

國立中央大學八十四學年度碩士班研究生入學試題卷

所別: 化學研究所

組

科目: 無機化學

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Inorganic Chemistry; 100 points totally.

- (1) Predict (or draw) the structure and also determine the point group for the following compounds; (14 points, 2 each)
- (a) PF_2Cl_3 (b) ICl_4^- (c) BrF_5 (d) ClF_3 (e) Cp_2TiCl_2 (Cp=cyclopentadiene)
(f) borazine; $[\text{RNBX}]_3$ (g) $[\text{CpFe}(\text{CO})_2]_2$
- (2) The 18e rule (EAN rule) is a way to help us decide whether a given d-block transition metal organometallic complex is likely to be stable. How could a complex of empirical formula, $\text{Cr}(\text{CO})_3(\text{C}_6\text{H}_5)_2$ or $(\text{CO})_3\text{ReCl}$ attain the 18e configuration without requiring any external ligands? (10 points, 5 each)
- (3) The addition of PEtPh_2 to NiBr_2 at -78°C in CS_2 or C_6H_6 gives a red complex with the formula $(\text{PEtPh}_2)_2\text{NiBr}_2$, which is converted to a green complex of the same formula on standing at room temperature. The red complex is diamagnetic, but the green complex has a magnetic moment of 3.2 B.M. However, in CH_2Cl_2 solution the effective magnetic moment of the compound is only 2.69 B.M. Rationalize and explain all phenomena described above. (20 points)
- (4) Account for the high conductivity of AlCl_3 in CH_3CN . (5 points)
- (5) The following data are available for $\text{Ni}(\text{H}_2\text{O})_6^{2+}$ and $\text{Ni}(\text{NH}_3)_6^{2+}$

$\text{Ni}(\text{H}_2\text{O})_6^{+2}$	$\text{Ni}(\text{NH}_3)_6^{+2}$	
$8,600\text{cm}^{-1}$	$8,600\text{cm}^{-1}$	
$13,500\text{cm}^{-1}$	$13,500\text{cm}^{-1}$	
$25,300\text{cm}^{-1}$	$25,300\text{cm}^{-1}$	
$15,400\text{cm}^{-1}$	$15,400\text{cm}^{-1}$	} Very weak peaks for both complexes
$18,400\text{cm}^{-1}$	$18,400\text{cm}^{-1}$	

Assign the bands. Calculate $10 Dq$ and the expected positions of the spin allowed bands. Account for any discrepancy between the experimental and calculated energies of the bands. Account for the relative position of corresponding bands for the two complexes. (10 points)

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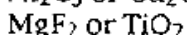
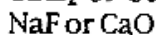
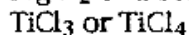
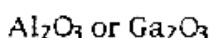
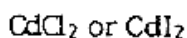
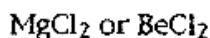
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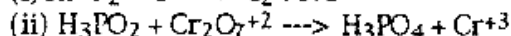
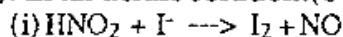
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- (6) For each of the following pairs indicate which substance is expected to be a. More covalent (fajans' rules): b Harder (from concept of soft and hard acid or base) and also explain why? (24 points, 4 each)

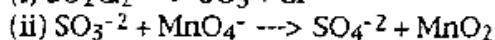
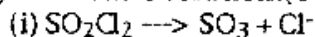


- (7) Balance the following equations

- (a). In an acidic solution. (6 points, 3 each)



- (b). In a basic solution. (6 points, 3 each)



- (8) Explain why comparing a normal melting point with a melting point taken with the compound under water sometimes helps distinguish between intra and intermolecular hydrogen bonding. (5 points)

		Atomic number																	
		Atomic mass																	
Group*	I	II	3	4	5	6	7	8	9	10	11	12	III	IV	V	VI	VII	VIII	
1	H 1.008																		He 4.003
2	Li 6.941	Be 9.012											B 10.81	C 12.01	N 14.01	O 16.00	F 18.99	Ne 20.18	
3	Na 22.99	Mg 24.30											Al 26.98	Si 28.09	P 30.97	S 32.07	Cl 35.45	Ar 39.95	
Transition Elements																			
4	K 39.10	Ca 40.08	Sc 44.96	Ti 47.88	V 50.94	Cr 52.00	Mn 54.94	Fe 55.85	Co 58.93	Ni 58.71	Cu 63.55	Zn 65.39	Ga 69.72	Ge 72.64	As 74.92	Se 78.96	Br 79.90	Kr 83.80	
5	Rb 85.47	Sr 87.62	Y 88.91	Zr 91.22	Nb 92.91	Mo 95.94	Tc 98.91	Ru 101.1	Rh 102.9	Pd 106.4	Ag 107.9	Cd 112.4	In 114.8	Sn 117.4	Sb 121.8	Te 127.6	I 126.9	Xe 131.3	
6	Cs 132.9	Ba 137.3	La 138.9	Hf 178.5	Ta 180.9	W 183.8	Re 186.2	Os 190.2	Ir 192.2	Pt 195.1	Au 197.0	Hg 200.6	Tl 204.4	Pb 207.2	Bi 209.0	Po 209	At 210	Rn 222	
7	Fr 223	Ra 226	Ac (227)	Uuq (231)	Uup (232)	Uuh (233)	Uuq (234)	Uuo (235)	Uuq (236)	Uuq (237)	Uuq (238)	Uuq (239)	Uuq (240)	Uuq (241)	Uuq (242)	Uuq (243)	Uuq (244)	Uuq (245)	Uuq (246)
Lanthanides																			
6	Ce (140.1)	Pr (140.9)	Nd (144.2)	Pm (144.9)	Sm (150.4)	Eu (152.0)	Gd (157.3)	Tb (158.9)	Dy (162.5)	Ho (164.9)	Er (167.3)	Tm (168.9)	Yb (173.0)	Lu (175.0)					
Actinides																			
7	Th (232.0)	Pa (231.0)	U (238.0)	Np (237.0)	Pu (244.0)	Am (243.0)	Cm (247.0)	Bk (247.0)	Cf (251.0)	Es (252.0)	Fm (257.0)	Md (258.0)	No (259.0)	Lr (260.0)					

*The main groups are numbered I to VIII following accepted practice, but due to the confusion created by the difference between European and American practice with respect to A and B groups, the distinction between A and B groups has not been made, and the transition metal groups have not been assigned numbers. Recently the American Chemical Society and the International Union of Pure and Applied Chemistry recommended a revised system in which the groups are numbered consecutively from 1 to 18 as shown here. However, this recommendation has not yet been generally accepted and remains a subject of controversy. We have not adopted it in this text.

*Elements 85 to 109 have unstable nuclei. Each atomic mass given in parentheses is the mass number of the single nuclide. The nuclides of Th and U have sufficiently long half-lives that their abundances and average atomic masses can be determined.