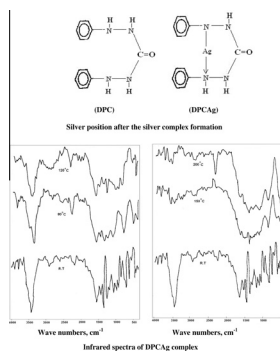


IR spectroscopic analysis of the new organic silver complex $C_{13}H_{13}N_4OAg$ F. El-Kabbany^a, S. Taha^b, M. Hafez^{a,*}^a Physics Dept., Faculty of Science, Cairo University, Egypt^b Physics Dept., Faculty of Science, Fayoum University, Egypt

HIGHLIGHTS

- IR analysis is used to investigate the changes in modes of DPCAg.
- The glass and the high temperature phase transitions are studied by IR spectroscopic parameters.
- A proposed silver position in the new complex DPCAg has been presented.

GRAPHICAL ABSTRACT



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ABSTRACT

IR analysis in the frequency range $400\text{--}4000\text{ cm}^{-1}$ is used here to investigate the changes in different modes of thermally treated new metal complex (diphenyl carbazide silver complex DPCAg, $C_{13}H_{13}N_4OAg$) during the glass transition at $91\text{ }^{\circ}\text{C}$ and the high temperature phase transition at $167\text{ }^{\circ}\text{C}$. These two phase transitions in this new metal compound are studied here by detecting the changes in some IR spectroscopic parameters (e.g., mode shift, band contour, peak height and peak intensity) during the elevation of temperature. All of the vibrations of DPCAg were found to be due to ionic fundamentals 3311 cm^{-1} , 3097 cm^{-1} , 3052 cm^{-1} , 1677 cm^{-1} , 1602 cm^{-1} , 1492 cm^{-1} , 1306 cm^{-1} , 1252 cm^{-1} , 887 cm^{-1} and 755 cm^{-1} . The results obtained can be considered as the first spectroscopic analysis of this new metal complex. These results strongly confirmed that the thermally treated DPCAg transverse a glass transition at $91\text{ }^{\circ}\text{C}$ and a high temperature phase transition at $167\text{ }^{\circ}\text{C}$. Anomalous spectroscopic changes near the glass transition temperature T_g could be recorded. A temperature dependence of peak intensity of the two modes 810 cm^{-1} and 3440 cm^{-1} could be observed beyond T_g . Also, the high temperature phase modification at $167\text{ }^{\circ}\text{C}$ showed anomalous change in the spectroscopic parameters before and after the phase transition process. A proposed silver position in the new silver complex DPCAg has been presented.

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Introduction

The importance of metal-complex formation stems from the fact that when a metal ion becomes part of a complex, it acquires new properties which may be strikingly different from those of the original ion. 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. The present work aims to study the optimum condition for the formation of one silver complex, and identify the new physical properties, which is probably found. A new work on silver complex formed by amorphous DPC and silver will be presented in this part. DPCAg complex sample is prepared by the chemical reaction between amorphous DPC [1–4] and silver nitrate. A special attention has been paid to the probable stability of the obtained silver complex.

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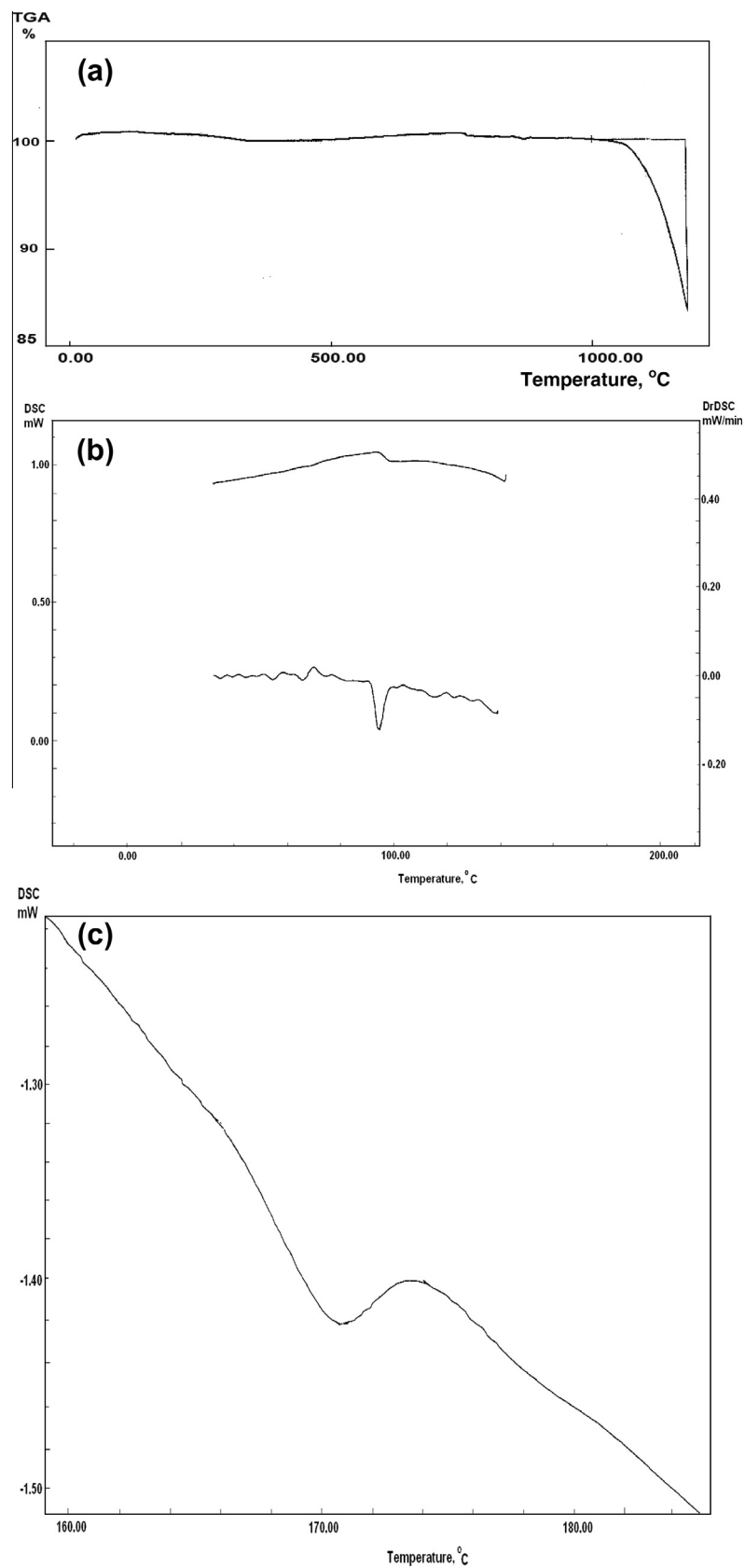


Fig. 1. (a) TGA thermogram for DPCAg complex. (b) DSC thermogram and its first derivative for AgDPC complex. (c) DSC thermogram for AgDPC organic complex.

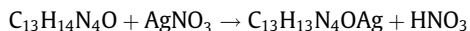
An important feature of many organic metal complexes is their extended linear chain structure. Transition metal organic complexes have attracted the interest of experimental and theoretical chemists and physicists for many years due to their fascinating chemical and photophysical properties [5,6]. Recent examples include the development of a vapochromic light emitting diode from a linear chain complex [7]. It has been reported that colorless trinuclear gold compounds that do not form extended chain structure by themselves can produce brightly colored complexes by sandwiching naked Ag^+ ions to form linear chain complexes with fascinating luminescence properties that include the luminescence thermochromism [8]. Recent results 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., Ag, into organic complex may create new important properties and new structures. The present study aims to use IR spectroscopic analysis to check the probable stability of this new silver complex compound.

The present work is considered as an extension of our work on DPCAg (includes thermal analysis such as DSC and electrical measurements) [9]. These thermal and electrical investigations give a detection for the first time of the existence of a probable glass transition at 91 °C and high temperature phase transition at 167 °C in DPCAg compound. Here DPCAg is subjected to an IR spectroscopic study under conditions similar to that performed before in thermal and electrical analysis. The nature of the temperature dependence of thermal activity of the vibrating groups is of great interest as its role that is fundamental in explaining many of the physical prop-

erties of this metal complex compound. We hope that infrared analysis might be successfully used to confirm the previously observed phase transitions through the spectral changes in DPCAg.

Experimental

DPCAg complex compound sample is prepared by the chemical reaction between amorphous DPC and silver nitrate (dissolved in acetone).



A precipitated powder is obtained in a solution of nitric acid. After filtrating the precipitated powder and drying it, the physical properties of this new organic complex $\text{C}_{13}\text{H}_{13}\text{N}_4\text{OAg}$ can be studied. We report for the first time here the properties and the crystal structure of the new silver complex.

The thermogravimetric analysis (TGA) was carried out in this study by Shimadzu system type 50 made in Japan. Differential scanning calorimetry (DSC) is an efficient and powerful tool for studying phase transition phenomena. Shimadzu DSC-60 is an accurate differential scanning calorimetry system with numerous features such as high sensitivity noise level as low as $1 \mu\text{W}_{\text{RMS}}$ (at 15 °C). The temperature range here is extended between – 140 °C and 1600 °C when liquefied nitrogen supplied.

X-ray diffraction patterns are carried out here by X-ray machine type, Bruker axs D8, Germany with $\text{Cu K}\alpha$ ($\lambda = 1.5406 \text{ \AA}$) radiation and secondary monochromator in the 2θ range from 20° to 70°. A good computer analysis program must be used for X-ray data

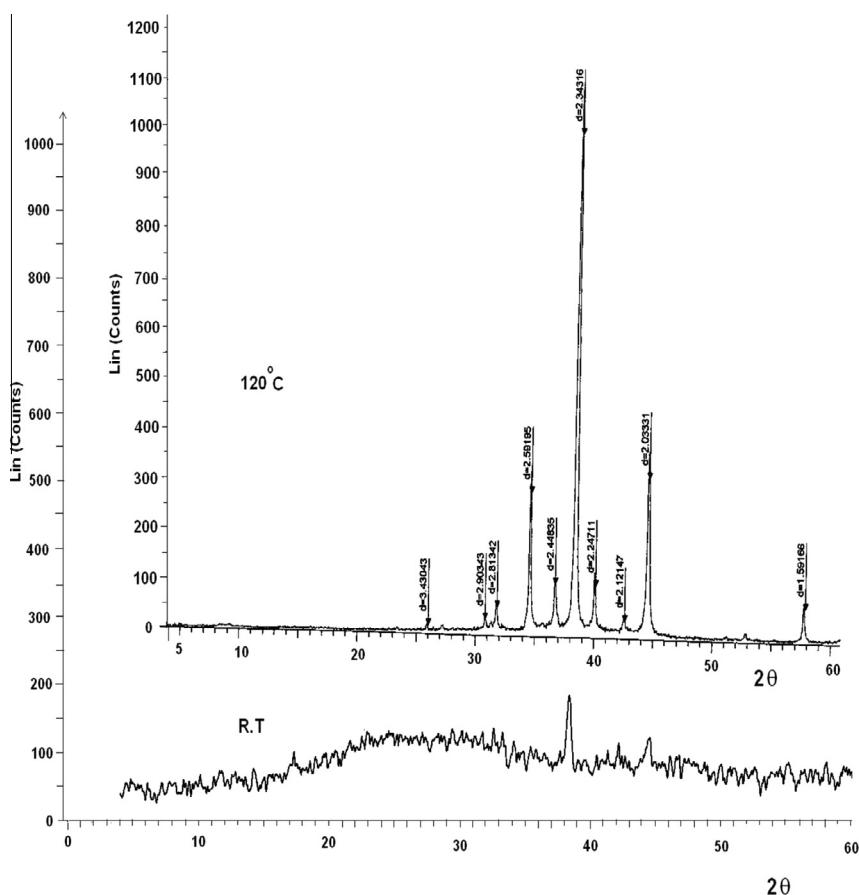


Fig. 2. X-ray diffraction patterns for DPCAg complex.

analysis. The program used in the present study is crysfire 2002 interactive powder indexing supports system. Crysfire program assists users to find the possible solutions to the powder indexing problems, in the form of complete or partial unit cells.

IR spectra were recorded using the FT-IR type Perkin–Elmer recorded on satellite 2000 spectrometer and the experimental technique employed has been reported [10]. The samples used were in the form of discs prepared by mixing 20 mg of DPCAg 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 the 400–4000 cm^{-1} region by a computerized system attached to a monitor and a printer.

Results and discussion

At first and as a fast check up of the dried precipitated material, a thermogravimetric analysis TGA is carried out as shown in Fig. 1a. According to this figure, the DPCAg sample is stable up to $\approx 1018^\circ\text{C}$. At this temperature, the sample starts a melting process and very little weight loss 12.4%. The amorphous DPC material has a melting point 162°C . This means that this new silver complex belongs to very high melting point. Thermal stability of this complex is very high and that is mainly depended on which of the bonds of the complex breaks first at elevated temperatures [11].

Fig. 1b shows a DSC thermograms and its derivative with time (DrDSC) for AgDPC complex sample in a temperature range between room temperature ($\approx 30^\circ\text{C}$) and 140°C . This DSC curve showed clearly a distinct kink at $\approx 91^\circ\text{C}$. Such kink in the DSC thermogram indicates a new type of transition, which takes place in this organic complex that contains silver. At this kink, the rate of

heat absorbed is reduced by 0.04 mW. This little change in heat absorbed indicates that this transition is not due to crystal structure change. It can be assigned to a glass transition in this organic silver complex. Non-crystalline solids are known as amorphous materials. Such materials do not have their atoms or molecules arranged on a lattice that repeats periodically in space. The kink point at 91°C is called a glass transition temperature T_g . In fact, T_g is the critical temperature that separates their glassy and rubbery behavior. If a material is at a temperature below its T_g , large-scale molecular motion is not possible because the material is essentially frozen. If it is at a temperature above its T_g , molecular motion on the scale of repeat unit takes place, allowing it to be soft or rubbery. The glass transition is the reversible transition in amorphous materials (or in amorphous regions within semicrystalline materials) from a hard and relatively brittle state into a molten or rubber-like state. An amorphous solid that exhibits a glass transition is called a glass. Despite the massive change in the physical properties of a material through its glass transition, the transition is not itself a phase transition of any kind; rather it is a laboratory phenomenon extending over a range of temperature and defined by one of several conventions [12–14]. Glass material at room temperature has an amorphous structure. Such state is called a glass state. AgDPC complex has amorphous structure at room temperature (glassy state). When AgDPC heated to 91°C , it transform to another state (with orthorhombic crystal structure). Here AgDPC transforms from amorphous state to the orthorhombic state. Such phase transformation in AgDPC is called glass transition.

Fig. 1c shows the DSC thermogram for AgDPC sample in a temperature range between 160°C and 185°C . A clear endothermic phase transition can be observed at 167°C .

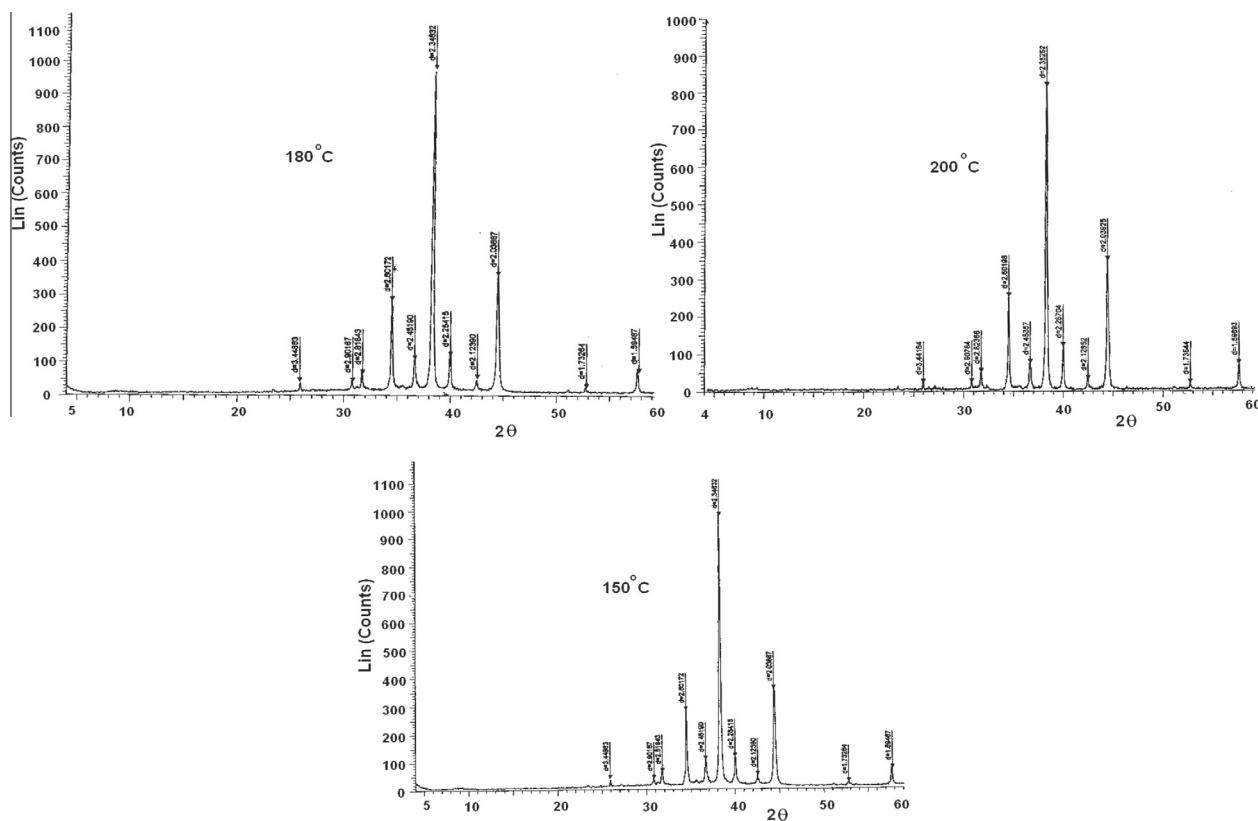


Fig. 3. X-ray diffraction pattern for DPCAg organic complex samples at three different temperatures 150°C , 180°C and 200°C .

Table 1

Principle modes of parent amorphous DPC and silver complex (DPCAg) at room temperature.

Modes	Amorphous DPC at R.T.	Organic complex (DPCAg) at R.T.
Asymmetric stretching of N–H	3311	3440
Symmetric stretching of N–H	3097	3186
Aromatic C–H stretching	3052	3124
Bending or deformation mode of N–H	1677	1628
N–N stretching symmetric vibrations	1602	1512
N–N stretching asymmetric vibrations	1492	1442
C–H stretching vibrations	1306	1342
C=O stretching vibrations	1252	1273
Out of plane C–H bending	887	933
Monosubstituted benzene	755	810
N–H oscillation	489	517

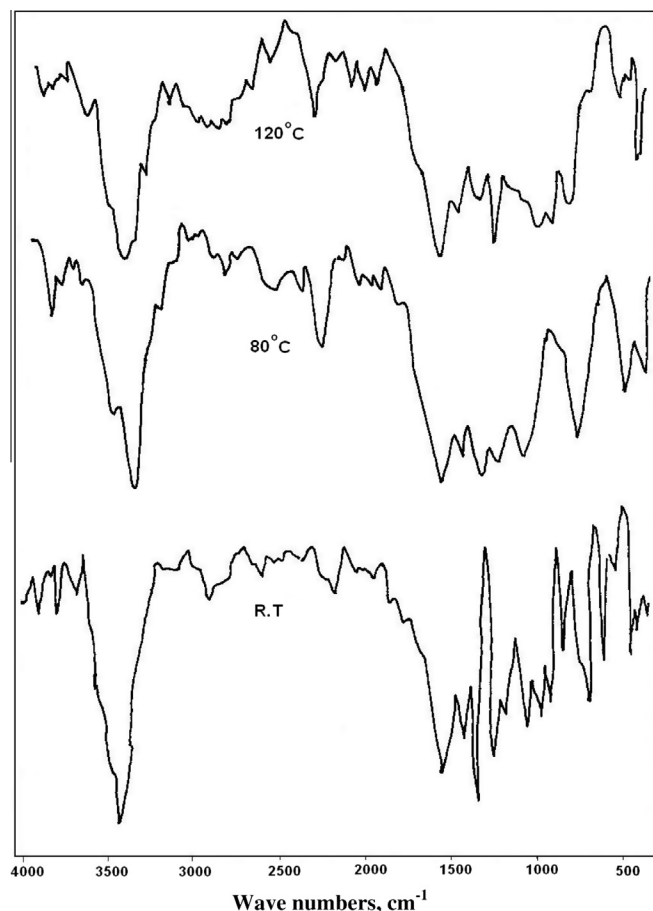


Fig. 4. Infrared spectra of DPCAg complex at room temperature (R.T. $\approx$ 30 °C), 80 °C and 120 °C.

X-ray analysis confirmed the presence of a probable glass transition at $T = 91$ °C and another high temperature phase transition at 167 °C as shown in Figs. 2 and 3.

The IR spectroscopic analysis is used here to study this probable glass transition in DPCAg at 91 °C and the high temperature phase transition at 167 °C. At first, the principle modes of the parent amorphous (DPC) and the silver complex DPCAg are checked at room temperature as given in Table 1. In order to do that, a set of IR spectra are fulfilled at different temperatures covering the regions before and after this glass transition. The selected temperatures are R.T., 60 °C, 70 °C, 80 °C, 100 °C, 110 °C and 120 °C. Fig. 4 shows examples of the recorded IR spectra at R.T., 80 °C and

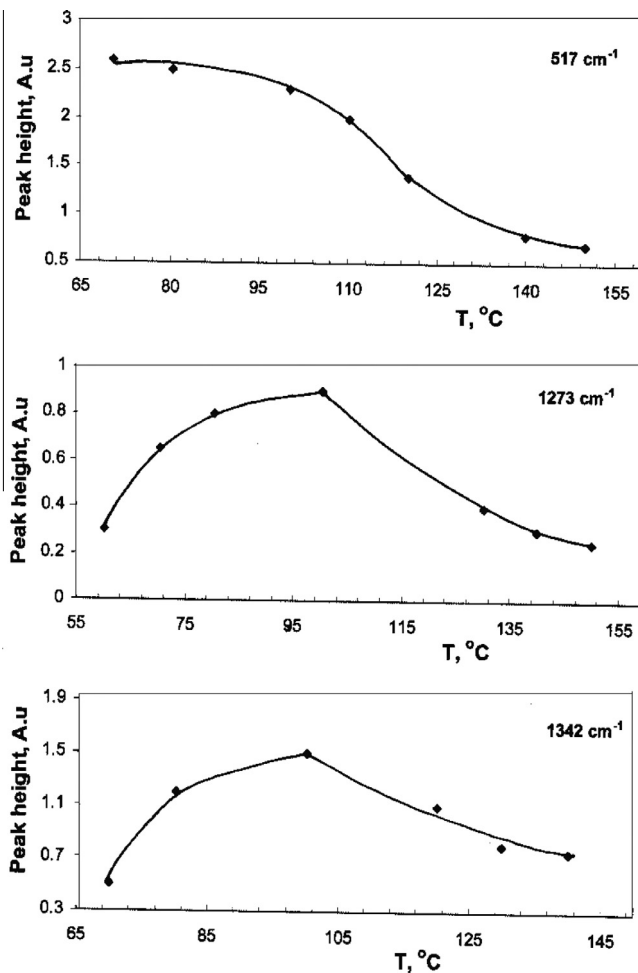


Fig. 5. Peak height temperature dependence of the IR modes 517 cm^{-1} , 1273 cm^{-1} and 1342 cm^{-1} during the glass transition in DPCAg.

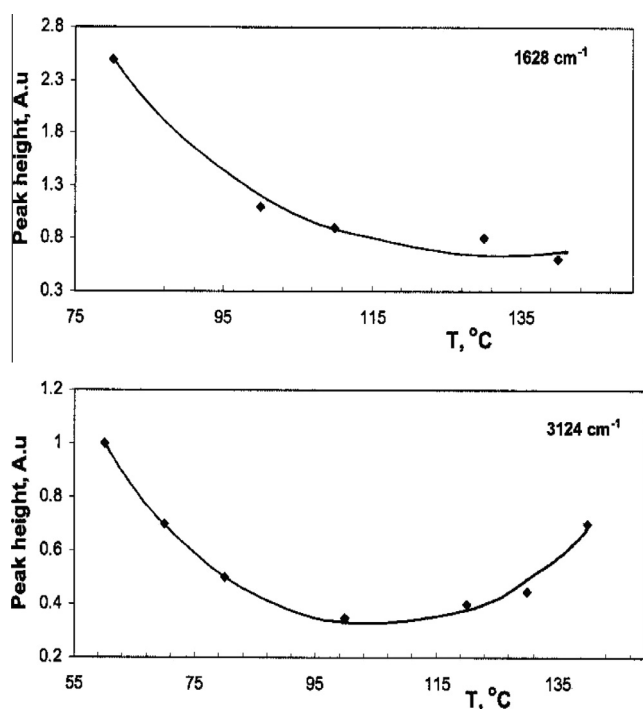
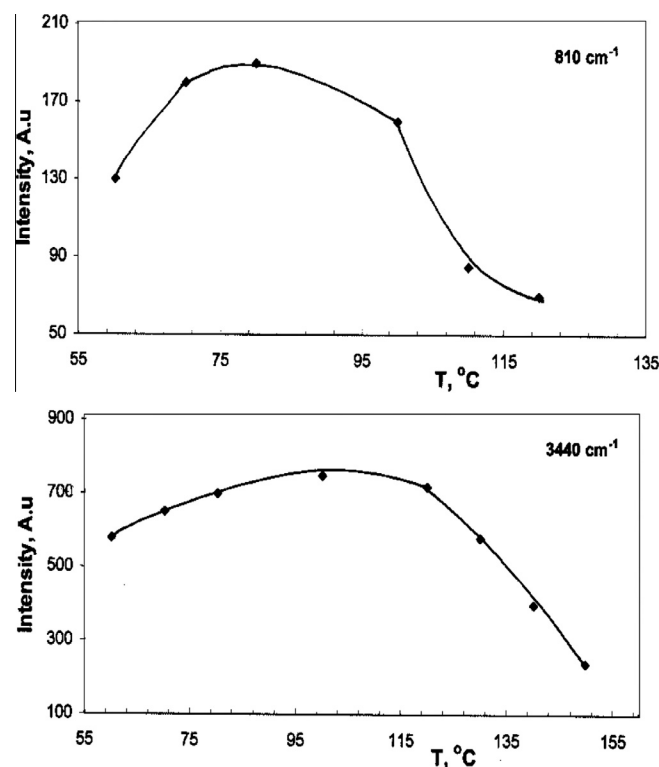
120 °C. However, the change in the principle IR different modes is due to the elevation of temperature which is given in Table 2. It was found that there is a clear change in the peak height of the principle modes 517 cm^{-1} , 1273 cm^{-1} , 1342 cm^{-1} , 1628 cm^{-1} and 3124 cm^{-1} as the DPCAg sample temperature traversing the glass transition temperature $T_g \approx 91$ °C as shown in Figs. 5 and 6. The peak height shows anomalous change near the glass transition point. The peak intensity of the two modes 810 cm^{-1} and 3440 cm^{-1} showed clear temperature dependence and fast reduction beyond T_g as shown in Fig. 7. By comparing the infrared spectra of the complex and ligand, one can see clear frequency shift of some peaks, due to silver metal. The scheme of the proposed reaction between DPC and silver metal cation is shown in Fig. 8. During the complex formation, the ligands coordinate to the central metal atom, and the newly established metal–ligand coordinate bond changes the electronic structure and the energy state. These changes affect the vibration of the ligand and consequently its vibrational spectrum [15].

The infrared spectroscopy is successfully used here to study the high temperature phase transition of DPCAg at 167 °C. Fig. 9 shows the infrared spectra of DPCAg complex at room temperature, 150 °C and 200 °C. The detailed wave number values of the principle mode are given in Table 3. Also, in the same table, the principle modes of the parent amorphous DPC are given. A fast review of the mode values showed that there is a clear positive and negative mode change between the parent material and the new complex DPCAg.

Table 2

Variation of the principle modes of the silver complex (DPCAg) with temperature.

Modes	R.T.	60 °C	70 °C	80 °C	100 °C	110 °C	120 °C
Asymmetric stretching of N–H	3440	3440	3425	3425	3471	3440	3471
Symmetric stretching of N–H	3186	–	–	–	3203	3186	3193
Aromatic C–H stretching	3124	3132	3119	3094	3093	–	3116
Bending or deformation mode of N–H	1628	1635	1620	1635	1620	1620	1620
N–N stretching symmetric vibrations	1512	1500	–	1512	1527	–	1512
N–N stretching asymmetric vibrations	1442	1404	1450	–	1450	–	–
C–H stretching vibrations	1342	–	1373	1388	1373	1388	1388
C=O stretching vibrations	1273	1234	1311	1311	1311	–	1296
Out of plane C–H bending	933	926	–	–	881	941	972
Monosubstituted benzene	810	848	864	848	818	863	879
N–H oscillation	517	540	551	555	509	585	551

**Fig. 6.** Peak height temperature dependence of the IR modes 1628 cm^{-1} and 3124 cm^{-1} during the glass transition in DPCAg.**Fig. 7.** Intensity temperature dependence of the two principle modes 810 cm^{-1} and 3440 cm^{-1} during the glass transition in DPCAg.

In addition, Fig. 9 shows two high temperature spectra for DPCAg complex at $150\text{ }^{\circ}\text{C}$ and $200\text{ }^{\circ}\text{C}$. As clear, the two spectra are completely different. However, the IR spectra are recorded in details for DPCAg samples at ten different temperatures started at R.T., $120\text{ }^{\circ}\text{C}$, $130\text{ }^{\circ}\text{C}$, $140\text{ }^{\circ}\text{C}$, $150\text{ }^{\circ}\text{C}$, $170\text{ }^{\circ}\text{C}$, $180\text{ }^{\circ}\text{C}$, $190\text{ }^{\circ}\text{C}$, $200\text{ }^{\circ}\text{C}$ and $210\text{ }^{\circ}\text{C}$. The mode changes at these temperatures are tabulated in Table 3. The change in peak height with temperature for the different modes of the IR spectra is given in Figs. 10 and 11. All of them showed anomalous change in the phase transition region. The variation of the peak intensity of both the monosubstituted benzene (810 cm^{-1}) and asymmetric stretching of N–H (3440 cm^{-1}) with temperature is given in Fig. 12. All of these changes in the spectroscopic parameters support the previously detected high temperature phase transition in DPCAg at $167\text{ }^{\circ}\text{C}$.

A phase transition process is considered as an indication of the regularity of the thermodynamic functions characterizing the state of a substance at a special point called the phase transition point. As soon as such a point is reached the initial phase can no longer exist and changes into a new phase. Near this critical point a sub-

stance acquires unusual properties. Accordingly, the phase transformations observed here in DPCAg may be experimentally observed by studying the temperature dependence of the vibrational spectra, especially near the glass transition point $91\text{ }^{\circ}\text{C}$ and high temperature phase transition point at $167\text{ }^{\circ}\text{C}$. The elevation of temperature increases the probability of reorientation of DPCAg molecules and in turn, this should lead to a change of the characteristics of the vibrational spectrum. This provides very important information about the dynamics of the process of phase transition in this metal complex. It is well known that a distinct shape of an absorption band for distinct molecule is related to the number of ions that undergo the various energy transitions. Thus, the most intense line is that represents the largest number of ions undergoing a particular transition. The intensity of each line depends here on the number of DPC ions undergoing a certain energy transition and hence the band envelope as a whole is a representation of the total number of DPC ions involved [16]. As the temperature of DPC ions increased, the contour of the absorption band will change, but the area under the envelope will remain constant, pro-

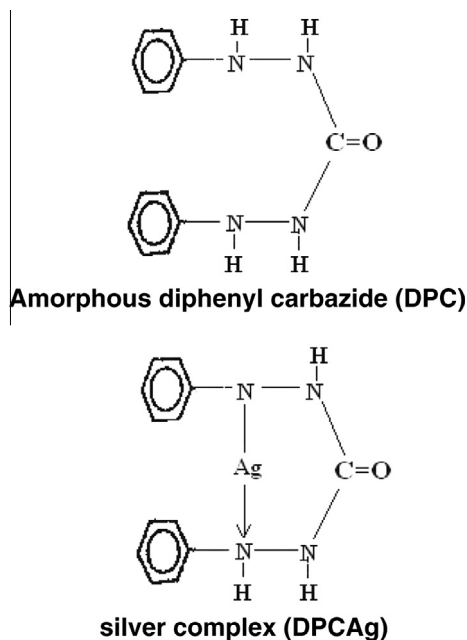


Fig. 8. Proposed silver position after the silver complex formation.

Table 3

Variation of the principle modes of the silver complex (DPCAg) during its high temperature phase transition.

Modes	130 °C	140 °C	150 °C	170 °C	180 °C	190 °C	200 °C	210 °C
Asymmetric stretching of N–H	3494	3484	3471	3417	3448	3456	3456	3456
Symmetric stretching of N–H	–	3209	3186	3155	3186	3178	3163	3197
Aromatic C–H stretching	3098	3101	3123	3086	3124	3078	3106	3109
Bending or deformation mode of N–H	1620	1628	1620	1612	1597	1658	1620	–
N–N stretching symmetric vibrations	1504	–	1504	1550	1504	1535	1520	1520
N–N stretching asymmetric vibrations	–	1435	1458	1442	–	–	–	–
C–H stretching vibrations	1381	1381	1381	1381	1388	1388	1381	1381
C=O stretching vibrations	1303	1288	1304	1280	1273	–	1273	1304
Out of plane C–H Bending	–	–	–	949	–	910	–	–
Monosubstituted benzene	841	864	856	802	864	825	856	810
N–H oscillation	–	557	517	508	532	532	517	532

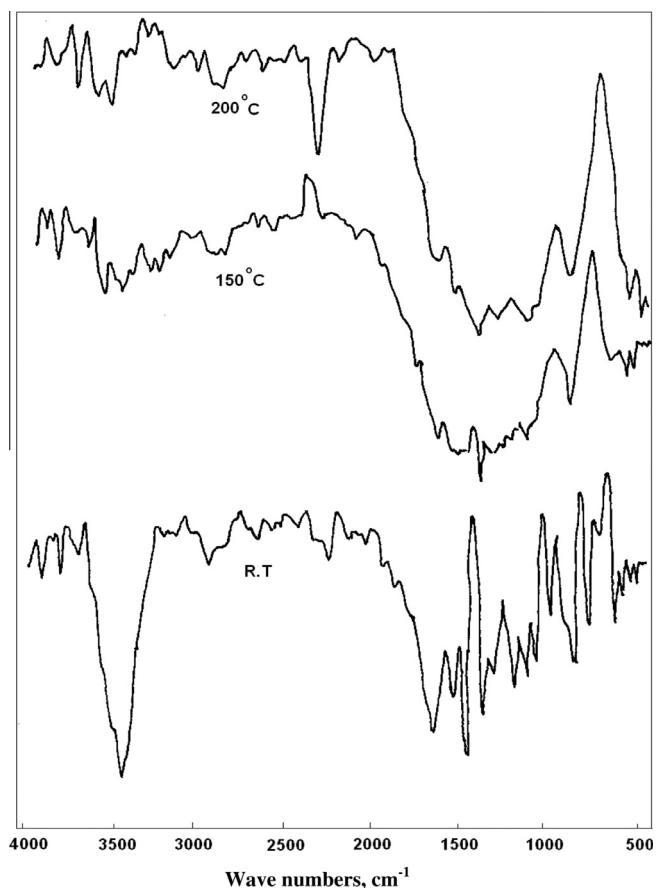
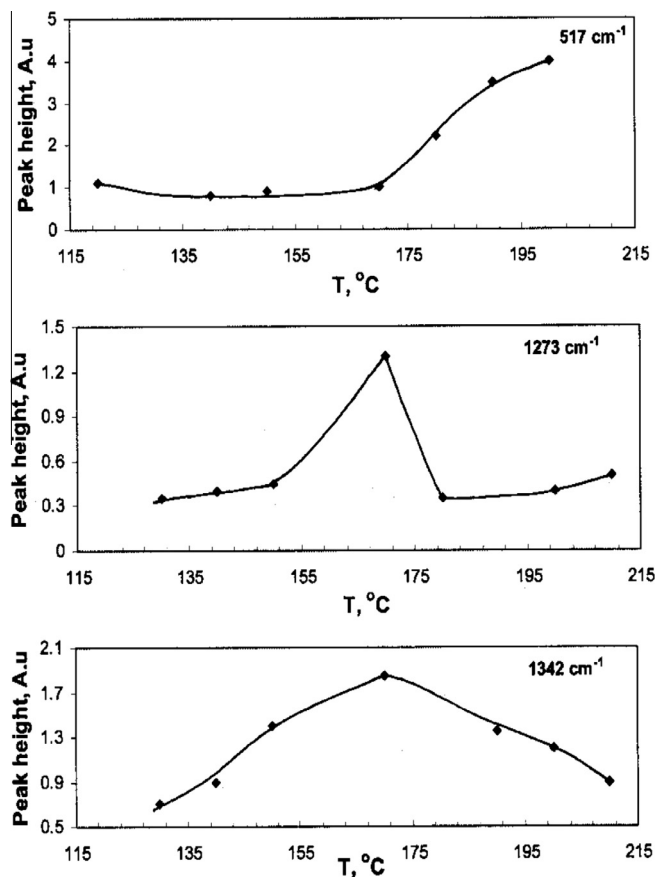


Fig. 9. Infrared spectra of DPCAg complex at room temperature (R.T. ≈ 30 °C), 150 °C and 200 °C.

Fig. 10. Peak height temperature dependence of the IR modes 517 cm^{−1}, 1273 cm^{−1} and 1342 cm^{−1} during the high temperature phase transition in DPCAg at 167 °C.

vided that the increase in temperature does not change the number of ions initially being in the vibrational level $\nu = 0$. The area

of a band remains constant for fairly large changes in temperature until the transition temperature is reached.

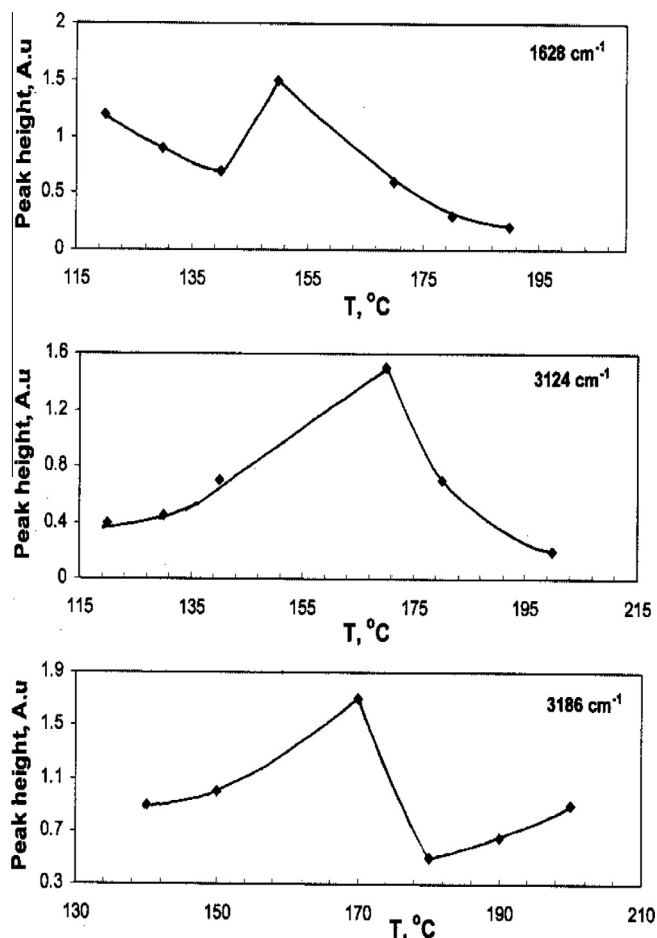


Fig. 11. Peak height changes of the modes 1628 cm^{-1} , 3124 cm^{-1} and 3186 cm^{-1} during the high temperature phase transition in DPCAg at $167\text{ }^{\circ}\text{C}$.

Conclusion

In conclusion, the infrared spectroscopy was successfully used for the prediction of the glass transition at $91\text{ }^{\circ}\text{C}$ and high temperature phase transition point at $167\text{ }^{\circ}\text{C}$ for the silver complex $\text{C}_{13}\text{H}_{13}\text{N}_4\text{OAg}$.

The IR of a metal complex compound in its solid state arises from lattice vibrations of the individual ions and internal vibrations of molecules. Since the vibrations occur throughout the lattice and are not concerned with a single unit cell, these vibrations are often observed as broad peaks which represent a composite band of several vibrations. For such compounds the mass of ions concerned plays an important role in determining the frequency of absorption. However, a regular change in frequency is observed with increasing size and mass and decreasing polarizing power of the cation.

For those lattice containing complex molecules, the vibrations likely to be observed in the IR spectrum arise from two sources:

- Molecular lattice vibrations which would occur at very low frequencies due to the mass of the molecule.
- Internal vibrations of the molecules.

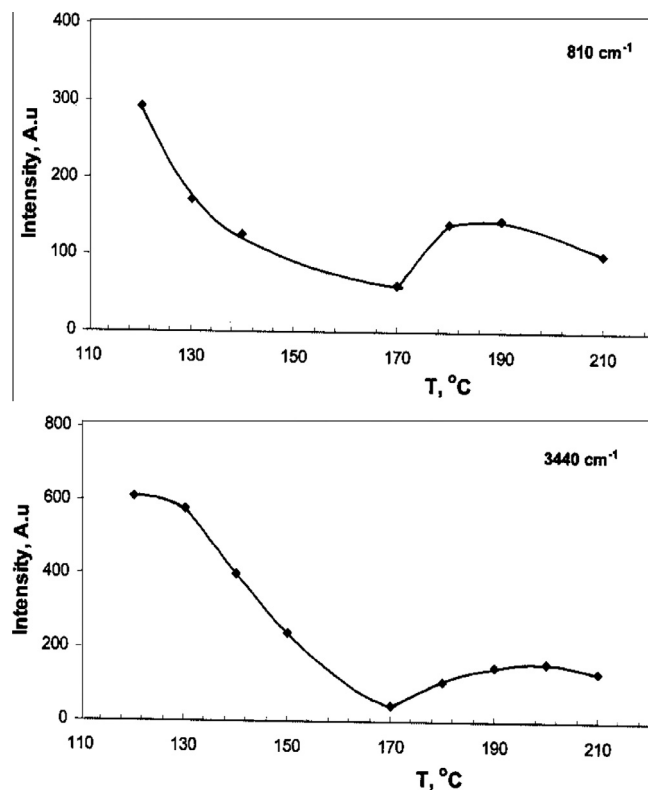


Fig. 12. Variation of the peak intensity of the monosubstituted benzene at 810 cm^{-1} and asymmetric stretching of N–H at 3440 cm^{-1} with temperature for DPCAg.

Within this second class there are stretching and bending vibrations which involve heavy atoms such as metal–oxygen and hindered rotation of ligands attached to central metal atom.

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