

1996 Inorganic Examination (total 100 points)

1. In the development of quantum mechanics (to describe the structure of atoms), three persons; Werner Heisberg, Louis De Broglie and Erwin Schrodinger, have more significant contribution. Briefly describe the contents of their theories (15 points).

2. How might one distinguish between the following isomers? (9 points).

- (a) $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$ and $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$.
 (b) $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$ and $[\text{Co}(\text{NH}_3)_6][\text{Co}(\text{NO}_2)_6]$.
 (c) cis- and trans- $[\text{Co}(\text{Cl}_3)_2(\text{en})_2]\text{Cl}$.

3. Draw a simple qualitative MO (molecular orbital) diagram for $\text{Mo}(\text{CO})_6$ or $\text{Mo}(\text{CN})_6^{4-}$ compound, and also explain that the metal binds to C atom, not O atom. (assuming the structure of the complexes is a perfect octahedron) (10 points)

4. Why are layer structures such as those of CdCl_2 and CdI_2 usually not encountered for metal fluoride or compounds of the most active metals? (5 points)

5. Give the bond order and the number of unpaired electrons for Be_2^+ , B_2^+ , C_2^+ , O_2^+ , and O_2^- . (5 points)

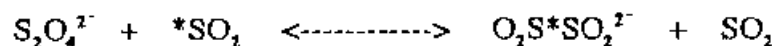
6. The intensity of an infrared absorption is proportional to the change in the dipole moment occurring during the vibration. The asymmetric stretching vibration in IHI^- is far more intense than that found for the stretching vibration of HI . Please give a reasonable explanation. (6 points)

7. Please calculate the LFSE values of transition metal complexes with electronic configuration of d^6 -octahedron in term of high- and low-field ligands. (6 points)

8. Replacement of a ligand by OH^- is called base hydrolysis. In fact, it was argued for some time that base hydrolysis provided an example of an A (Association) reaction involving rate-determining attack by OH^- . However it would be extremely suprising if OH^- were the only nucleophile in aqueous solution capable of attack. Please propose a reasonable mechanism for the following reaction. (6 points)



9. Propose a mechanism for the following incorporation reaction. (5 points)



國立中央大學八十五學年度碩士班研究生入學試題卷

所別: 化學研究所 不分組

科目: 無機化學

共 2 頁 第 2 頁

10. In compounds containing terminal carbonyls, the electron-donor abilities of the metal and other ligands are reflected in the CO stretching vibration frequencies ν_{CO} . Given the following IR data, please rationalize the observed trend in frequencies. (7 points)

$\text{Ti}(\text{CO})_6^{2-}$	1748 cm^{-1}
$\text{V}(\text{CO})_6^-$	1858 cm^{-1}
$\text{Cr}(\text{CO})_6$	1984 cm^{-1}
$\text{Mn}(\text{CO})_6^+$	2094 cm^{-1}
CO	2143 cm^{-1}

11. Give the valence electron count for the following species. (16 points; 2 each. show the calculation for credit)

- (a) $\text{CpMo}(\text{CO})_3(\eta^1\text{-C}_3\text{H}_5)$ (b) $\text{Ir}(\text{PPh}_3)_2(\text{CO})\text{Cl}(\eta^1\text{-C}_3\text{H}_5)$ (c) $\text{Co}_2(\mu\text{-CO})_2(\text{CO})_6$
 (d) $\text{Mn}(\text{CO})_5\text{CH}_2\text{C}_6\text{H}_5$ (e) $\text{IrRh}(\text{CO})_5$ (f) $\text{Ru}_3(\text{CO})_{12}$ (g) $[\eta^4\text{-COD}]\text{Ru}(\mu\text{-Cl})_2$
 (h) $\text{CpCr}(\text{NO})_2\text{Me}$

12. Propose a mechanism for the stoichiometric decarbonylation of $\text{C}_6\text{H}_5\text{CH}_2\text{C}(\text{O})\text{Cl}$ by $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ giving benzyl chloride. Keep in mind the 16- and 18-electron rule. (6 points)

13. Solution of triethylamine in POCl_3 as solvent becomes conducting. Please explain this phenomenon. (4 points)

Representative Elements		d-Transition Elements										Representative Elements					Noble gases
I A Group no. numbers												III A	IV A	V A	VIA	VII A	8A
1 H 1.00794	II A											5 B 10.811	6 C 12.011	7 N 14.00674	8 O 15.9994	9 F 18.9984032	10 Ne 20.1797
3 Li (6.941)	4 Be 9.012182											13 Al 26.981539	14 Si 28.0855	15 P 30.973762	16 S 32.066	17 Cl 35.4527	18 Ar 39.948
11 Na 22.989768	12 Mg 24.3050	II B	IV B	V B	VI B	VII B	VIII		IB	II B	31 Ga 69.723	32 Ge 72.61	33 As 74.92159	34 Se 78.96	35 Br 79.904	36 Kr 83.80	
19 K 39.0983	20 Ca 40.078	21 Sc 44.955910	22 Ti 47.867	23 V 50.9415	24 Cr 51.9961	25 Mn 54.93805	26 Fe 55.845	27 Co 58.93320	28 Ni 58.6934	29 Cu 63.546	30 Zn 65.39	32 Ge 72.61	33 As 74.92159	34 Se 78.96	35 Br 79.904	36 Kr 83.80	
37 Rb 85.4678	38 Sr 87.62	39 Y 88.90585	40 Zr 91.224	41 Nb 92.90638	42 Mo 95.94	43 Tc (99)	44 Ru 101.07	45 Rh 102.90550	46 Pd 106.42	47 Ag 107.8682	48 Cd 112.411	49 In 114.818	50 Sn 118.710	51 Sb 121.760	52 Te 127.60	53 I 126.90447	54 Xe 131.29
55 Cs 132.90543	56 Ba 137.327	57 La 138.9055	72 Hf 178.49	73 Ta 180.9479	74 W 183.84	75 Re 186.207	76 Os 190.23	77 Ir 192.217	78 Pt 195.08	79 Au 196.96654	80 Hg 200.59	81 Tl 204.3833	82 Pb 207.2	83 Bi 208.98037	84 Po (210)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	89 Ac (227)	104 Unq (281)	105 Unp (282)	106 Unh (283)	107 Uns (284)	108 Uno (285)	109 Une (286)									

● Lanthanides

58 Ce 140.115	59 Pr 140.90765	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.965	64 Gd 157.25	65 Tb 158.92534	66 Dy 162.50	67 Ho 164.03032	68 Er 167.26	69 Tm 168.93421	70 Yb 173.04	71 Lu 174.967
---------------------	-----------------------	--------------------	-------------------	--------------------	---------------------	--------------------	-----------------------	--------------------	-----------------------	--------------------	-----------------------	--------------------	---------------------

▲ Actinides

90 Th 232.0381	91 Pa 231.03588	92 U 238.0289	93 Np (237)	94 Pu (239)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (252)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)
----------------------	-----------------------	---------------------	-------------------	-------------------	-------------------	-------------------	-------------------	-------------------	-------------------	--------------------	--------------------	--------------------	--------------------