CHEMISTRY

Name:..... Roll No:.....

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National Institute of Technology Calicut

Second Semester B. Tech. (Winter Semester)
End Semester Examination April-May 2014
CY1001 CHEMISTRY

Time: 3 hours **Maximum Marks: 50**

(Answer all questions)

1. The primary UV absorption band of phenol and benzoic acid appears at 210 (ε = 7400) and 230 (ε = 11600) nm respectively. When dilute NaOH is added, phenol shows red shift but benzoic acid shows blue shift. Account for the observation. (2 marks)

2. The solution of $[Co(H_2O)_6]^{2+}$ is pink in colour, but when it is treated with excess of Cl^- intense blue coloured solution of $[CoCl_4]^{2-}$ is obtained. Explain the change in colour of the solution by drawing crystal field splitting diagram. (2 marks)

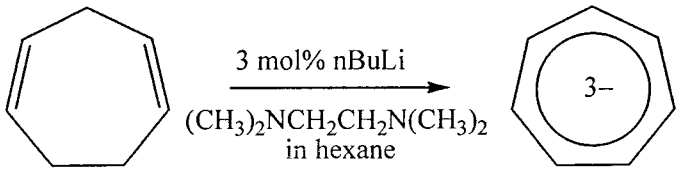
3. One δ–bond is formed between the transition metals (M) in L_4M–ML_4 complex (L = mono-dentate ligand). If both the metal atoms lie on the Z axis, which d-orbital is responsible for the δ–bond formation? Sketch a neat diagram showing the formation of the δ–bond. (2 marks)

4. Draw appropriate structural formulae of **A**, **B** and **C** that are consistent with the following observations. When the spectrum is recorded in D_2O the spectrum of A remains unchanged, but the peak at 5.5 ppm of the compound **C** disappears.

	A	**B**	**C**
	$C_6H_2N_3O_6Cl$	⟶	$C_6H_3N_3O_7$
^{1}H NMR (ppm)	9.5 (2H, singlet)		9.4 (2H, singlet) 5.5 (1H, singlet)

(3 marks)

5. Predict the ^{1}H NMR spectrum for **D** and **E** in the following reaction.



D **E**

(3 marks)

6. Trans azo-benzene (C_6H_5–N=N–C_6H_5) shows two UV-Vis absorption bands at 365 and 512 nm. Upon irradiation, it converts to cis isomer and blue shift is observed for both the bands. Further, the blue shifted band at the longer wavelength become more intense. Give reasons for the above observations. (3 marks)

(P.T.O.)

7. The force constant of HCl is 483 Nm^{-1}. Calculate the fundamental vibrational frequency and zero point energy of HCl. (3 marks)

8. Draw the Huckel molecular orbital diagram with correct electronic configuration for vinylic ($H_2C{=}CH^+$) and allylic ($H_2C{=}CH{-}CH_2^+$) carbocations. Comment on their relative stability. (3 marks)

9. The complex $[Fe^{II}L_6]^{2+}$ (L = mono-dentate ligand) absorbs UV-Vis radiation at 10400 cm^{-1}. Calculate the crystal field stabilization energy and spin only magnetic moment for the complex (The pairing energy of Fe^{2+} is 17600 cm^{-1}). (3 marks)

10. Draw the molecular orbital diagram of CO and sketch the shape of HOMO and LUMO. (3 marks)

11. Predict the approximate product distribution for the mono-nitration of $C_6H_5{-}CH_2Cl$, $C_6H_5{-}CHCl_2$ and $C_6H_5{-}CCl_3$. (3 marks)

12. An aqueous solution of copper (II) sulphate, $[Cu(H_2O)_6]SO_4$, turns blue when treated with 4 equivalents of aqueous ammonia. The resultant solution gives intense blue crystals of $[Cu(NH_3)_4]^{2+}$, when treated with ethanol and kept for some time. Use crystal field splitting diagram and comment on the Cu–O and Cu–N bond lengths in the complexes $[Cu(H_2O)_6]^{2+}$ and $[Cu(NH_3)_4]^{2+}$. (4 marks)

13. Compare the I–O bond length and O–I–O bond angle between IO_3^- and IO_6^{5-}. (4 marks)

14. Draw an appropriate structural formula for the compound $C_8H_8O_3$, which gives the following peaks in the IR (only prominent peaks) and ^1H NMR spectrum.

IR (cm^{-1}) : 3600 (sharp), 1745, 1250

^1H NMR (ppm): 11.0 (1H, singlet), 7.69 (1H, doublet), 7.64 (1H, singlet), 7.36 (1H, multiplet), 7.11 (1H, doublet), 3.73 (3H, singlet) (4 marks)

15. Starting from benzene prepare

(i) diphenyl ether (C_6H_5-O-C_6H_5) via benzyne mechanism.

(ii) diphenyl ether (C_6H_5-O-C_6H_5) via addition-elimination mechanism.

(iii) 2-bromo-4-nitro benzoic acid.

(iv) 3-bromo-5-nitro benzoic acid. (4×2 = 8 marks)

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