

University of Canterbury

# Mid Year Examination and Test Period 2009

Prescription Number(s):	CHEM 231
Paper Title:	Introduction to Inorganic Chemistry

Time Allowed: 1.5 HOURS

Number of pages: SIX

Answer **ALL** questions.

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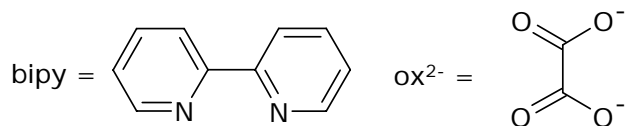
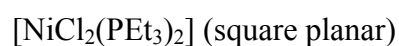
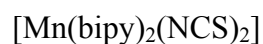
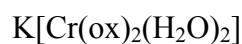
1. (10 marks)

Using diagrams as appropriate provide definitions for the following terms used within the field of coordination chemistry:

- (a) Multi-dentate chelating ligand
- (b) Octahedral field and crystal-field stabilisation energy
- (c) Paramagnetic and diamagnetic
- (d) Overall/cumulative stability constant.

2. (25 marks)

(a) For each of the following complexes:

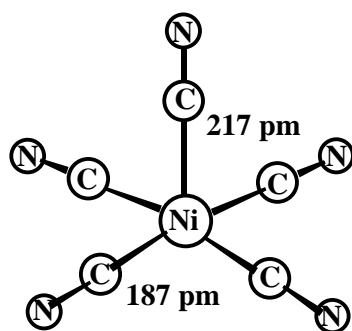


- (i) Give the metal oxidation state and the number of d-electrons on the metal ion.
  - (ii) Each of the three compounds may exist in isomeric forms. Draw the isomers and describe the kind of isomerism exhibited.
  - (iii) Draw the crystal-field splitting diagram for each. Assuming, where appropriate, that each is in the high-spin state, calculate their expected magnetic moments.
- (b) How would the magnetic moment of the nickel complex in (a) differ if it were in tetrahedral geometry? Explain.

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3. (20 marks)

- (a) Draw all possible isomers of the five-coordinate complex  $[M(\text{bipy})(\text{Br})_2(\text{H}_2\text{O})]$  in trigonal bipyramidal geometry ( $M$  = metal ion; bipy = 2,2'-bipyridine). Identify the situations in which optical isomers are possible.
- (b) Develop a crystal-field splitting diagram for the  $d$ -orbitals of the metal in the square pyramidal complex  $[\text{Ni}(\text{CN})_5]^{3-}$  (pictured below). Show, qualitatively, how the energy of each of the  $d$ -orbitals changes.

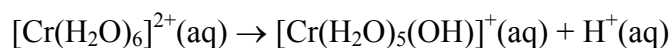


Structure of  $[\text{Ni}(\text{CN})_5]^{3-}$  showing the different axial and basal nickel to cyanide bond lengths.

Given that the magnetic moment for this complex is 2.83 B.M. show on your diagram the electron occupation of the  $d$ -orbitals in this complex.

4. (10 marks)

A sky-blue aqueous solution of  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$  undergoes hydrolysis readily according to the following equation:

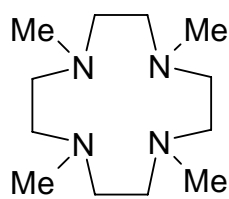


- (a) With the aid of a crystal-field splitting diagram of  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ , explain the origin of the sky-blue colour of the solution.
- (b) The absorption maximum of  $[\text{Cr}(\text{H}_2\text{O})_5(\text{OH})]^+$  is at a longer wavelength than that of  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ . What does this tell you about the effect of hydroxide ligands compared to water on the magnitude of the crystal-field splitting parameter,  $\Delta$ ?

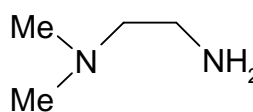
5. (25 marks)

The following table summarizes UV-visible and magnetic data for three nickel complexes:

Complex	UV-visible spectrum $\lambda_{\max}$ ; $\epsilon_{\max}$	Magnetic moment (B.M.)
$(\text{Et}_4\text{N})_2[\text{NiBr}_4]$	650 nm; $550 \text{ M}^{-1} \text{ cm}^{-1}$	3.1
$[\text{Ni}(\text{Me}_2\text{en})_2\text{Cl}_2]$	544 nm; $8.5 \text{ M}^{-1} \text{ cm}^{-1}$	2.8
$[\text{Ni}(\text{Me}_4\text{cyclen})]\text{Cl}_2$	500 nm; $200 \text{ M}^{-1} \text{ cm}^{-1}$	0



$\text{Me}_4\text{cyclen}$



$\text{Me}_2\text{en}$

Using these data, determine the configuration of the nickel centre in each of the complexes. Fully explain your answers, using diagrams where appropriate.

Account for the observed differences in colour and why the intensity of these colours varies between each complex.

**END OF PAPER**

**(Periodic Table on following page)**

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## Periodic Table

1 H 1.008																	2 He 4.00
3 Li 6.94	4 Be 9.01											5 B 10.8	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.0	10 Ne 20.2
11 Na 23.0	12 Mg 24.3											13 Al 27.0	14 Si 28.1	15 P 31.0	16 S 32.1	17 Cl 35.5	18 Ar 39.9
19 K 39.1	20 Ca 40.1	21 Sc 45.0	22 Ti 47.9	23 V 50.9	24 Cr 52.0	25 Mn 54.9	26 Fe 55.9	27 Co 58.9	28 Ni 58.7	29 Cu 63.5	30 Zn 65.4	31 Ga 69.7	32 Ge 72.6	33 As 74.9	34 Se 79.0	35 Br 79.9	36 Kr 83.8
37 Rb 85.5	38 Sr 87.6	39 Y 88.9	40 Zr 91.2	41 Nb 92.9	42 Mo 95.9	43 Tc (99)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.3	57-71 see below	72 Hf 178.5	73 Ta 181.0	74 W 183.9	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (210)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	89-103 see below	104 Rf (257)	105 Db (260)	106 Sg (263)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110	111	112						

57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (147)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
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89 Ac (227)	90 Th 232.0	91 Pa (231)	92 U 238.1	93 Np (237)	94 Pu (242)	95 Am (243)	96 Cm (247)	97 Bk (245)	98 Cf (251)	99 Es (254)	100 Fm (253)	101 Md (256)	102 No (254)	103 Lr (257)
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