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# Chemical and physical investigations on the charge transfer interaction of organic donors with iodine and its application as non-traditional organic conductors

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## HIGHLIGHTS

- The *iso*-leucine-iodide and methionine-iodide charge-transfer complexes were prepared and characterized.
- The structures of iodide charge-transfer complexes are discussed with Raman laser spectra.
- The electrical properties of both complexes were investigated.
- The positron annihilation Doppler broadening spectroscopes were performed.

## ARTICLE INFO

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## ABSTRACT

The *iso*-leucine-iodide and methionine-iodide charge-transfer complexes were prepared and characterized using different spectroscopic techniques. The iodide charge-transfer complexes were synthesized by grinding KI-$I_2$-amino acid with 1:1:1 M ratio in presence of few drops of methanol solvent. The structures of both solid amino acid iodide charge-transfer complexes are discussed with the help of the obtained results of the infrared and Raman laser spectra, Uv–vis. electronic spectra and thermal analyses. The electrical properties (AC resistivity and dielectric constant) of both complexes were investigated. The positron annihilation Doppler broadening (PADB) spectroscopies were also used to probe the structural changes of both complexes. The PADB line-shape parameters (S and W) were found to be dependent on the structure, electronic configuration of the charge transfer complex. The PADB technique is a powerful tool to probe the structural features of the KI-$I_2$-amino acid complexes.



## Introduction

Charge-transfer (CT) complexes may be formed between a donor (D) molecule and an acceptor (A) molecule in their ground states and almost all CT complexes have unique absorption bands in the ultraviolet–visible region of spectra [1–4]. The interaction between donor and acceptor is not only a charge-transfer interaction but also an expression of electrostatic force action [5–7]. The interaction between donor and acceptor is usually much weaker than inter actions responsible for formation of the hydrogen bond and the covalent bond, but nevertheless it is useful for constructing crystal structure [6–10].

The solid charge-transfer complexes formed between iodine and several types of electron donors such as aromatic hydrocarbons, polycyclic amines, mixed oxygen/nitrogen-containing cyclic bases, aromatic/aliphatic amines have been studied and classified [1–10]. The triiodide ion $I_3^-$, pentaiodide ion $I_5^-$, and enneaiodide ion $I_9^-$ were formed in the reaction of iodine with various donors, such as metal acetylacetonates [11–13], polyazacyclic [14–16], and crown ethers [17–20]. Some of charge-transfer complexes show very interesting applications in the analysis of some drugs in pure form or in pharmaceutical preparations [21,22]. The

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charge-transfer in fullerene-based [23,24] compounds is currently of great interest since these materials can be utilized as superconductors [25] and produce non-linear optical activity [26].

The positron annihilation spectroscopy has been accepted as a sensitive microprobe for studying defects and open-volumes in solids [27–33]. The method relies on the fact that positron, the anti–particle of electron, can be preferentially localized at a vacuum defect or open-volume in solids and annihilate with an electron of the atoms of materials via 2γ- or 3γ-decay. These γ rays carry information about the electronic environment around the annihilation site. In polymers or porous materials, a positron may annihilate via a positronium (Ps), the bound state of a positron and an electron. There are two positronium states: a singlet state (para-Ps, p-Ps) and a triplet state (ortho-Ps, *o*-Ps), depending on the spin combination of the electron and the positron. The ratio of the formation probability of p-Ps to *o*-Ps is 1:3. The utility of positrons in polymer studies is enhanced by the fact that Ps is preferentially localized in the free volume holes.

The positron annihilation Doppler broadening (PADB) Spectroscopy is a well-established tool to characterize defects [34]. The motion of the electron–positron pair causes a Doppler shift on the energy of the annihilation radiation. As a consequence, the line-shape gives the distribution of the longitudinal momentum component of the annihilating pair. Since the positrons are thermalized, the Doppler broadening measurements provide information about the momentum distributions of electrons at the annihilation site.

The Doppler broadening measurements have been performed using either slow positron beams or wide-energy-spectrum positron beams from radioactive sources. Two parameters S (for shape), and W (for wings) [35] are usually used to characterize the annihilation peak. The S-parameter is more sensitive to the annihilation with low momentum valence and unbound electrons. The S-parameter is defined by Mackenzie et al. [36] as the ratio of the integration over the central part of the annihilation line to the total integration. The W-parameter is more sensitive to the annihilation with high momentum core electrons and is defined as the ratio of counts in the wing regions of the peak to the total counts in the peak. The equation used to calculate the S- and W-parameters are reported in Ref. [37].

In relation to our interest in the study of intermolecular charge-transfer complexes (CTC) [38–45], we report here the results obtained from electronic, infrared, and Raman spectra of the two CT complexes formed in the reaction of iodine with the donors, *iso*-leucine and methionine. The aim of the work is to study the supposed structures and bonding of the resulting two iodine-amino acid complexes and also to investigate the electrical conductivity behavior.

## Experimental

### *Materials and reagents*

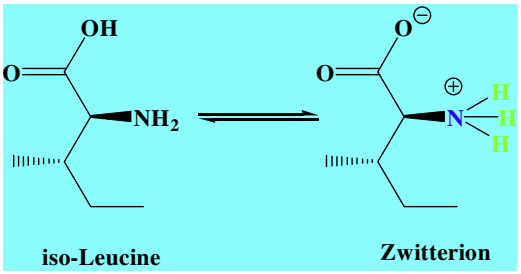
All chemicals used in this study were of high purity grade. Iodine and potassium iodides were obtained from BDH, *iso*-leucine (Formula I) and methionine (Formula II) were obtained from Merck and Aldrich Chemical Co.

### *Synthesis of iso-leucine/methionine iodine complexes*

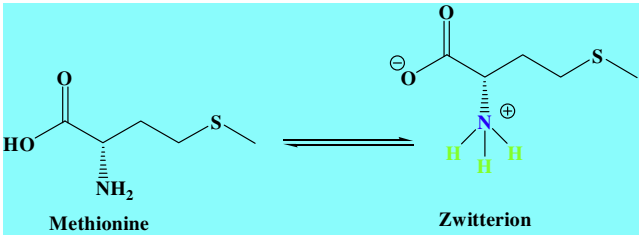
The *iso*-leucine-$KI_3$ and methionine-$KI_3$ charge-transfer complexes were prepared as a dark brown solid by addition of iodine, KI and *iso*-leucine/methionine with 1:1:1 M ratio as (*iso*-leucine-$KI_3$; 1.32 g: 2.54 g: 1.66 g of *iso*-leucine: $I_2$: KI) and (methionine-$KI_3$; 1.5 g: 2.54 g: 1.66 g of methionine: $I_2$: KI). Add *iso*-leucine/methionine to the definite weight of both iodine and KI in porcelain mortar with continuous grinding in presence of few drops of methanol solvent. Dry the reactions of amino acids with $KI/I_2$ systems by continuous suction and transfer them to a dry beaker. Store the beaker overnight in a dessicator filled with activated anhydrous calcium chloride, then transfer solid powders of iodine complexes to clean vial. The vial was capped well to exclude moist air. The contents of C, H, N, and I of the solid reaction products are as follows:

[(*iso*-leucine)] $K^+ \cdot I_3^-$. (*M* 550.98 g/mol). Found,%: C 13.06; H 2.35; N 2.52; I 69.07. Calculated,%: C 13.08; H 2.38; N 2.54; I 69.10.

[(methionine)] $K^+ \cdot I_3^-$. (*M* 569.02 g/mol). Found, %: C 10.49; H 1.94; N 2.45; I 66.87. Calculated, %: C 10.55; H 1.95; N 2.46; I 66.91.




**Formula I.** *iso*-Leucine and its zwitterions structures.




**Formula II.** Methionine and its zwitterions structures.

### *Instrumentals and spectroscopic techniques*

The elemental analyses of the carbon, hydrogen and nitrogen contents were performed using a Perkin–Elmer CHN 2400 (USA). The electronic absorption spectra of chloroform solutions of the amino acids, iodine and resulting CT complex were recorded over a wavelength range of 200–800 nm using a UV/Vis double-beam JASCO-V-670 spectrophotometer. The instrument was equipped with a quartz cell with a 1.0 cm path length. The molar conductivities of freshly prepared $1.0 \times 10^{-3}$ mol/cm$^3$ dimethylsulfoxide (DMSO) solutions were measured for the dissolved free amino acids and its iodine charge-transfer complexes using Jenway 4010 conductivity meter. The mid-infrared (IR) spectra within the range of 4000–400 cm$^{-1}$ for the solid powder of free amino acids and its iodine charge-transfer complexes were recorded on a Bruker FT-IR spectrophotometer with 30 scans at 2 cm$^{-1}$ resolution, while, Raman laser spectra of samples were measured on the Bruker FT-Raman with laser 50 mW. Thermogravimetric analysis (TG/DTG) was performed under static nitrogen atmosphere between room temperature and 800 °C at a heating rate of 10 °C/min using a Shimadzu TGA-50H thermal analyzer.

The Doppler broadening line-shape parameters (S and W) were measured using a p-type high-purity germanium detector (Ortec, GEM series) with an energy resolution (FWHM) of 1.6 keV for 1.33 MeV gamma line of $^{60}$Co and relative efficiency of 25%. The amplified signals from an Ortec 570 amplifier were acquired with