FINAL B. SC. EXAMINATION, 2019

(2nd Semester)

CHEMISTRY (HONOURS)

PAPER - XVII

INORGANIC CHEMISTRY

Time : Two hours Full Marks : 50

1. a) Write a brief account on ***any two*** of the following :

   i) Cryptands and their utilities.

   ii) Synthesis of $[NMe_4]_2[Si(oxalate)_3]$ starting from $SiCl_4$.

   iii) Synthesis and structure of tris (diethy ldithio-carbamato) arsenic (III).

   b) Describe the structure of ***any two*** of the following :

   i) Calcium oxalate dihydrate

   ii) $[Pb(acac)_2]$

   iii) As_6Ph_6 $(2\frac{1}{2}+2\frac{1}{2})+(1\frac{1}{2}+1\frac{1}{2})$

2. a) Describe the general method of preparation for a cross linked two dimensional silicone clearly mentioning the starting materials involved.

   b) What are silicone oils and how are they prepared ?

   c) How is N, N, N trimethyl borazine prepared ?

   d) What are the two structural forms of Boron Nitride ?

Mention the carbon analogues of these two forms. Under what condition does the form which is known to show electrical conductivity, convert to the harder form ? Compare the harder form of Boron Nitride to its carbon analogue in terms of mechanical strength.

e) What happens when $[NPCl_2]_3$ reacts with catechol in the presence of Et_3N ? Why is a similar reaction not known for resorcinol ?

f) Discuss structure and bonding in $[NPCl_2]_3$.

$1\frac{1}{2}+1\frac{1}{2}+1+2+1\frac{1}{2}+1\frac{1}{2}$

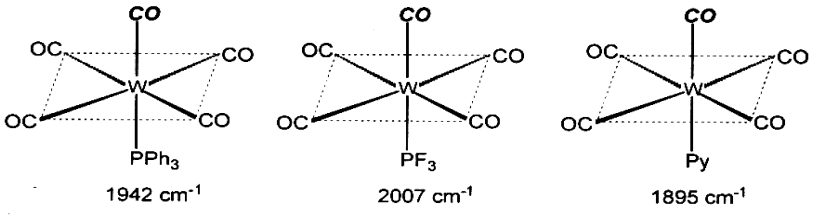
3. a) Interpret the C-C and Pt - C bond distances in $Pt(C_2H_4)Cl_3$ ($d_{c\text{-}c}$, 1.37 Å , $d_{Pt\text{-}C}$, 2.55 Å), and $Pt(C_2H_4)(PPh_3)_2$ ($d_{C\text{-}C}$, 1.43 Å , $d_{Pt\text{-}C}$, 2.11 Å) and $Pt(C_2(CN)_4(PPh_3)_2$ ($d_{c\text{-}c}$, 1.49 Å , $d_{Pt\text{-}C}$, 2.09 Å)

b) Give a brief account on the structure and bonding in metal-allyl complexes.

c) Give examples of η^1, η^3 and η^5 cyclopentadienyl complexes. Give an example of triple-decker cyclopentadienyl complex.

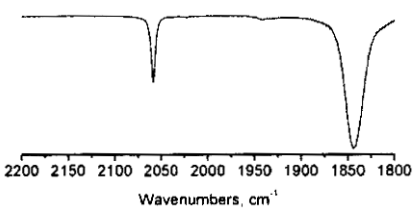
d) Give examples of 1,1 - and 1,2- migratory insertion reactions. 2+3+(2+1)+1

d) Determine the relative π -acidity order of Lfrom the ν_{co} value of the following $[W(CO)_5L]$ complexes along with the illustration of π bonding for {OC–W–L} moiety.



The ν_{CO} of **CO** lying *trans* to L.

e) Give a synthetic scheme of $Me\text{-}C(O)Mn(CO)_5$ starting from $Mn_2(CO)_{10}$ and provide the mechanistic aspect of the final reaction. 2+(2×3)

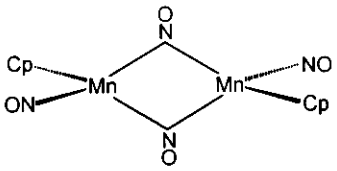


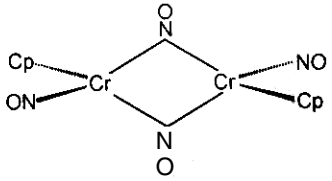
b) Using 18-electron rule

i) find the value of 'x' of the following complexes (any one).

$[Co_3(CO)_x(CH)]$ $[Fe_4(CO)_x(Cp)_2]$

ii) determine the number of metal—metal bonds (any one), C_P = Cyclopentadiene.





c) Match the ν_{co} frequency with the relevant complex with justification and comment on the nature of bonding of CO (ν_{co} of free CO : 2143 cm^{-1})

Complex	ν_{co} cm^{-1}
$[Au(CO)_2]^+$	1836
$[(Cp)Ni(CO)]_2$	2000
$[Cr(CO)_6]$	2217

4. a) Comment on the ligand field strength of dioxygen and its effect on magnetic behavior in the case of oxy-haemoglobin.

b) Draw the schemes and assign the different modes of dioxygen binding.

c) Write down Three chemical reasons of "As" poisoning.

d) Explain the prevention mechanism of carbon monoxide poisoning of haemoglobin.

e) Which properties of chlorophyll make it an antenna in the photosynthesis process ? $1\frac{1}{2}+2+1\frac{1}{2}+2+1$

5. a) How does partial molal volumes of aquated lanthanoides (in 3 +oxidation states) vary with their f^n configurations ? Explain.

b) Discuss lanthanoid contraction in terms of relativistic effect.

c) Between La^{3+} (aquated) and Lu^{3+} (aquated) which one is more acidic ? Explain. $3+3\frac{1}{2}+1\frac{1}{2}$

6. Attempt 6a and any three from the rest :

a) Discuss the bonding of metal — carbon bond in $[Fe(CO)_3(CN)_2]^{2-}$ from the IR spectrum and crystallographic data (Fe-CO: 1.78 $\mathring{A}$, Fe–CN: 1.93 $\mathring{A}$) and hence predict its structure. Justify your answer with the Bent's rule.