



Synthesis and Characterization of Metal Complexes of Phloroglucinol

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Abstract : Manganese(II), iron(III), cobalt(II), nickel(II), copper(II) and zinc(II) complexes of phloroglucinol have been prepared and characterized by molar conductivity, magnetic susceptibility measurements, estimation of metal ion and by their IR and electronic absorption spectra. The analytical data shows that all the complexes are of octahedral geometry. The non electrolytic and electrolytic nature of these complexes is evidenced by their magnetic susceptibility and conductance data. The electronic and IR spectral data suggests octahedral geometry and coordination mode of the ligand.

Keywords : phloroglucinol, metal complexes, Copper(II), Nickel(II), Iron(III)

(Received July 2013, Accepted August 2013)

1. Introduction

Phloroglucinol and its compounds, both synthetic as well as natural, have shown a vast array of biological activities such as anti-inflammatory[1], antitumor[2], anti-microbial[3], anti-allergic, enzyme inhibitory[4], neuro-regenerative and antioxidant[5-6]. There are a wide range of

applications of phloroglucinol compounds in pharmaceuticals, cosmetics, textiles, paints and dyeing industries. Although many of the phloroglucinols have shown promising results in various biological assays, very few have reached clinics. It is also used in the treatment of gallstones, spasmodic pain and other related gastrointestinal disorders[7]. It has a non-specific spasmolytic action on the vessels, bronchi, intestine, ureters and gall bladder, and is used for treating disorders of these organs. Daniel Plaul and Winfried Plass carried out studies on synthesis, crystal structures, and magnetic properties of Phloroglucinol-bridged trinuclear complexes with three paramagnetic octahedral nickel(II) ions[8]. An extensive literature survey revealed that phenolic compounds have used in complexing with certain metal ions. It also revealed, transition metal ions were used to form complexes with phloroglucinol derivatives not with pure phloroglucinol. In this present work we report the synthesis and characterization of manganese(II), iron(III), cobalt(II), nickel(II), copper(II) and zinc(II) complexes of pure phloroglucinol.

2. Materials and Methods

The metal salts and the reagents employed were BDH/AR products and they were used as received. All the solvents used were purified by method given in the literature[9] and treated under nitrogen prior to use. IR measurements were carried out in KBr using a Perkin-Elmer model 1600 FT-IR spectrometer. Commercially obtained phloroglucinol(Merck) is used as a ligand in this present work. The magnetic susceptibility was measured on powdered sample using Gouy balance. The electronic spectra of the complexes in ethanol were recorded on Hitachi 3400 spectrophotometer. Estimation of metal ion was determined by EDTA complexometric titration method [10]. Toshiniwal's conductivity bridge and dip type platinum electrodes were employed for molar conductivity measurements.

3. Synthesis of Metal Complexes

Metal chlorides and phloroglucinol were mixed in the molar ratio of 1:3 in 40 ml of ethanol and were refluxed about 7 h with the help of water condenser. The complex formed was separated from excess ligand by using ether as a solvent and dried under vacuum. For the zinc complex the excess ligand is separated by using solvent 80% of benzene and 20% of acetone.

4. Result and Discussions

4.1 Molar Conductance

Molar conductance of 0.001 M aqueous solutions of the complexes are given in Table-I. Manganese(II), iron(II), nickel(II), copper(II) and zinc(II) complexes show conductance values in the range 40-68 $\text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$ indicating 1:0 electrolytic nature, for which Λ_m is expected to be in the range up to 80 $\text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$. The cobalt complex shows conductance value (110 $\text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$) close to 1:1 electrolyte.

4.2 Magnetic Studies

The observed magnetic moments, μ_{eff} of the complexes are given in the table-I. The theory of magnetic susceptibility of cobalt (II) ion was given originally by Schlapp and Penny[11] and the best summary of the results on the magnetic behavior of cobalt compound is that of Figgis and Nyholm[12]. The octahedral and tetrahedral cobalt (II) complexes differ in their magnetic properties because of the intrinsic orbital angular momentum in the octahedral ground state, there is consistently a considerable orbital contribution and μ_{eff} for such compounds at room temperature are between 4.8 to 5.2 BM. For tetrahedral complexes the ground states acquires orbital angular momentum indirectly through mixing in the 4T_2 state by a spin orbit coupling perturbation. So the tetrahedral complexes have slightly lower μ_{eff} 4 BM when compared with

the octahedral complexes. The cobalt (II) chloride complex is found to have a magnetic moment of 4.45 BM which is less than the expected value for octahedral cobalt complex. We conclude that the lower value is because of mixture of octahedral cation and tetrahedral anion.

Nickel (II) has the electronic configuration $3d^8$ and should exhibit a magnetic moment higher than the expected for two unpaired electrons in octahedral (2.8 – 3.2 BM) and tetrahedral complexes have much higher magnetic moments (3.4-4.2 BM) due to effective orbital contribution while the square planar complexes would be diamagnetic. The magnetic moment of nickel (II) complex of phloroglucinol is 2.9 BM suggesting octahedral geometry and copper (II) complex exhibit magnetic moment of 1.8 BM. The magnetic moment of manganese (II) complex is 5.9 B.M.

S.No	Complex	Colour	Percentage of metal Experimental/(calcd)	Λ_m	μ_{eff} (B.M)
				$\Omega^{-1}\text{mol}^{-1}\text{cm}^2$	
1	Cobalt	Pink	11.30 (11.45)	110	4.45
2	Copper	Brown	12.38(12.55)	40	1.8
3	Iron	Black	10.33(10.10)	45	6.05
4	Manganese	Pink	10.90(11.20)	47	5.9
5	Nickel	Green	11.62(11.30)	68	2.9
6	Zinc	Pale yellow	12.71(12.55)	55	-----

TABLE - I. Analytical, conductivity and magnetic data of metal complexes of phloroglucinol

4.3 Infrared Spectra

Comparison of IR spectrum of ligand and those of the complexes were confirmed the coordination of phenolic oxygens with the metal ion. There are three phenolic groups in the ligand. In the spectra it is found that OH stretch at $3200\text{-}3400\text{ cm}^{-1}$ is shifted to lower region and also it is broad due to probably non coordination of one of the phenolic groups. The OH deformation found at 1418 cm^{-1} is also shifted to 1385 cm^{-1} in the spectra of copper complexes.

In cobalt complex the peak of the OH deformation found at 1418 cm⁻¹ in the spectrum of ligand is shifted to 1414 cm⁻¹ and 1364 cm⁻¹. The absorption band at 1414 cm⁻¹ may be due to uncoordinated phenolic and the absorption band at 1364 cm⁻¹ is due to coordinated phenolic groups. The absorption bands at 1616 cm⁻¹ and 1498 cm⁻¹ are assigned to C=C stretching of the benzene ring which one not affected in the spectra of the complexes. The bond found at 567 cm⁻¹ which is absent in the spectrum of the ligand is assigned to the M-O stretch of the complexes.

4.4 Electronic spectra

The cobalt (II) complex shows peak at (650nm) 15,350 cm⁻¹ and (550nm) 18,000 cm⁻¹ suggesting tetrahedral and octahedral coordination. Based on the investigation cobalt complex is found to have the structure [CoL₃]²⁺[CoCl₄]²⁻. The conductance study also confirms that structure. The nickel (II) complex exhibits a band at 23,500 cm⁻¹(350 nm) assigned to ³A_{2g} → ³T_{1g}(P) transition and band at 18,800 cm⁻¹ (530nm) assigned to ²A_{2g} → ³T_{1g}(F) transition of octahedral geometry for the complex. The copper(II) complex showed a band at 11,700 cm⁻¹ assigned to ²E_g → ²T_{2g} transition.

5. Conclusion

The present work describes a simple and convenient route to synthesize metal complexes of phloroglucinol. The IR studies suggest that in these complexes the metal ions are coordinated by the two phenolic oxygens present in phloroglucinol and thus phloroglucinol acts as a bidentate ligand. Electronic spectra revealed that the cobalt complex has the octahedral cation and tetrahedral anion such as [CoL₃]²⁺[CoCl₄]²⁻. The electronic spectra of other complexes showed octahedral structure and the chlorides are involved in the coordination. A conductance study shows that the cobalt complex is in 1:1 electrolytic nature and the other complexes are in non

electrolytic nature. Magnetic moments of the complexes reveal that they are all of high spin type with paramagnetic nature except zinc(II) complex is diamagnetic.

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