give the point group for  $[\text{Co}(\text{NH}_2\text{C}_2\text{H}_4\text{NH}_2)_3]^{3+}$ , shown below, (put it beside the structure).
- (b) Give the *reducible representation* of the d orbitals of the Co.



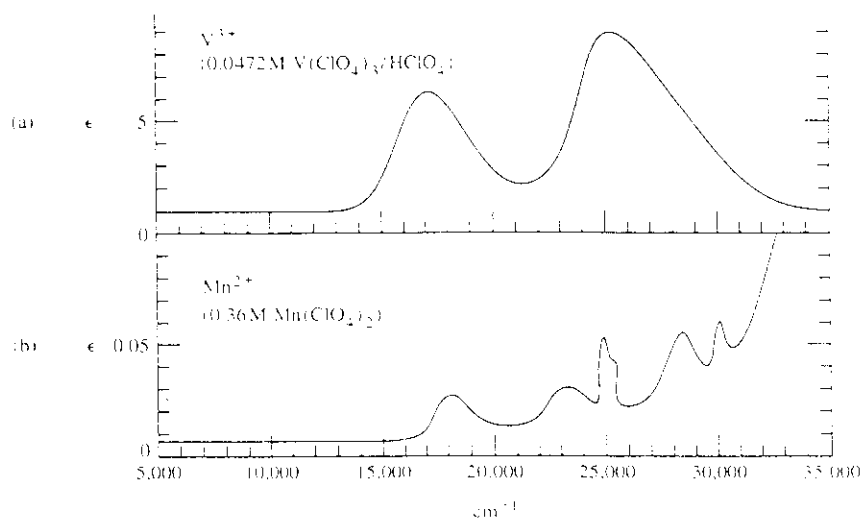
- Q3** Which of the following molecules have *both* a center of symmetry *and* a mirror plane? (Circle your choice(s)).



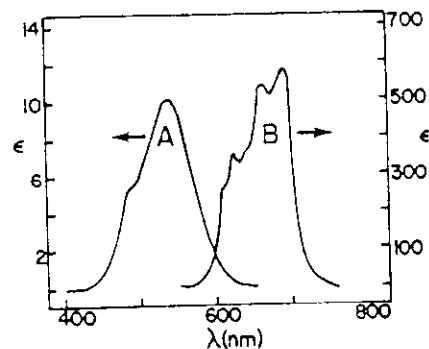
Isomers of  $[(\text{gly})_2\text{Co}(\text{OH})_2\text{Co}(\text{gly})_2]$



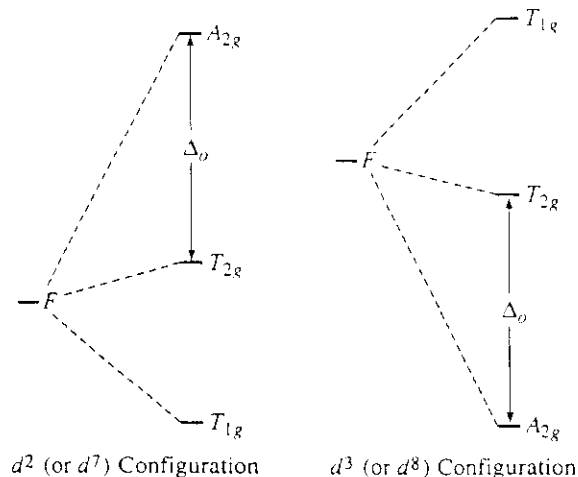
- Q4** The spectra below show  $V^{3+}$  and  $Mn^{2+}$  aqueous salts respectively.  
 (a) Why do manganese (II) salts have weak coloration?  
 (b) Why is the manganese (II) spectrum so complicated?



- Q5** The following visible spectra may represent  $[Co(H_2O)_6]^{2+}$  and  $CoCl_4^{2-}$ . If so, which is which? (Circle your choice).  
 (a) A =  $[Co(H_2O)_6]^{2+}$  B =  $CoCl_4^{2-}$   
 (b) A =  $CoCl_4^{2-}$  B =  $[Co(H_2O)_6]^{2+}$   
 (c) Neither.  
 (d) Not enough information to judge.



- Q6** The figure below shows the term symbol splitting for  $d^2$  and  $d^3$  in an octahedral field. Why are the ground state split terms reversed in going from a  $d^2$  to a  $d^3$  configuration?



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- Q7 In the diagram of question 6 why is it not reasonable to measure  $\Delta_o$  from the *ground state* in the  $d^2$  configuration? (Answer in the space below *only*).
- Q8 Why does the thiocyanate ion appear *twice* in the spectrochemical series? (Answer in the space below *only*). Note: you do not need the series to answer this question.
- Q9 Draw the correlation diagram for a  $T_d$   $d^2$  complex.

Q10

- (a) Two complexes of Ni(II) are believed to be Oh and Td. Each has three uv/visible absorption bands, but **complex A** has  $\epsilon = 10$  and **complex B** has  $\epsilon = 150$ . Which is probably the Oh complex?
- (b) What *physical* measurement would you make to prove that neither complex was square planar?

Q11 How many microstates are there for  $d^3$ ?

Q12 Find the ground state term symbol for  $d^7$ .

Q13 For which  $d^n$  configurations would no Jahn-Teller splitting be expected in the Td case? (Ignore possible low-spin cases).

Q14 The *Racah parameter B* is: (Circle your choice(s)).

- (a) an electron repulsion term in an ion.  
(b) a function of the ligands surrounding a metal ion.  
(c) represented by the nephelauxetic series.  
(d) smaller for a complex than for a free metal ion.

Q15 What factor differentiates a Tanabe-Sugano diagram from an Orgel diagram?

Q16 Why do some lines bend on Tanabe-Sugano diagrams?

**Q17** The terms for the  $p^2$  electronic configuration are given below with LS coupling only. Show how these are affected by spin-orbit coupling. (Give full term symbol information in your answer).

$^1S$  \_\_\_\_\_

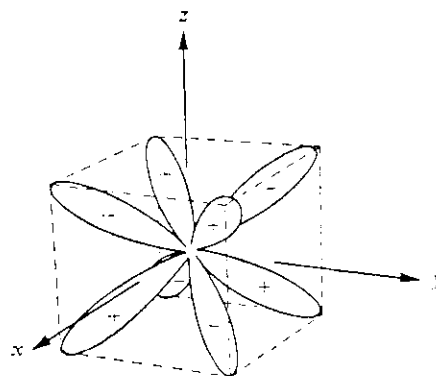
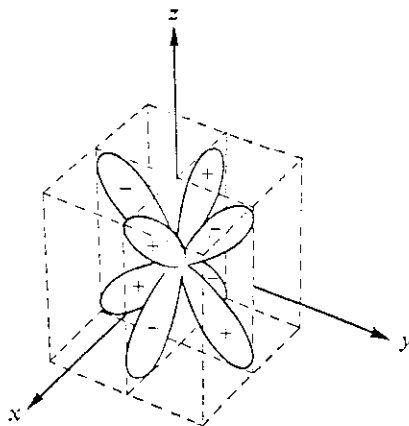
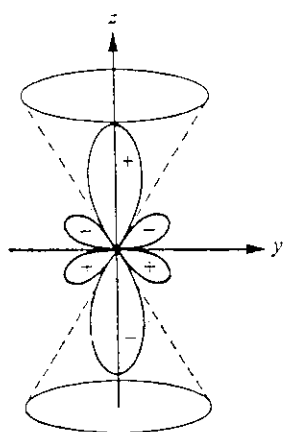
$^1D$  \_\_\_\_\_

$^3P$  \_\_\_\_\_

LS coupling only

**Q18** State Laporte's rule.

**Q19** Which one of the following  $f$  orbitals is represented by  $A_{2u}$ ? (Circle your choice).



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

Q20

- (a) The electronic absorption spectra of octahedral  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  is shown below. There are three main d-d bands located at  $17400\text{cm}^{-1}$ ,  $24600\text{cm}^{-1}$  and  $37800\text{cm}^{-1}$ . Use the appropriate Tanabe-Sugano diagram to find **B** (the *Racah* parameter) and  $\Delta_o$ . (Graph paper is attached).

$$\mathbf{B} =$$

$$\Delta_o =$$

- (b) Assign each of the three bands to an appropriate transition.

<u>Band</u>	<u>Transition</u>
-------------	-------------------

$17400\text{cm}^{-1}$

$24600\text{cm}^{-1}$

$37800\text{cm}^{-1}$

- (c) The value of **B** in this complex is only 75% of the value for the free  $\text{Cr}^{3+}$  ion. Give a very brief explanation.

