УДК 547.796.1+541.49

ТЕОРЕТИЧЕСКОЕ И ИК-СПЕКТРОСКОПИЧЕСКОЕ ИССЛЕДОВАНИЕ СТРУКТУРЫ ПОЛИ-5-ВИНИЛТЕТРАЗОЛАТА МЕДИ(II) И ПРОДУКТА ЕГО ТЕРМОЛИЗА

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Методами теории функционала плотности и ИК-спектроскопии исследовано строение поли-5-винилтетразолата меди(II) и продукта его термолиза. Путем анализа вычисленного распределения молекулярного электростатического потенциала, а также сопоставления рассчитанного для модельных структур и экспериментального ИК-спектров установлены преимущественные способы координации ионов меди и тетразольных лигандов в поли-5-винилтетразолате меди(II). Показано, что наилучшее согласие между расчетными и экспериментальными данными наблюдается для модельной структуры с трехкоординированными ионами меди, которая включает тетразольные циклы, координирующие два иона меди(II) через атомы N(1) и N(3), и циклы, координирующие один ион меди через атом азота N(2) или N(3). На основании анализа экспериментального ИК-спектра продукта термолиза с учетом возможностей расщепления связей в условиях термолиза предложены семь структур возможных продуктов, рассчитаны их ИК-спектры и результаты расчетов сопоставлены с экспериментом. Показано, что основным продуктом термолиза является *цис*-полицианоацетилен.

Ключевые слова: теория функционала плотности; ИК-спектроскопия; поли-5-винилтетразол; термолиз; поли-5-винилтетразолат меди(II).

Образец цитирования:
Матулис Виталий Э, Рагойжа ЕГ, Зураев АВ, Григорьев ЮВ, Ивашкевич ОА. Теоретическое и ИК-спектроскопическое исследование структуры поли-5-винилтетразолата меди(II) и продукта его термолиза. *Журнал Белорусского государственного университета. Химия.* 2020;1:19–31 (на англ.).
https://doi.org/10.33581/2520-257X-2020-1-19-31

For citation:
Matulis Vitaly E, Ragoyja EG, Zuraev AV, Grigoriev YV, Ivashkevich OA. Theoretical and infrared spectroscopy study of the structure of copper(II) poly-5-vinyltetrazolate and the products of its thermolysis. *Journal of the Belarusian State University. Chemistry.* 2020;1:19–31.
https://doi.org/10.33581/2520-257X-2020-1-19-31

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Журнал Белорусского государственного университета. Химия. 2020;1:19–31
Journal of the Belarusian State University. Chemistry. 2020;1:19–31

THEORETICAL AND INFRARED SPECTROSCOPY STUDY OF THE STRUCTURE OF COPPER(II) POLY-5-VINYLTETRAZOLATE AND THE PRODUCTS OF ITS THERMOLYSIS

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The structure of copper(II) poly-5-vinyltetrazolate and the products of its thermolysis has been studied by means of density functional theory and infrared spectroscopy. Copper(II) poly-5-vinyltetrazolate has been obtained and subsequently subjected to thermolysis. Infrared spectra of copper(II) poly-5-vinyltetrazolate and the products of its thermolysis have been recorded. The possible ways of coordination of copper(II) ions with tetrazole-containing ligands were established by analyzing the calculated molecular electrostatic potential distribution and comparing the calculated IR-spectra of the model structures to the experimental ones. It has been shown that the best agreement between the calculated and experimental data is observed for the model with three-coordinated copper(II) ions, which includes both the tetrazole-containing ligands coordinating two copper(II) ions through N(1)- and N(3)-atoms of the tetrazole ring, and the tetrazole-containing ligands coordinating one copper(II) ion through either the N(2)- or the N(3)-atom. Recently we have shown that the product of thermolysis of copper(II) poly-5-vinyltetrazolate exhibits high catalytic activity in homocoupling of phenylacetylene and Huisgen [3 + 2]-cycloaddition. To establish the structure of the products of thermolysis of copper(II) poly-5-vinyltetrazolate, seven possible products have been proposed based on the analysis of the structure of copper(II) poly-5-vinyltetrazolate and the experimental IR-spectrum. IR-spectra of all proposed products have been calculated and the results of the calculations have been compared with the experimental IR-spectrum of copper(II) poly-5-vinyltetrazolate thermolysis product. It has been shown that the main product of thermolysis is *cis*-polycyanoacetylene.

Keywords: density functional theory; IR spectroscopy; poly-5-vinyltetrazole; thermolysis; copper(II) poly-5-vinyltetrazolate.

Introduction

Tetrazole is a five-membered heterocycle containing four nitrogen atoms and possessing a unique combination of properties caused by very high energetics along with sufficient thermal stability and compatibility with substances and materials of various nature [1–4]. This attracts a lot of attention to tetrazole derivatives as efficient components of various combustible and thermally decomposed systems including solid rocket propellants, burning catalysts, auxiliary initiators and ignitors, as well as other high-energetic materials [5–7]. The particular and increasing interest is attracted now to tetrazole-containing polymers and some of their metal-containing derivatives as binders of solid propellants and precursors of a wide variety of products with unusual properties [8–11].

The methods for preparation of tetrazole-containing polymers and their metal-containing derivatives, as well as properties of their thermolysis products have been studied extensively [6; 8–11]. Recently we have established that the product of thermolysis of copper(II) poly-5-vinyltetrazolate is a highly efficient catalyst for some reactions such as homocoupling of phenylacetylene and Huisgen [3 + 2]-cycloaddition [12; 13].

However, the structure of initial metal-containing polymers, determining the mechanism of thermal decomposition, along with the structure of thermolysis products that, in their turn, provide the catalytic activity, have not been studied in details [12; 13].

Here we present a study of the structure of copper(II) poly-5-vinyltetrazolate, as well as the products of its thermolysis based on the comparison of the calculated IR-spectra of the corresponding model structures with the experimental data. The possible ways of copper(II) ions coordination with tetrazole-containg ligands were established by analyzing the calculated molecular electrostatic potential (MESP) distribution. The IR spectroscopy has been chosen for the experimental part of the study, as this method is not affected by the insolubility of copper(II) poly-5-vinyltetrazole and the products of its thermolysis.

Experimental and theoretical methods

Quantum chemical calculations

All calculations have been carried out within density functional theory (DFT). Since calculations of large polymer molecules are time-consuming, for theoretical prediction of IR-spectra of poly-5-vinyltetrazole, copper(II) poly-5-vinyltetrazolate and its thermolysis products, we have used the model structures in which heavy polymer chains were substituted by iodine atoms. Thus, all calculations in such cases were carried out for corresponding single monomeric units terminated by iodine atoms. We assume that heavy iodine atoms will have almost no effect on the calculated vibrational properties of remaining atoms in model structures. The geometry optimization and vibrational frequencies calculations of possible products of thermolysis of copper(II) poly-5-vinyltetrazolate were carried out using hybrid B3LYP [14] functional and 6-311+G(d, p) [15] basis set for all atoms except iodine for which Def2-TZVPD [16] basis was applied. Taking into account a much larger size of the model structures used for theoretical investigation of copper(II) poly-5-vinyltetrazolate itself, the geometry optimization and vibrational frequencies calculations of such systems were carried out using smaller 6-31G(d) [17] basis set for H, C, N and SDD basis for Cu [18] and I [19]. To prevent the interaction between the N-atoms of the tetrazole rings and the H-atoms of the substitute, which can lead to unphysical conformations, a polar aprotic medium was used for geometry optimization and vibrational frequencies calculations of copper(II) poly-5-vinyltetrazolate model structures. Dimethylsulfoxide (DMSO) was chosen as a solvent and the solvation effects were considered within the PCM model [20]. All calculations were performed using the *Gaussian 09* program [21].

Experimental section

Synthesis of poly-5-vinyltetrazole. Poly-5-vinyltetrazole was obtained through the polymer-analogous transformation of polyacrylonitrile [9]. Polyacrylonitrile (25 g) was dissolved in dimethylformamide (250 mL). To the resulting solution a mixture of sodium azide (32 g) and ammonium chloride (27 g) was added. The reaction mixture was stirred at 100 °C for 25 h. Afterwards the solution was diluted with water, and the resulting mixture was added to a solution of hydrochloric acid (0.7 $\mathrm{mol \cdot cm^{-3}}$). The obtained product was filtered out, washed with water, and dried in a vacuum oven for 8 h.

Preparation of copper(II) poly-5-vinyltetrazolate and the products of its thermolysis. For the preparation of copper(II) poly-5-vinyltetrazolate, poly-5-vinyltetrazole (6.5 g) was dissolved in an aqueous solution of sodium hydroxide (200 mL, 1.2 wt. %). The resulting solution of sodium poly-5-vinyltetrazolate was added to an aqueous solution of copper(II) nitrate (100 mL, 25 wt. %). The reaction mixture was stirred at room temperature for 2 h. Afterwards the solution was filtered through the cellulose membrane. The obtained precipitate was washed with water and ethanol, and dried in a vacuum oven for 4 h Subsequently, copper(II) poly-5-vinyltetrazolate was subjected to thermolysis in a muffle oven at 300 °C for 5 min. As a result of the thermolysis of copper(II) poly-5-vinyltetrazolate, a black powder product was obtained [12].

IR spectroscopy investigation. Infrared spectra of poly-5-vinyltetrazole, copper(II) poly-5-vinyltetrazolate and the products of their thermolysis were recorded on Bruker «Vertex 70» FT-IR system (Blackman – Harrys apozidation) over the 4000–400 $\mathrm{cm^{-1}}$ range in «Pike» diamond cavities.

Results and discussion

Structure of copper(II) poly-5-vinyltetrazolate

With a purpose of proving the feasibility of the chosen method, model structure of poly-5-vinyltetrazole was optimized (fig. 1) and its vibrational frequencies were calculated and compared with the experimental data. Calculated vibrational frequencies together with the corresponding displacement vectors, as well as the experimental IR data are shown in table 1.

As can be seen from table 1, the calculated frequencies are in good agreement with the experimental ones especially in the region below 1600 $\mathrm{cm^{-1}}$. We therefore focus on the comparison of calculated and experimental IR-spectra of copper(II) poly-5-vinyltetrazolate in this region. The application of the larger basis set allows improving the agreement with experiment only for frequencies above 1100 $\mathrm{cm^{-1}}$.

In our previous work [22] we have shown that in silver(I) and palladium(II) 1-R-tetrazole-5-thiolates Ag^+ and Pd^{2+} ions are located in the areas of minimal MESP. Therefore, in order to determine the most probable Cu^{2+} coordination sites we carried out the calculations of MESP for the model structure corresponding to the poly-5-vinyltetrazolate anion. The B3LYP/6-311+G(d, p) calculated plot of MESP distribution is shown in fig. 2.

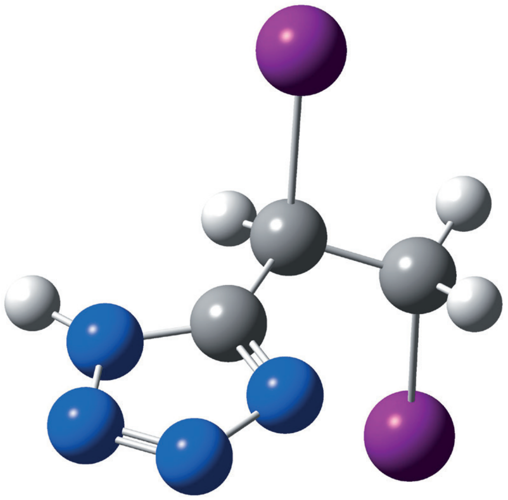
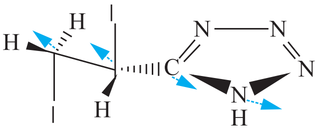
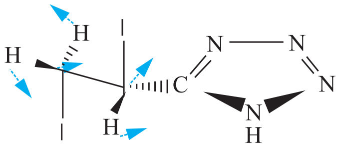
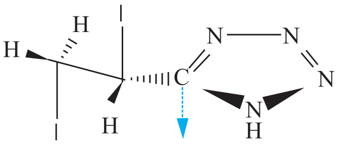
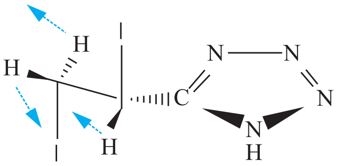
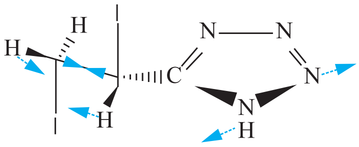
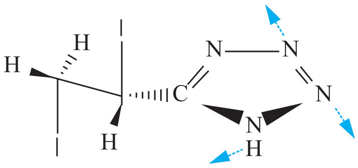
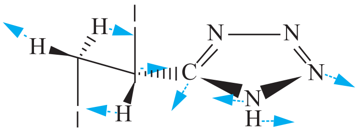
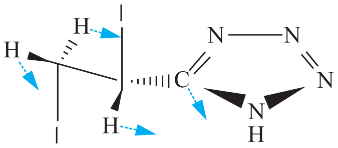
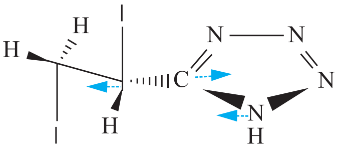


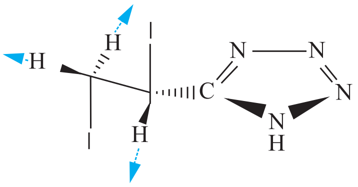
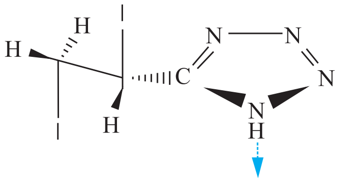
Fig. 1. Optimized model structure of poly-5-vinyltetrazole

Table 1

Comparison of calculated (corresponding to the model structure shown in fig. 1) and experimental vibrational frequencies of poly-5-vinyltetrazole: ***a*** **– B3LYP/6-311+G(d, p), Def2-TZVPD level of theory;** ***b*** **– B3LYP/6-31G(d), SDD level of theory**

Vibrational frequencies, cm^{-1}			Displacement vectors
Experimental	Calculated		
	a	*b*	
462	452	453	
668	672	675	
766	757	762	
892	872	891	
1053	1058	1055	
1251	1257	1266	
1387	1393	1407	
1448	1452	1470	
1556	1566	1577	

Ending table 1

Vibrational frequencies, cm^{-1}			Displacement vectors
Experimental	Calculated		
	a	*b*	
3021	3125	3170	
3398	3640	3645	

It can be seen from fig. 2 that the most negative areas of MESP are located in the plain of the tetrazole ring near the N(2)- and the N(3)-atoms, but the values of MESP near the N(1)- and the N(4)-atoms are very similar to those for N(2) and N(3). It should be noted that the interaction of Cu^{2+} with the N(4) nitrogen atom is likely to be prohibited by the steric effects caused by the spatial arrangement of the polymer chain. As such, we can suppose that the favorable interaction of the polymer chain with Cu^{2+} should be mediated through the N(1)-, N(2)- or N(3)-atoms.

Considering a large number of possible configurations of copper(II) poly-5-vinyltetrazolate, while the only experimental data available is IR-spectrum as well as the fact that the initial salt is amorphous, it is practically impossible to determine the actual structure of copper(II) poly-5-vinyltetrazolate. Therefore, the main goal of our study was to establish the possible coordination between tetrazole-containing ligand and copper(II) ions. We have investigated the possibility of interaction of one tetrazole ring with one or two copper(II) ions through nitrogen atoms N(1), N(2) or N(3) (see fig. 1), and studied various model structures, starting with the smallest ones, including one copper(II) ion and two poly-5-vinyltetrazolate ligands, and ending with models including up to four copper(II) ions and five poly-5-vinyltetrazolate ligands. In view of a large size of the poly-5-vinyltetrazolate ligand, we have considered only those models in which the copper ions are three-coordinated. The geometries of all considered structures were fully optimized and vibrational frequencies were calculated to simulate the IR-spectrum of copper(II) poly-5-vinyltetrazolate.

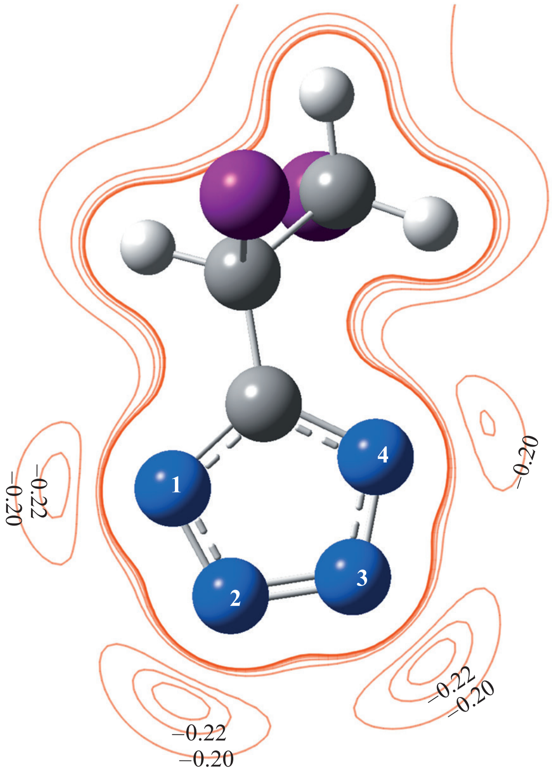


Fig. 2. B3LYP/6-311+G(d, p) calculated plot of MESP distribution for the model structure of the poly-5-vinyltetrazolate anion

The best agreement between the calculated and experimental spectra occurs for the model structures given in fig. 3, which includes both tetrazole-containing ligands coordinating two copper(II) ions through the N(1)- and N(3)-atoms of the tetrazole ring and those coordinating one copper(II) ion through N(2). The corresponding B3LYP/6-31G(d), SDD optimized structures in DMSO solution are given in fig. 4.

The calculated vibrational frequencies for the model ***D*** (see fig. 4) in the gas phase and in DMSO solution are compared in table 2.

As can be seen from table 2, the values of vibrational frequencies calculated in gas phase and in DMSO solution are very close. As such, we did not use any scale factors for the frequencies calculated in DMSO.

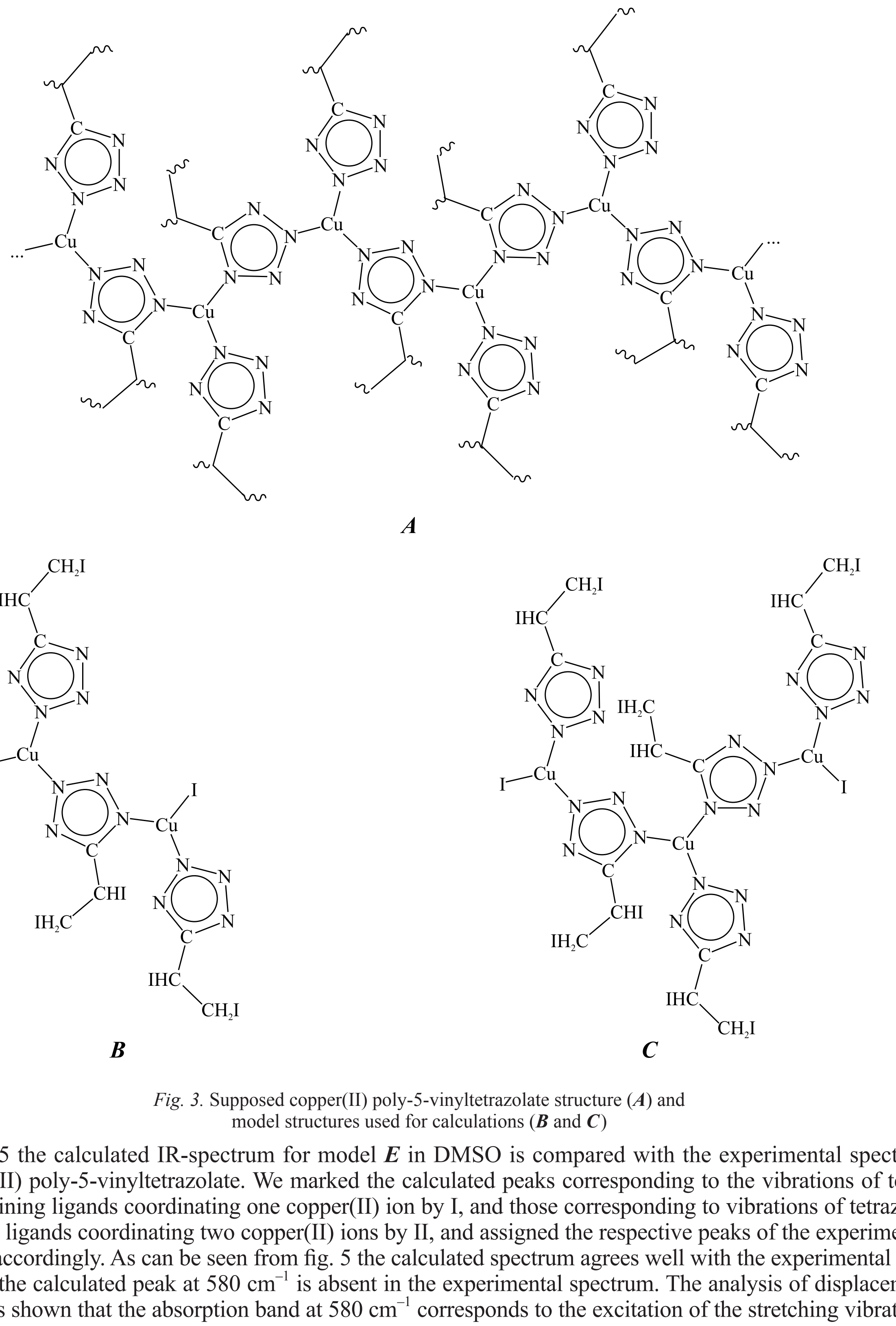


Fig. 3. Supposed copper(II) poly-5-vinyltetrazolate structure (***A***) and model structures used for calculations (***B*** and ***C***)

In fig. 5 the calculated IR-spectrum for model ***E*** in DMSO is compared with the experimental spectrum of copper(II) poly-5-vinyltetrazolate. We marked the calculated peaks corresponding to the vibrations of tetrazole-containing ligands coordinating one copper(II) ion by I, and those corresponding to vibrations of tetrazole-containing ligands coordinating two copper(II) ions by II, and assigned the respective peaks of the experimental spectrum accordingly. As can be seen from fig. 5 the calculated spectrum agrees well with the experimental one. However, the calculated peak at 580 cm^{-1} is absent in the experimental spectrum. The analysis of displacement vectors has shown that the absorption band at 580 cm^{-1} corresponds to the excitation of the stretching vibrations of C—I bonds that are available in model structures and absent in real copper(II) poly-5-vinyltetrazolate. The results of our calculations indicated that in order to describe all peaks in the experimental spectrum, a model structure must contain tetrazole rings coordinating two copper(II) ions as well as one copper(II) ion. Experimental vibrational frequencies, together with those calculated for the model ***E***, as well as the corresponding displacement vectors are given in table 3. The deviation between calculations and experiment is smaller than 20 cm^{-1}, with the exception of the peak at 1560 cm^{-1} (see table 3).

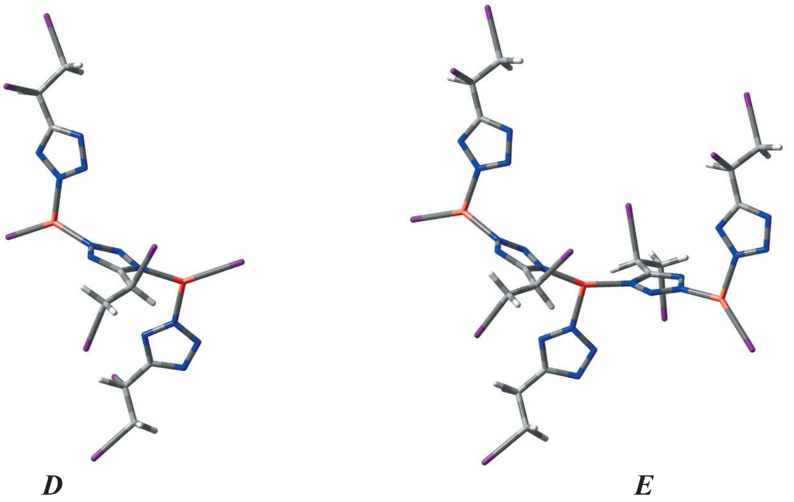


Fig. 4. B3LYP/6-31G(d), SDD optimized model structures (***D*** and ***E***) of copper(II) poly-5-vinyltetrazolate in DMSO solution

Table 2

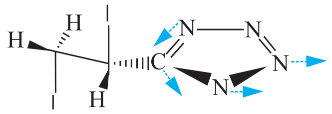
Comparison of B3LYP/6-31G(d), SDD calculated vibrational frequencies for model *D* (see fig. 4) in the gas phase and in DMSO solution

Calculated vibrational frequencies, cm^{-1}	
Gas phase	DMSO solution
486.4	487.2
689.8	690.8
784.3	787.3
1042.4	1044.2
1125.2	1127.9
1230.3	1231.0
1330.2	1327.7
1427.4	1428.3
1473.3	1478.2
1521.7	1522.0

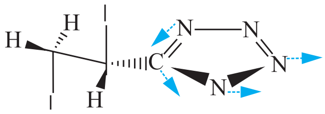
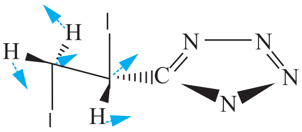
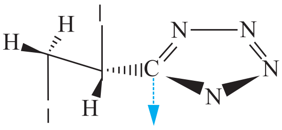
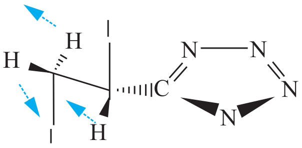
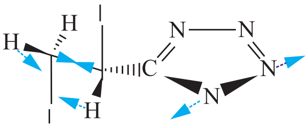
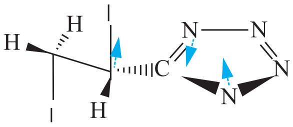
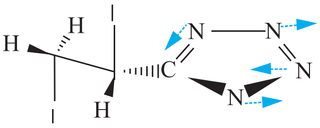
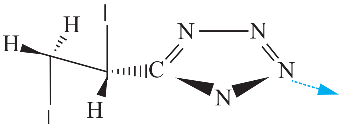
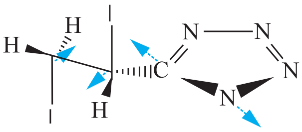
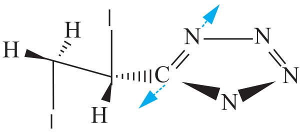
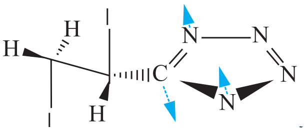
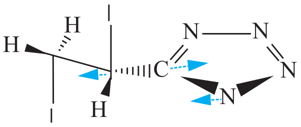
Thus, the obtained results allow concluding that copper(II) poly-5-vinyltetrazolate should contain both tetrazole-containing ligands coordinating two copper(II) ions through the N(1)- and N(3)-atoms of tetrazole ring and through N(2)- or N(3)-atom. Taking into account a rather good agreement between the calculations and experiment, we are confident in the validity of the proposed three-coordinated copper model.

Table 3

Comparison of the experimental vibrational frequencies of copper(II) poly-5-vinyltetrazolate with the ones calculated for the model *E*

Vibrational frequencies, cm^{-1}		Displacement vectors
Experimental	Calculated	
471	491 (II)	

Ending table 3

Vibrational frequencies, cm^{-1}		Displacement vectors
Experimental	Calculated	
516	515 (I)	
670	687 (II)	
764	781 (I)	
823	839 (I) 898 (II)	
1042	1044 (I) 1047 (II)	
1129	1124 (I) 1144 (II)	
	1201 (II)	
1250	1231 (I)	
1333	1332 (II)	
1411	1426 (I)	
1477	1467 (II)	
1560	1526 (II)	

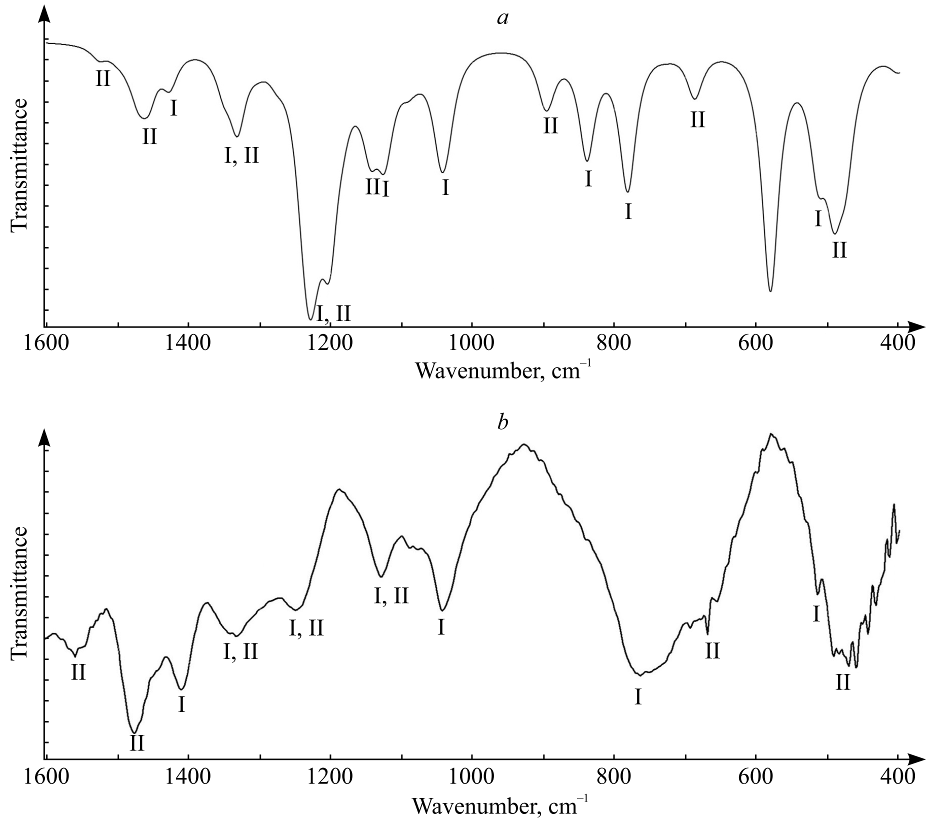


Fig. 5. Calculated IR-spectrum for model ***E*** (see fig. 4) (*a*);
experimental IR-spectrum of copper(II) poly-5-vinyltetrazolate (*b*)

Thermolysis products

The comparison of the experimental IR-spectra of the products of thermolysis of poly-5-vinyltetrazole and its copper salt shown that they are very similar. We therefore assume that in both cases the products of thermolysis contain the same organic matrix. However, the IR-spectrum of the copper(II) poly-5-vinyltetrazolate thermolysis product features lower resolution in comparison with the product of thermolysis of poly-5-vinyltetrazole. This can be explained by the presence of copper nanoparticles in a polymeric matrix of the product of thermolysis of copper(II) poly-5-vinyltetrazolate. To determine the composition of such polymeric matrix we calculated the corresponding vibrational spectrum and compared it to the experimental data.

Before proposing possible structures of the thermolysis products, preliminary analysis of the experimental IR-spectrum was carried out. According to the characteristic frequencies data we can assume the presence of cyano-groups. This assumption is based on the fact that no other fragments that could be formed from poly-5-vinyltetrazole are able to absorb in the spectral region of 2200–2400 cm^{-1}. Double C═C bond was suggested to be formed in the thermolysis product based on the absorption bands at 1596 cm^{-1} (stretching vibration typical for double bond attached to heavy substituents such as a polymer chain) and 807 cm^{-1} (typical for out-of-plane C—H vibrations in the trisubstituted double bond). Finally, peaks at 1382 and 3371 cm^{-1} are common to C—N and N—H stretching vibrations, respectively.

Considering the presence of the above mentioned chemical bonds and fragments together with the structure of poly-5-vinyltetrazole and tendencies of bonds cleavage for similar substances seven possible products have been suggested (fig. 6). The geometries of all chosen structures were fully optimized and the calculated IR-spectra were compared with experimental data.

As can be seen from fig. 6 the polymeric products **1**, **3** and **4** have system of conjugated double bonds. It is therefore incorrect to consider only one monomeric unit for calculation of their IR-spectra. We have calculated the IR-spectra of model structures of polymers **1**, **3** and **4**, including up to six monomeric units. For polymer **1** (polycyanoacetylene), both *cis*- and *trans*-isomers have been considered. According to the results of our calculations, the *cis*-isomer is more stable, therefore only the calculated spectrum of this isomer is discussed below. Calculated IR-spectra for models **3** and **4** remain practically unchanged starting with tetramers. On the other hand, the structure of the polymer **1** becomes non-planar starting from hexamer. In addition, there is an intense peak at ~1000 cm^{-1} in the tetramer spectrum, corresponding to the deformation vibrations of terminal protons. It is obvious, that the

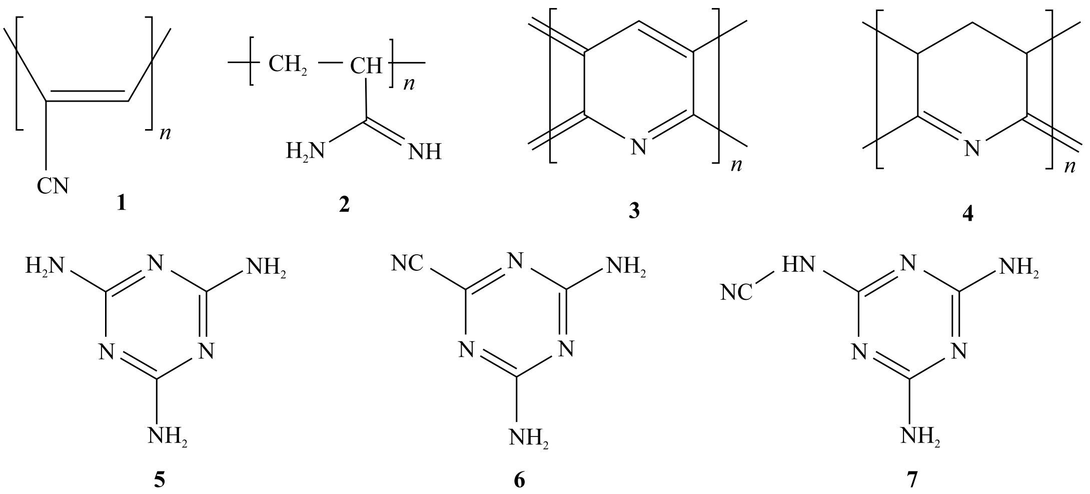


Fig. 6. Structural formulas of possible products of the poly-5-vinyltetrazole thermolysis

contribution of these protons to the IR-spectrum and, consequently, the relative intensity of this peak should decrease with the number of monomeric units, becoming negligible in an actual polymer. To verify this statement, we have calculated IR-spectra for models of *cis*-polycyanoacetylene comprising 8 to 16 monomeric units. Indeed, the relative intensity of the peak at ~1000 cm^{-1} decreases rapidly with the increasing number of monomer units in the model structure, while the position and relative intensity of the remaining peaks are practically unchanged. Therefore, the IR-spectra discussion below assumes tetramers for polymers **3** and **4**, and an octamer for the polymer **1**.

The optimized structures of possible poly-5-vinyltetrazole thermolysis products and their calculated vibrational frequencies are shown in fig. 7 and table 4, respectively.

The comparison of calculated and experimental frequencies revealed that the best agreement with the experimental data is observed for structure **1** (fig. 7), modeling *cis*-polycyanoacetylene. In fig. 8 the IR-spectrum

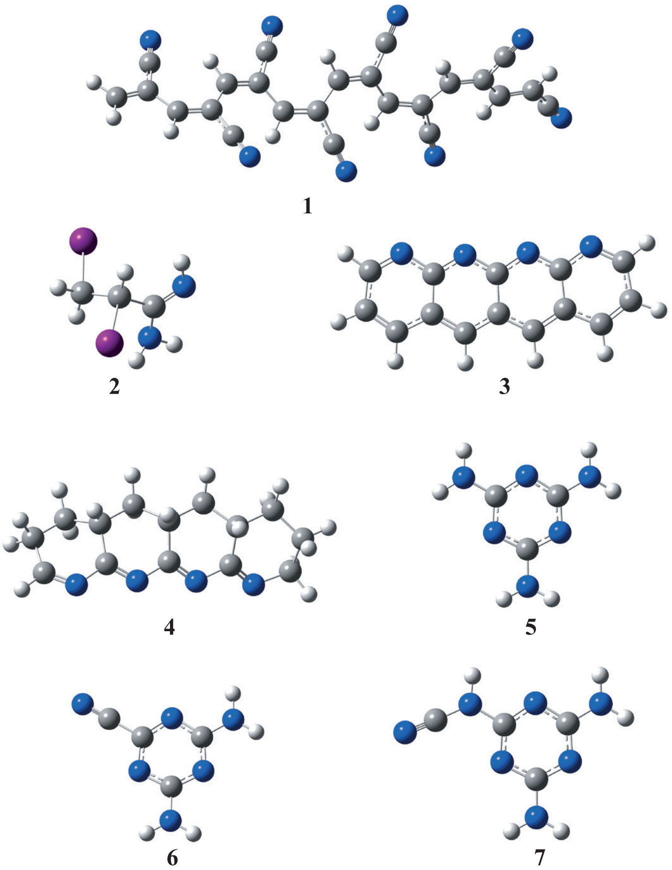


Fig. 7. B3LYP/6-311+G(d, p), Def2-TZVPD optimized model structures
of possible products of the poly-5-vinyltetrazole thermolysis

calculated for this structure is compared with the experimental one. If, as discussed above, we take into account that in *cis*-polycyanoacetylene the relative intensity of the peak at ~1000 cm^{-1} should be negligible, the wave numbers of all calculated peaks are in good agreement with the experimental data (see fig. 8, table 4).

Table 4

Comparison of the experimental vibrational frequencies of poly-5-vinyltetrazole thermolysis product with the corresponding values calculated for the structures suggested in fig. 7

Experimental vibrational frequencies, cm^{-1}	Calculated vibrational frequencies, cm^{-1}						
	1	2	3	4	5	6	7
631	640	634	–	–	–	–	–
807	810	824	789	–	829	834	828
880	916	906	933	–	–	963	–
1382	1390	1410	1216, 1453	1230, 1350	1465	1400, 1460	1386, 1465
1596	1596	1625	1554, 1627	1604	1602, 1625	1602, 1635	1586, 1644
2219, 2356	2332	–	–	–	–	–	2356
3215, 3371	3212	3515	3164, 3195	3060	3612	3615	3605, 3618

Thus, *cis*-polycyanoacetylene is unambiguously assigned as a component of the thermolysis product. It should be noted that the black color of the thermolysis product can be explained in this case by the presence of a large conjugated system of double bonds, which is present in *cis*-polycyanoacetylene. The calculated IR-spectra for polymeric structures **2** and **4** are in worse agreement with the experiment and the presence of these structures among the thermolysis products is unlikely. On the other hand, structure **3** may be among the thermolysis products, since the peaks of this structure could be hidden by the peaks of *cis*-polycyanoacetylene.

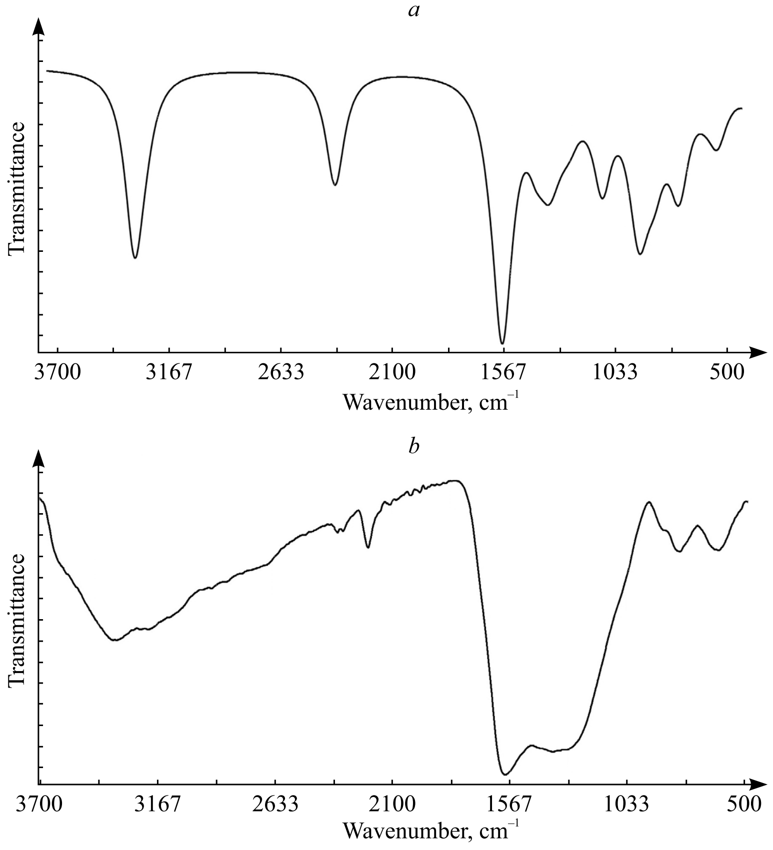


Fig. 8. Calculated IR-spectrum for structure **1** (see fig. 7) (*a*) and experimental IR-spectrum of the product of thermolysis of poly-5-vinyltetrazole (*b*)

Among possible low-molecular products, the best agreement with the experimental IR-spectrum is observed for structure **7**.

We can therefore conclude that the *cis*-polycyanoacetylene is the main product of thermolysis of poly-5-vinyltetrazole. However, structures **3** and **7** may also be present.

Conclusions

The structure of copper(II) poly-5-vinyltetrazolate as well as the products of its thermolysis have been studied by comparing the DFT calculated IR-spectra of model structures with experimental data. It has been shown, that for poly-5-vinyltetrazole the calculated frequencies are in good agreement with the experimental ones in the region below 1600 cm^{-1}. The possible ways of coordination of copper(II) ions with tetrazole ligands were established by analyzing the MESP distribution, which shows that the favorable interaction of initial polymer with copper(II) ions should pass through N(1)-, N(2)- or N(3)-atoms. Among various considered copper(II) poly-5-vinyltetrazolate model structures, the best agreement between the calculated and experimental spectra is observed for the model with three-coordinated copper which includes both tetrazole-containing ligands coordinating two copper(II) ions through N(1)- and N(3)-atoms of tetrazole ring and one copper(II) ion through N(2) or N(3).

Based on the analysis of the experimental IR-spectrum of the copper(II) poly-5-vinyltetrazolate thermolysis products and taking into account tendencies of bonds cleavage under thermolysis conditions, seven possible thermolysis products have been supposed. The calculations of IR-spectra of all supposed products have been carried out and the obtained results were compared with experimental data. The best agreement with the experiment was found in the case of structure **1** (see fig. 7), modeling polycyanoacetylene. Thus, we can conclude that the main thermolysis product of poly-5-vinyltetrazole is *cis*-polycyanoacetylene.

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Received by editorial board 13.10.2019.