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Infrared study and phase transformation of the new lithium–diphenyl carbazide complex (LiDPC)

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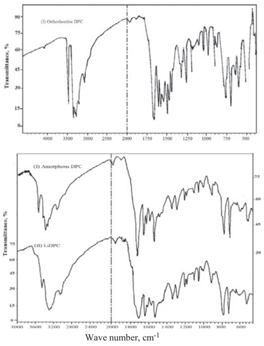
HIGHLIGHTS

- A complete IR investigation of orthorhombic, amorphous DPC and crystalline LiDPC is performed.
- The presence of an order–disorder phase transition in LiDPC complex at 60 °C.
- An energy model is suggested for the interpretation of the phase transition process.

GRAPHICAL ABSTRACT

IR bands of amorphous DPC (I) and LiDPC (II) complex samples at room temperature.



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ABSTRACT

A complete IR investigation (400–4000 cm^{-1}) of orthorhombic, amorphous DPC and crystalline LiDPC (at room temperature and 80 °C) is performed and new results are reported. Introducing lithium ions into diphenyl carbazide $C_{13}H_{14}N_4O$ forms a completely new complex associated with new properties. The IR spectroscopic analysis includes measurements and interpretation of the IR spectral band shape, intensities, and frequencies of the internal modes of vibrations.

The principle modes of vibrations of amorphous DPC found to be 3445 cm^{-1}, 3292 cm^{-1}, 3052 cm^{-1}, 1670 cm^{-1}, 1602 cm^{-1}, 1495 cm^{-1}, 1305 cm^{-1}, 1254 cm^{-1}, 974 cm^{-1}, and 577 cm^{-1} correspond to normal vibrations of N—H, C—H, N—N, C═O and monosubstituted benzene. A marked change could be recorded for these modes of vibrations in the presence of Li^+ ions. The results strongly confirm the formation of a metal–organic complex. Anomalous spectroscopic changes could be recorded in LiDPC spectra. A proposed Li^+ position in LiDPC complex is proposed. X-ray diffraction analysis is used to find out the crystal structure and parameters of LiDPC complex. The results obtained show triclinic crystal structure with $a = 5.6929$ Å, $b = 7.6378$ Å, $c = 17.8739$ Å, $\alpha = 119.176°$, $\beta = 63.322°$, $\gamma = 85.378°$. The results reveal the presence of an order–disorder phase transition in LiDPC complex at 60 °C. The transformation process is monitored by clear variations in the spectral shape, band intensities and new eight different modes appeared in the high temperature disordered phase. An energy model is suggested for the interpretation of such phase transition process.

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Introduction

The design and preparation of materials with desired properties are among the principle goals of chemists, physicists, materials scientists, and structural biologists. Achieving that goal depends critically on understanding the relationship between the structure of a material and the properties in question. To be most effective studies of structure–property relationships generally require systematically eliminating as many as possible of the structural and composition variables that play the most important role in determining the particular property under investigation. For molecular materials, a typical strategy might involve for instance, a methodical variation in the mode or type of substitution on one part of the molecule in order to test a particular hypothesis about the causal relationship between structure and properties. Variations in substituents while they do often result in changes in structure, and the corresponding changes in properties, also lead to perturbations in the geometric and electronic structure of the molecules in question. In such cases, changes in properties cannot always be correlated directly with changes in structure. The existence of polymorphic forms provides a unique opportunity for the investigation of structure–property relationships, since by definition the only variable among polymorphs is that of structure and one of the most effective strategies for studying structure–property relations has been to follow the behavior of a physical property through a polymorphic phase change. The study of the spectroscopic, the thermodynamics, kinetic of phase transitions by most or all analytical or physical techniques is a discipline in itself. The present IR spectroscopic investigations go on to this direction.

Diphenyl carbazide (DPC) deserves a special attention as it has been used for more than century in the field of trace metal determination [1]. Despite this wide range of applications of DPC, little was known about the mechanism of its reactions with metals. Also, it has various applications, especially in the field of biophysics and microbiology. DPC is used, for example, in differential regulations of high light tolerance in the mutant and wild type Anacystis cells. With the help of exogenous electron donors DPC photo-chemical reactions in activated sites on the electron transfer chain were delineated [2]. It is also used as an artificial donor during charge separation in photochemical reactions [3], and also photosynthetic electron transport [4–6]. The crystal structure for DPC ($C_{13}H_{14}N_4O$) as determined by De Ranter et al. [7] was found to be orthorhombic (at room temperature) with space group *pbnm*. In this crystalline structure two phenyl hydrazide groups lie on either side of a crystallographic symmetry plane passing along the bond direction of the carbonyl group.

In the last few years, much attention has been paid round the studies on the structure and properties of manufactured metal–organic complex compounds. Such studies are great interest in both scientific and technological stand points. It is quite obvious that investigation and interpretation of the various physical properties of such metal organic complexes depends mainly on the molecular ratios of constituents. The literature survey shows that the available results were deficient in spectroscopic properties in LiDPC and no data in this field are available. The present study tries to overcome such deficiencies. Although LiDPC complex has not been prepared before other metal–carbazide complexes were studied only through chemical reactions and nothing has been reported about their physical properties. Lithium polymer batteries researches are one of the most up to date branches in the field of applied physics [8,9]. Diphenyl carbazide (DPC) is one of the organic compounds processing polymorphic and thermoplastic properties [10]. Researchers are working to improve the properties of such type of batteries.

The present work is devoted to revise and analytically exploit the reaction between lithium ions Li^+ and DPC. A completely new complex LiDPC will be obtained. Important information about this reaction is given and some further experimental evidence regarding the nature of the complexometry of this new product is provided. The significance of metal–organic complex formation is attributed to the fact that when a metal ion becomes part of a complex, it acquires new properties which may strikingly different from those of the original organic compound. These changes may include new crystalline form of the formed compound and the different physical properties. These new properties, which are used in the identification or determination of either the metal ion or the coordinating agents, illustrate applications of such complexing process.

Diphenyl carbazide is one of the organic compounds processing polymer properties. Researchers are working to improve the properties of such type of batteries using new Lithium–polymer complex compounds [8–10].

In our previous studies, we have reported the new organic silver complex $C_{13}H_{13}N_4OAg$ [11]. In this paper, we present a study regarding the interaction between lithium and DPC. The obtained complex compound is studied here by FT-IR. X-ray diffractometry is used to give an accurate structural analysis for this new complex. A group of hyperfine structure lines (of IR spectra) corresponding to the Li^+ ion is reported here for the first time. This research is paramount importance for understanding the precise location of Li ion in LiDPC complex compound.

The present work aimed to study the optimum condition for the formation of one lithium organic complex, and identify the new physical properties, which is probably found. LiDPC complex sample is prepared by the chemical reaction between amorphous DPC [12–15] and lithium nitrate. A special attention has been paid to the probable stability of the obtained lithium complex. Recent results [16] have demonstrated that the electron rich complexes can interact with organic Lewis acids to produce infinite linear chain complexes. This means that the introduction of electron rich metal element, e.g., Li, Ag, etc. into organic complex may create new important properties and new structures.

Experimental

In the present study, LiDPC complex compound sample is prepared by the chemical reaction between amorphous DPC and lithium nitrate (dissolved in acetone).

$$C_{13}H_{14}N_4O + LiNO_3 \rightarrow C_{13}H_{13}N_4OLi + HNO_3$$

A precipitated powder is obtained in a solution of nitric acid. We report here the properties and the crystal structure of this new lithium–organic complex.

The IR spectra were recorded using the FT-IR type Shimadzu (IR Affinity-1). The samples used were in the form of discs prepared by mixing 20 mg of LiDPC complex with one gram of KBr in a cylindrical die of 10 mm diameter. The die was then evacuated to ensure dryness and the sample was pressed. The spectra were recorded in 400–4000 cm^{-1} region by a computerized system attached to a monitor and a printer.

X-ray diffraction patterns are carried out here by X-ray machine type, Bruker axs DS, Germany with Cu Kα (λ = 1.5406 Å) radiation and secondary monochromator in the 2θ range from 20° to 70°. A computer program (Crysfire) is used for data analysis of X-ray spectra. Crysfire program assists users to find the possible solutions to the powder indexing problems in the form of complete or partial unit cells.