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INVESTIGATION OF SYMMETRICAL TETRAPHENYL PORPHYRIN METAL COMPLEXES THROUGH INFRARED AND RAMAN SPECTROSCOPY

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ABSTRACT

The porphyrins importance is increasing day by day. Tetraphenyl porphyrin metal complexes are comparable to chlorophyll and hemoglobin molecules. Infrared spectroscopy is a powerful tool for the elucidation of structure and symmetry of molecules along with Raman spectroscopy. The symmetry of molecule is directly related with properties and applications of tetraphenyl porphyrin metal complexes. In this paper various IR spectra of 11 tetraphenyl metal complexes have been discussed.

KEYWORDS: Nanomaterial, Solar Cell, Symmetry

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Original Article

INTRODUCTION

Infrared spectroscopy is concerned with the infra-red region of light. It is concerned with longer wavelength and low frequency. It may be analyze in three ways absorption, emission and reflection. It is used to determine a particular functional group in an organic compound. Absorption of IR is meant for vibration and rotation of molecules in allowed energy states. Molecular vibration like bending, stretching are more important than molecular rotation. Infrared analysis has scope in the field of environmental chemistry [1], in the analysis of medicinal field [2] and forensic chemistry [3]. Infra-red spectroscopy is an excellent tool for the identification of structures of lipids, proteins and carbohydrates [3-6]. The infrared 23 spectra of proteins shows absorption due to particular Amide group [7-8]. The spectra of nucleic acid is based on three component base, sugar and phosphate group [9]. It also plays an important tool for disease 25 diagnoses. It provides important information for the malignant cells causing dysplasia [10]. The particular band of CaCO3 in kidney disease is 875 cm-1 and for cholesterol in hyperlipidemia is 1050 cm-1. Infra-red spectroscopy can also provide valuable informations regarding presence of E-Coli, a notorious pathogens 28 caused urinary tract infection and Thyroid fever [11]. In this paper infra-red and Raman spectra of tetraphenyl porphyrin metal complexes has been elucidated and various stretching and bending modes.

Have been discussed to clarify the symmetry of tetraphenyl porphyrins.

MATERIALS AND INSTRUMENTS

Materials

The chemicals used in the research were of analytical grades and purchased sigma and Aldritch chemicals. Solvents used in the research work were tetrahydrofuran, carbon tetrachloride, dichloromethane, n-36 hexane and cyclohexane. As all the chemicals were pure hence used without purification.

Instruments for Analysis

Instruments

FT-IR model FTS 4800 MX spectrophotometer (USA) was employed in the frequency range of 4000-400 41 cm-1 using KBr pellets.

RESULTS AND DISCUSSIONS

Synthesis of Tetraphenyl Porphyrins

The amount of 20.6 g of 4-chlorobenzaldehyde was taken in the round bottom flask and it was fitted with water condenser. Round bottom flask was placed on the heating mental. The amount of 350 ml of propanoic acid was added in the round bottom flask and refluxed it for 5 to 10 minutes. The temperature 48 of heating mantle was set around 60 centigrade after 10 to 15 minutes, pyrrole was added from the top of 49 the condenser in 10 ml and the reflux time is 20 to 30 minutes [23]. Propanoic acid is separated by 50 vacuum distillation and the compound is washed with methanol and mixture was allowed to cool and the 51 crystals of TPP were filtered through Buckner funnel [24]. The crystal was dried in vacuum desiccators. 52 Purple color compound was obtained and the yield is 13%. Melting point is 350 0C. The compound name is 53 5, 10, 15, 20-tetrakis (4'-chlorophynyl) porphyrins (TCPP).

Purification of Tetraphenyl Porphyrins

The tetrachlorophenyl porphyrin was developed by Edler [12] and Ruthmend Synthesis [13]. The formation of compound was confirmed by IR method. The main problem in porphyrin separation is the 68 formation of side reaction. In this regard there are so many impurities like propanoic acid derivatives and 69 pyrrole impurities. Purification of crystals can be obtained by using a column. These purpose different 70 solvents were selected along with silica gel. Firstly the column was filled with silica gel along with THF 71 solvent. But the final solvent in column was dichloromethane. Porphyrins elute in a second step [12]. During the formation of porphyrin the reaction can be checked by using TLC. The solvents would be chloroform and n-hexane in 1:3 ratios. The formation of green color in HCl solution confirms the formation of porphyrins.

Synthesis of Tetraphenyl Porphyrin metal Complex

The synthesis of 5, 10, 15, 20-tetrakis (4-chlorophynyl) porphyrinatometalr (II) was carried out as follows. The amount of 0.5 g of tetrachlorophenyl porphyrin was dissolved in 1.766g of cupric chloride or cupric acetate with the presence of DMF (50 ml) and refluxed it for 5 to 6 hours. These chemicals were 80 taken in the round bottom flasks and a condenser is set on a heating mental. The temperature was set at 81 60 to 70 0C. It is the continuation of two pot synthesis. The scheme of complex formation has been 82 discussed in the scheme 1 [12]. The formation of the complex can be confirmed by TLC after every half an hour. The solvent mixture is in the ratio of 1:3 of chloroform and normal hexane. TLC analysis will show 84 the two bands of which one will be of TCPPCu and after the reflux the DMF will remove in half of quantity 85 through vacuum distillation. In the final step the complex will be treated with 6M HCl solution. In this respect 20 ml of 6 M HCl solution will be taken. The complex formed was filtered and TLC analysis 87 confirmed color change in HCl solution.

Table 1: IR Data of the Porphyrin and its Transition Metal Complexes Compound

	1νN-H cm-1	νC-H cm-1	NC=C cm-1	νC-N cm-1	νM-N cm-1	νM-Cl cm-1	2νN-H cm-1	ν(CH2)n cm-1
TCPP	3305.7	2926	1511	1177	---	---	981	730
TCPPFe	---	3024	1395	1232	1012	416	997	723
TCPPCo	---	2780	1634	1350	1014	434	965	715
TCPPNi	---	2780	1626	1350	1014	440	1003	791
TCPPCu	---	2170	1368	1218	980	411	986	702

An infrared spectrum of tetra phenyl porphyrin is presented in figure 1 and indicates that at 3305.7 cm-1 is 94 the peak because of N-H bond of pyrrole whereas at 2926 cm-1 and 2844cm-1 is the peak because of C-H 95 bond of pyrrole. It further shows that at 1558 cm-1 is the peak due to the C=C of TCPP and 1174 cm-1 is the 96 peak due to C-N bond. It is clear from the result that at 981cm-1 is another peak of N-H of pyrrole,

IR Analysis of Tetraphenyl Porphyrin Nickel Complex

The peak for stretching frequency of N-H of pyrrole is absent whereas presence of peak at 2780 cm-1 is for 100 (C-H) of pyrrole whereas the C=C and C-N Stretching frequency of benzene and pyrolle respectively explain the formation the complex [13], (CH2)n peak is at 721 cm-1. For N-H of pyrrole absorption occur at 102 1014 cm-1.

IR Analysis of Tetraphenyl Porphyrin Iron Complex

The peak due to stretching frequency of N-H of pyrrole is absent which is due to the insertion of Fe ion 106 whereas 3024 cm-1 is the peak of(C-H) of pyrrole whereas the C=C and C-N stretching frequency of benzene and pyrrole respectively explains the formation the complex, (CH2)n peak is 723 cm-1

IR Analysis of Tetraphenyl Porphyrin Cobalt Complex

IR absorption frequencies were different for free base porphyrins and TCPPCo. The absence of stretching 111 frequency of (N-H) bond of free base is due to the coordination of Co metal ion with nitrogen.37 When 112 cobalt atom is inserted into the free base porphyrins (N-H) bond vibration of free porphyrin is eliminated 113 and the characteristics functional group of Co-N bond is formed and vibrates at 1000 cm-1 [14]. This 114 indicates the formation of TCPPCo. The band at 2923-3133 cm-1 is due to C-H bond between benzene ring

IR Analysis of Tetraphenyl Porphyrin Copper Complex

The peak at 2173 cm-1 is the peak of pyrrole C-H bond whereas the peak of 1733 cm-1 is the peak of C=C 126 shows that the complex has been developed. The peak at 980 cm-1 confirms the stretching frequency of (Cu-N), whereas the Peak at 411 cm-1 shows the stretching frequency of (Cu-Cl). At 1218 cm-1 is the peak 128 of (C-N) of TCCPCu and at 702 cm-1 is the peak of (CH2)n of pyrrole [14]. 129

Raman Spectroscopic Studies 131

The representative Raman spectra of compounds TCPPFe, TCPPCo and TCPPNi are presented in figure 5. The optical spectra of metalloporphyrins are in general dominated by QV to Q* transitions of the porphyrin 133 core, which provides soret, Q and Qv features in the absorption spectra [25]. It is based on D4h symmetry. 134 The phenyl ring of porphyrins are exactly perpendicular to the porphyrin plane, the porphyrins has 71 in 135 plane modes [40] while normal spectrum contains 27 in plane vibrations. 9 of 27 are polarized (A1g) and 136 18 are depolarized (B1g) and (B2g). The

infra-red spectrum is maximum 18 modes with EU symmetry. Porphyrin core has D4h model has 34 out of plane mode of vibrations.

G out of plane = 3A1U + 6A2U (IR) + 4B2U + 5B1U + 8Eg (R)

The 8 Eg modes are Raman active and 6 A2g modes are infrared active. Raman spectra is based on 1statistics analysis, the in plane modes are dominant than out of plane modes. There is also number of phenyl vibrations as compared to central TCPP core. In order to consider phenyl group chlorobenzene has been set as a model. The TCPP ligand has four phenyl groups which is bounded to meso carbon atom of 148 porphyrin core. So there are four asymmetry adaptation combinations in TCPP. These interactions are 149 small so obtained splitting among four phenyl rings are small (5-10 cm-1). So it is of C2V (Point group of 150 chlorophenyl), four different symmetry blocks are found. There are 169 normal modes, 44% are Raman active and 27% are IR active. Interaction (C1) intense sort and weak Q band can be observed. The band is 152 observed on the higher side of Q. This band QV is due to vibronic mixing between sort and Q band. Both 153 excitation vibrations are of EU Symmetry. The Q and QV spectrum confirms the formation of complexes. There are three effects which can affect the D4h. The first effect is phenyl ring, coupling between core and 155 strong phenyl ring vibration. The second effect is different mixed modes. The third effect is symmetry 156 lowering beyond C4V is the degenerate EU vibration split in IR spectra [15].

CONCLUSIONS

Raman spectroscopy and infra-red spectroscopy successfully explained the structure and properties of tetraphenyl porphyrin metal complexes.

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