PHENAZINE BASED ORGANIC CONDUCTING MATERIALS FOR HEALTHY GLOBAL CLIMATIC SCENARIO

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Abstract: Global warming has become a biggest threat to the existing environment. Most of the fossil fuel consumption and production leads to release of enormous amounts of carbon dioxide in to the environment. This paper focuses on the synthesis of organic molecular substances as conducting materials to help in avoiding of huge coal burning and chemical processes involved in the metallurgical extractions of different metals. In the present investigation synthesis of Phenazine based material, a charge transfer complex namely bis methyl phenazenium hexa cyano tri methylene cyclopropanide (M_2P-HCTMCP) preparation and its characterization along with its conducting properties, uses and scope for further investigation are reported.

Keywords: Charge Transfer, Global Warming, Organic Conductors, Phenazine.

Introduction: Materials are often classified on the basis of their electrical conductivities. Those which offer strong resistance to electrical transport are called insulators; metals on the other hand display facile conduction of electricity. Observation of electrical conductivity in organic solids generally known for their electrically insulating nature was first reported in 1940's. But the discovery of semi conduction in the organic charge transfer complex Perylene-Bromine in 1954 by Akamatsu et al [1]. is considered as the landmark event that lead to the new field of organic conducting materials. Phenazine is a typical van der Waals molecular crystal which is a weak π-acceptor. However, N-methyl Phenazinium (MP^+) complex with tetracyano quinodimethane anion ($TCNQ^-$) is one of the best known organic metals [2]. In the present study we are interested in the new complexes of M_2P^+ with stable anion radicals. The synthesis of Phenazine based material, a charge transfer complex namely bis methyl phenazenium hexa cyano tri methylene cyclopropanide (M_2P-HCTMCP) preparation and its characterization along with its conducting properties, uses and scope for further investigation are reported in this paper.

Materials and Methods:

Materials: Phenazine and Methyl phenazinium methosulphate were purchased from Aldrich Chemical Company. They were dried under vacuum and used. All methyl halides are procured from Fluka Chemicals Ltd. The solvents used namely, dimethyl ether (DME), Ethanol,

Acetonitrile and Ether were purified using standard procedures. All solvents are freshly dried and distilled prior to the reaction.

Synthesis: Dialkyl Phenazines are prepared from Phenazine following the procedure of Gilman and Dietrich [3]. Phenazine (0.041 g) was added to the working compartment of the cell containing 10 ml of 0.3 M solution of tetra methyl ammonium per chlorate in acetonitrile so that the total concentration is 0.023 M in Phenazine. The solution was degassed for 10 minutes with Nitrogen gas prior to the addition of the alkylating agent Bromo ethane. An excess of Bromo methane was added to give a total concentration of 0.092 M. The solution was electrolyzed at 1.90 V until the current has decayed to 1% of its initial value. The solution turned dark green by the end of the reaction. After completion of the electrochemical reduction the solvent is removed on rotary-evaporator. The solid residue was partitioned between 1:1 mixture of benzene-water system. The benzene fraction was evaporated.

9 mg of N-methyl phenazenium methosulphate was dissolved in minimum amount of acetonitrile. The solution of $K^+HCTMCP^-$ was dissolved in minimum amount acetonitrile. The solution of $K^+HCTMCP^-$ in acetonitrile was added drop wise to N-methylphenazinium methosulphate solution. The mixture was cooled to about 5^oC and kept for 10-12 hours. Crystalline material is precipitated out. This product was collected and washed with cold acetonitrile. The yield of the complex was around 8 mg.

FT-IR spectrum of the product in KBr pellet is recorded using JASCO FT- IR 5300 Spectrometer. The conductivity measurements are made using two-probe method. ESR Study was carried out on JEOL X-Band ESR Spectrometer using 100 kHz modulation. The microwave power used is 0.1 mW. DPPH was used for calibration of g-value and calculation of the spin concentration.

Results and Discussion: FT - IR spectrum of the M_2P-HCTMCP complex in KBR pellet is presented in Figs 1-2. The peak at 2100 cm^{-1} is a characteristic of the cyano stretch in $HCTMCP^-$ [2]. From the experimental electrical conductivity measurements made in this investigation it is concluded that M_2P- HCTMCP is behaving like a semi conducting material with a specific conductivity value approximately 10^3 S cm^{-1}.

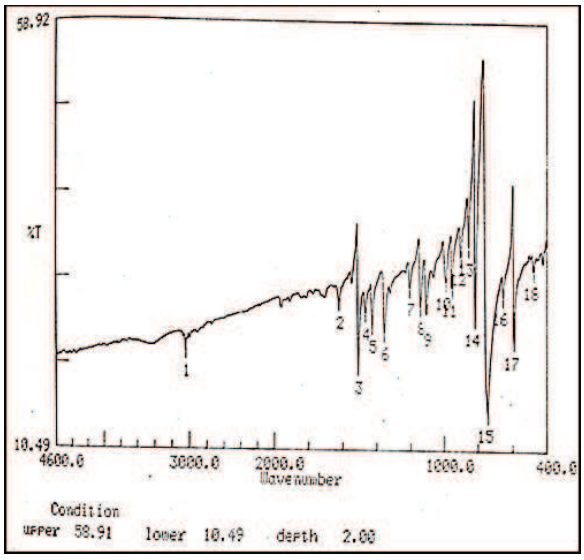

Fig. 1: The FT-IR Spectrum of M_2P

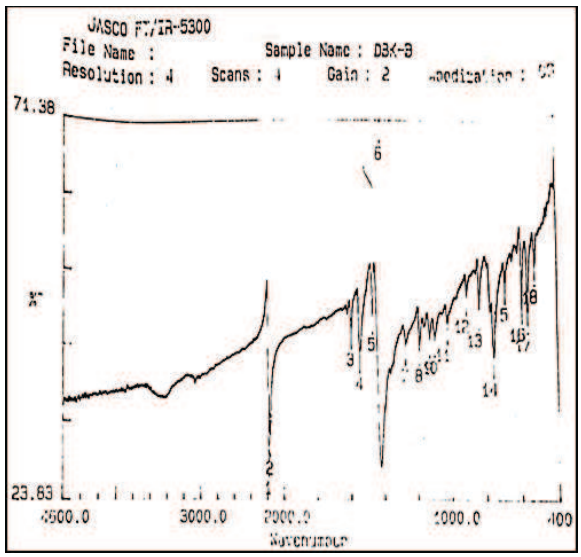

Fig. 2: The FT-IR Spectrum of M_2P HCTMCP complex

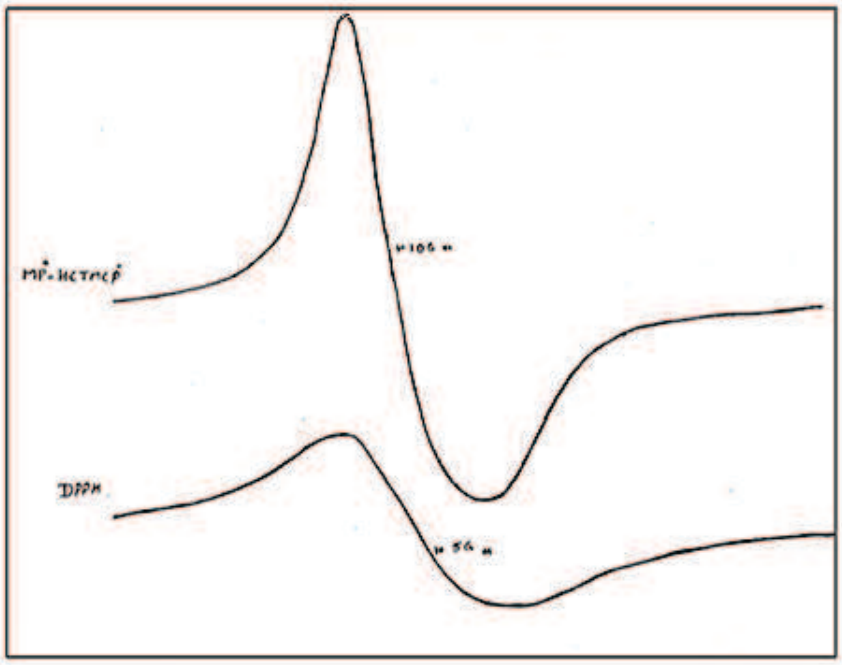

Fig 3: ESR Spectra of M2P+ - HCTMCP- and DPPH

The EPR spectrum $HCTMCP^-$ and of the reference DPPH is also shown in the same figure (Fig 3). The g-value calculated for the $HCTMCP^-$ is found to be 2.0029. The spin concentration is calculated from the experimental data and it was found as 0.077 mol^{-1}. This indicates that the material has strong anti-ferromagnetic interaction. This would be consistent with a stacked arrangement of $HCTMCP^-$ which is quite likely in the complex. Direct exchange interaction between anion radicals often leads to anti-ferromagnetic coupling of spins [4]. The exchange interaction leads to narrow line width of 1.1 G seen in this material. Similar stacked

arrangement is also observed by S. Jayanthi etal., in a complex of Phenazine with hexacarbomethoxy cyclopentadenide anion [5]

Conclusion: M_2P-HCTMCP complex is synthesized and it is characterized using FT-IR and EPR Spectra. From the conductivity measurements it can be concluded that M_2P-HCTMCP has semiconducting nature (σ = ~10^3 S Cm^{-1}). However, further research can be carried out by increasing the chain length of the alkyl group on Phenazine which enables the donating ability of Phenazine leading to form a better Donor-Acceptor complex, behaving like a conducting metal!

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