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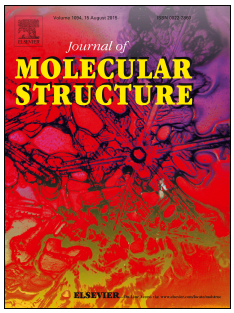

ATR-FTIR spectroscopic investigation of the *cis*- and *trans*-bis-(*α*-amino acids) copper(II) complexes

Tatyana V. Berestova, Lyudmila G. Kuzina, Natalya A. Amineva, Ilshat S. Faizrakhmanov, Ismail A. Massalimov, Akhat G. Mustafin

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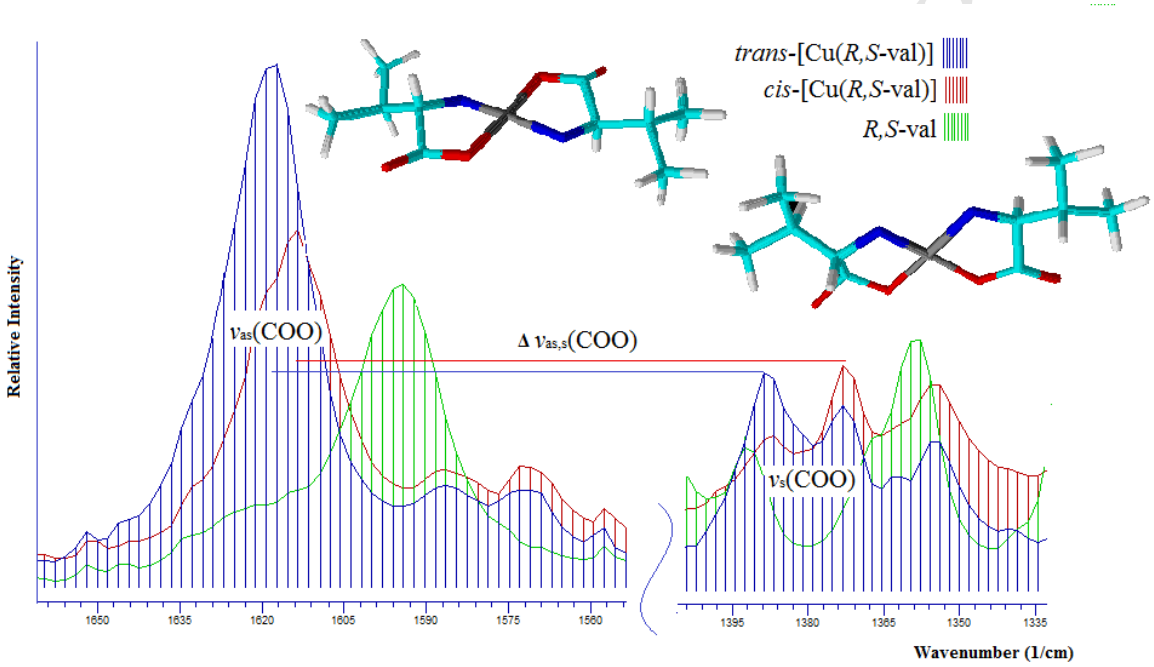
Graphical Abstract

The *cis*-isomers and *trans*-isomers bis-(*α*-amino acids) copper(II) complexes were studied by ATR-FTIR spectroscopy. It was established that asymmetric ν_{as}(COO) and symmetric ν_{s}(COO) stretching vibrations of carboxylic groups have different maxima for the *trans*- and *cis*-isomers. It found that ν_{as}(COO) and ν_{s}(COO) stretching vibrations of *cis*-isomers are shifted to longer wavelengths as compared with *trans*-isomers.



ATR-FTIR Spectroscopic Investigation of the *Cis*- and *Trans*-Bis-(*α*-Amino Acids) Copper(II) Complexes

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Abstract

The crystalline phases of the *trans*-(**a**) and *cis*-(**b**)-isomers of bis-(*α*-amino acids) copper(II) complexes $[Cu(^bL)_2]$ **1-5** (^bL - bidentate ligand: gly (**1**), *S*-ala (**2**), *R,S*-val (**3**), (±)-thr (**4**), *R,S*-phe (**5**)) were studied by ATR-FTIR spectroscopy in the mid region IR spectrum.

It was established that asymmetric ν_{as}(COO) and symmetric ν_s(COO) stretching vibrations of carboxylic groups of **1-5** are sensitive to change of the geometric structure and have a different maxima for the *trans*(**a**)- and *cis*(**b**)-isomers. It found that ν_{as}(COO) and ν_s(COO) stretching vibrations of *cis*-isomers are broadened and shifted to longer wavelengths (**b**) as compared with *trans*-isomers (**a**). Shown that peculiarities of crystal packing molecules of geometric isomers may affect on carboxylate stretching vibration bis-α-amino acids complexes copper(II) **1-5 a,b**.

Keywords: Bis-(*α*-Amino Acids) Copper(II) Complexes, C*is*-, *Trans*-isomers, Glycine, *S*-alanine, *R,S*-valine, (±)-Threonine, *R,S*-phenylalanine, ATR-FTIR-spectroscopy, XRD, Bond Distances.

1. Introduction

Synthesis and identification of individual isomers of biologically active compounds is one of the priority areas of pharmaceutical chemistry and fine chemical technology.

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It is known that nature of enzymes is strictly stereospecific and the amino acid and peptide complexes of Cu(II) may be regarded as simplified model systems for studying biochemical processes [1]. For example, amino acid chelate complexes of Cu(II) are active intermediates in metabolic and enzymatic processes of the body [2-4]. Their usage in the capacity of pharmaceuticals promotes rapid absorption of ions of biometals [5]. Also it is known that the chelates Cu(II) can exhibit antibacterial, anticancer and other bioactivity [6-8], which is dependent on the structure of ligands and the molecular design of the resulting compounds [9-10].

The structural isomers of *cis*- and *trans*-bis-glycinate copper(II) [11-12] are studied most of all. So, processes of *cis*-*trans*-isomerization of the bis-glycinate copper(II) were studied through experimental and theoretical methods [13-16]. Recently, much attention has been paid to their analogues [17]. Further, it was revealed that structural isomers of the bis-glycinate Cu(II) have different characteristic strectching vibrations in the mid-IR spectra in aqueous solutions [18]. This indicates their sufficient stability and probably different functional activity in biological systems. In particular, was shows that mixed and bis-*cis*-isomers copper(II) complexes can take part in the processes of the formation of biomolecules [19].

The previously published data include information about the identification of solid *cis*- and *trans*-isomers by IR characteristics of stretching vibrations of N-Cu, O-Cu as the most informative region [20-22]. Assuredly, the geometric isomers of amino acid complexes have differences in the IR spectra, but their identification in the field of "fingerprint" causes difficulties. Some aspects to identify the *cis*- and *trans*-isomers at characteristic frequencies in the medium area are described in [23], but these data are fragmented and need to be generalized.

In this work the characteristic stretching vibrations of *trans*-(**a**) and *cis*-(**b**) isomers of bis-α-amino acids copper(II) complexes [Cu(^{b}L)$_2$] **1-5** (^{b}L = gly(**1**), *S*-ala(**2**), *R*,*S*-val(**3**), (±)-thr(**4**), *R*,*S*-phe(**5**)) were studied by ATR-FTIR-spectroscopy in mid region IR spectrum.

2. Experimental

All reagents and chemicals were purchased from commercial sources (Avilon-companychem, Russia; Sigma Aldrich) and used as received without further purification. All used solutions were prepared by standard methods.

The FTIR spectra of the complexes **1-5** as compressed into thin plates, were recorded on FTIR-8400S spectrometer (Shimadzu) in the mid-infrared attenuated total reflectance (ATR) spectroscopy (HART Horizontal, PIKE, USA) (4000 – 850 cm^{-1}, 2 cm^{-1} resolution, 20 scans) at 25^{o}C. Frequency accuracy is estimated as ±1 cm^{-1}. The final spectra were baseline corrected and normalized.

The XRD patterns were recorded using DRON-4 diffractometer (CuK*a*: λ=1.5406 Å). For

simulating of molecular structure of compounds, the ACD/3D viewer 8.04 version program was used [24].

2.1. Method A. Synthesis of bis-*cis*-(amino acidato) copper(II) (1b) and bis-*trans*-(amino acidato) copper(II) (2-5a(a′)) [Cu(^{b}L)$_2$] (^{b}L = gly (1), *S*-ala (2), *R,S*-val (3), (±)-thr(4), *R,S*-phe (5)

The complexes were prepared according to the published method [25] in which in the 100 ml flask equipped with a magnetic stirrer a solution of amino acid (6.6 mmol) in distilled water (30 ml)was prepared. To a solution of amino acid an aqueous solution of $CuSO_4$ (0.82 g, 3.3 mmol $CuSO_4 \cdot 5H_2O$ in 15 ml) was added. The reaction mixture was stirred for 1 h at room temperature. Further, in the mixture $Ba(OH)_2$ water solution (3.3 mmol) was added. The reaction mixture was stirred for 1 h at room temperature. The resulting blue solution was twice filtered and dried over anhydrous $CaCl_2$. The blue powder of **1b** was obtained. The light blue-violet powder of **2-4a(a′)** and **5a+b** was obtained, including diastereomers **4a:4a′** in a ratio of 1:1. The received complexes were analyzed by ATR FTIR spectroscopy (br. broad; vs. very strong; s. strong; m. medium; w. weak).

Yield ***cis*-[Cu(gly)$_2$] (1b)**: 91%. ATR FTIR (powder, cm^{-1}): 3331w, 3289br (NH_2, ν_{as}); 3268m (NH_2, ν_s); 2925br, 2853br (CH, CH_3, $\nu_{as,s}$); 1605vs, 1593vs, 1580vs (COO, ν_{as}); 1576 – 1456w (NH_2, $\delta_{as,s}$); 1392s, 1404m (COO, ν_s).

Yield ***trans*-[Cu(*S*-ala)$_2$] (2a)**: 87%. ATR FTIR (powder, cm^{-1}): 3306m, (NH_2, ν_{as}); 3250m (NH_2, ν_s); 2983m, 2970m, 2935m, 2877m (CH, CH_3, $\nu_{as,s}$); 1620vs (COO, ν_{as}); 1576-1551w (NH_2, $\delta_{as,s}$); 1396s (COO, ν_s), 1356m (CH_3,δ_s).

Yield ***trans*-[Cu(*R,S*-val)$_2$] (3a)**: 87%. ATR FTIR (powder, cm^{-1}): 3300m (NH_2, ν_{as}); 3254br (NH_2, ν_s); 2962m, 2908m (CH, CH_3, $\nu_{as,s}$); 1618vs (COO, ν_{as}); 1587 – 1466w (NH_2, $\delta_{as,s}$); 1389s, 1373m (COO, ν_s), 1354m (CH_3, δ_s).

Yield ***trans*-[Cu((±)-thr)$_2$] (4a,a')**: 66%. Ratio **4a:4a′** ~ 1:1. ATR FTIR (powder, cm^{-1}): ***trans*-[Cu(*S*-thr)$_2$], [Cu(*R*-thr)$_2$] (4a)**: 3307m, 3294br (NH_2, ν_{as}); 3232br, 3208br (NH_2, ν_s); 2988br, 2982m, 2919br, 2851br (CH, CH_3, $\nu_{as,s}$); 1614vs (COO, ν_{as}); 1578-1444w (NH_2, $\delta_{as,s}$); 1395s (COO, ν_{as}), 1352m (CH_3, δ_s); ***trans*-[Cu(*R*-thr)(*S*-thr)], [Cu(*S*-thr)(*R*-thr)] (4a'):** 1612vs (COO, ν_{as}); 1383s (COO, ν_s).

Yield ***trans*-[Cu(*R,S*-phe)$_2$] (5a)**: 59%. ATR FTIR (powder, cm^{-1}): ***trans*-[Cu(*R,S*-phe)$_2$] (5a)** (major) 3342m (NH_2, ν_{as}); 3269m (NH_2, ν_s); 2921w, 2855 br (CH, $\nu_{as,s}$); 1651vs (COO, ν_{as}); 1588 – 1456w (NH_2, $\delta_{as,s}$); 1397 (COO, ν_s). ***cis*-[Cu(*R,S*-phe)$_2$] (5b)** (minor) 1647vs (COO, ν_{as}); 1388s (COO, ν_s).

2.2. Method B. Synthesis of bis-*cis*-amino acidato copper(II) 1-5b [Cu(^{b}L)$_2$] (^{b}L = gly (1), *S*-ala (2), *R,S*-val (3), (±)-thr(4), *R,S*-phe (5)

According to the published method [26] in the 100 ml flask equipped with a magnetic stirrer solution of amino acid (6.6 mmol) in distilled water (20 ml) was prepared. To an aqueous solution of amino acid 1M solution NaOH (6.6 mmol) was added. An aqueous solution of $CuSO_4$ (0.82 g, 3.3 mmol $CuSO_4 \cdot 5H_2O$ in 10 ml) to protonated amino acid was added. The reaction mixture was stirred for 2 days at room temperature and violet powder of **2-4b** and light violet powder of **5b** were formed. The received complexes were analyzed by ATR FTIR-spectroscopy.

Yield ***cis*-[Cu(gly)$_2$] (1b)**: 75%.

Yield ***cis*-[Cu(*S*-ala)$_2$] (2b)**: 71%. ATR FTIR (powder, cm^{-1}):, 3309m, (NH_2, ν_{as}); 3267m (NH_2, ν_s); 2983br, 2970br, 2935br, 2877br (CH, CH_3, $\nu_{as,s}$); 1616vs (COO, ν_{as}); 1385s (COO, ν_s), 1354m (CH_3, δ_s).

Yield ***cis*-[Cu(*R,S*-val)$_2$] (3b)**: 87%. ATR FTIR (powder, cm^{-1}): 3304m (NH_2, ν_{as}); 3240m (NH_2, ν_s); 2962br, 2908br (CH, CH_3, $\nu_{as,s}$); 1615vs (COO, ν_{as}); 1587 – 1466w (NH_2, $\delta_{as,s}$); 1387m, 1373s (COO, ν_s), 1356m (CH_3, δ_s).

Yield ***cis*-[Cu((±)-thr)$_2$] (4b,b′)**: 66%. Ratio **4b:4b′** ~ 1:1. ATR FTIR (powder, cm^{-1}):

***cis*-[Cu(*S*-thr)$_2$], [Cu(*R*-thr)$_2$] (4b)**: 3354-3224br, (NH_2, ν_{as}, ν_s); 2988-2851br (CH, CH_3, $\nu_{as,s}$); 1610vs (COO, ν_{as}); 1576-1505w (NH_2, $\delta_{as,s}$); 1373s (COO, ν_{as}); ***cis*-[Cu(*R*-thr)(*S*-thr)], [Cu(*S*-thr)(*R*-thr)] (4b′):** 1610vs (COO, ν_{as}); 1368s (COO, ν_s).

Yield ***cis*-[Cu(*R,S*-phe)$_2$] (5b)**: 46%.

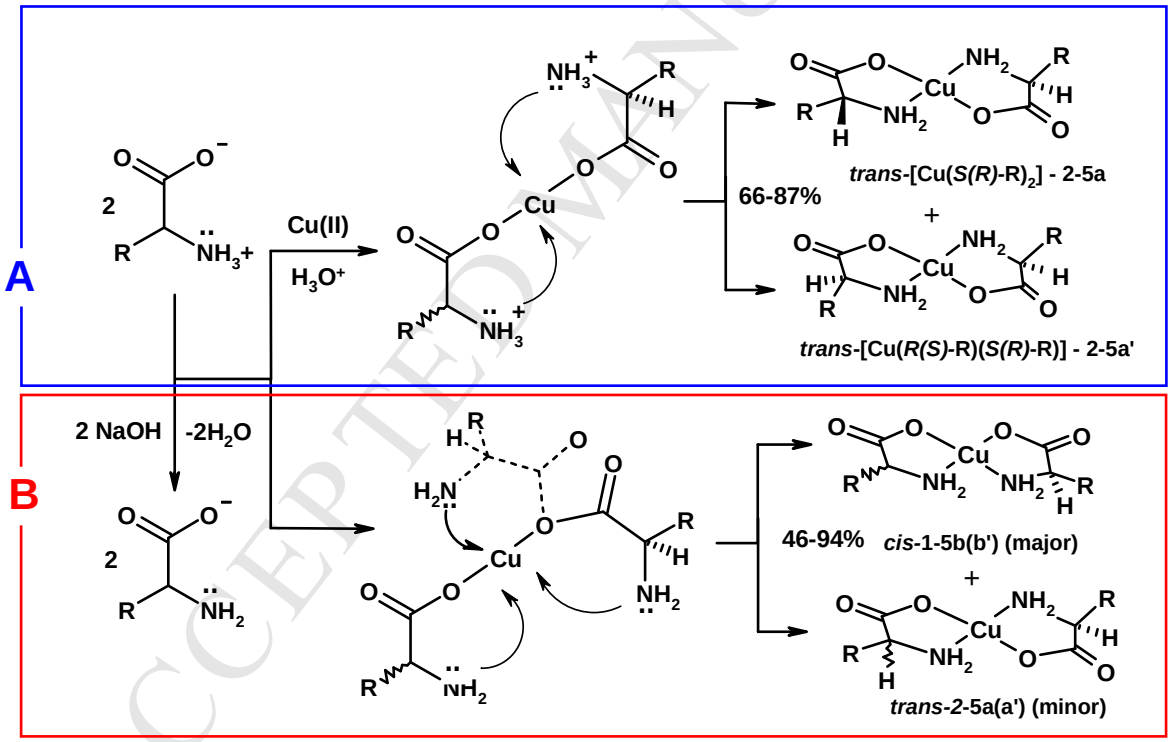
3. Results and discussion

3.1. Synthesis and characterization of the geometric isomers 1-5a(a′),b(b′)

Vibrational criteria for *cis*- and *trans*-bis amino acid complexes of Cu(II) **1-5**, which were prepared by two methods [25, 26] (Scheme 1, Table 1) were studied by ATR-FTIR-spectroscopy.

Predominantly *trans*-isomers (**2-4a(a')**) (Scheme 1, **A**) were obtained by procedure **A**.

Scheme 1



Sometimes impurity of *cis*-isomers (**2-4b(b')**) up to 20% in IR spectra **2-4a(a′)** were observed. But *cis*-isomers were poorly soluble in water and after recrystallization almost pure *trans*-isomers (**2-4a(a')**) were obtained. Regardless of method of synthesis of bis-glycinate complexes Cu(II) (**1b**) was obtained only as *cis*-isomers, that is consistent with the literature data

[27]. Apparently, this is due to the peculiarities of crystal packing effects of the *cis*-isomer [11,15].

Following the procedure of **B** complexes **1-5** were obtained as a mixture of *cis*- and *trans*-isomers (Scheme 1, **B**), but *cis*-isomers **1,3,5b** are predominant. According to this procedure, to solution of amino acid in deprotonated form a solution of $CuSO_4$ was added. During the reaction the suspensions of the complexes **1-3,5b** were obtained.

Apparently, in most cases the acidity of an aqueous solution (pH<7) promotes the formation of *trans*-isomers of **2-4a**(**a´**) because protonated form of amino groups may push away. But in neutral solution predominantly *cis*-isomers are formed although it is theoretically possible formation of two isomers (Scheme 1, **B**). In addition, contribution to the formation of a particular isomer will make substituent (R) of amino acids NH_3^+-CH(R)-COO^-, which is able to influence geometric structure of the complex due to additional interactions of functional groups with the metal.

Initially, from solutions hydrated complexes **1-5a,b** were isolated, evidenced by the presence of absorption bands $\delta(H_2O)$ in the IR spectra of the obtained compounds [28]. For example, $\delta(H_2O)$ were found in the region 1647 cm^{-1} for *trans*-[Cu(*R,S*-val)$_2$]$\cdot 2H_2O$ and *cis*-[Cu(*R,S*-val)$_2$]$\cdot H_2O$, but it didn't effect the shift of the maxima of the absorption bands of **1-5a(a'),b(b')** (table 1). After drying of **1-5a(a'),b(b')** in the desiccators, the deformation vibrations of water $\delta(H_2O)$ are invisible in the infrared spectrum and are not detected in stretching vibrations for hydroxyl group ν(OH) 3400 cm^{-1}.

3.2. FTIR-spectral analysis and identification of structural isomers 1-5a(a'),b(b')

Structural isomers of **1-5a(a'),b(b')** were identified on the basis of experimental data of IR, XRD [29] and an analysis of published data [11, 23, 26, 30-35] (Table 1).

The most informative absorption bands for identification of *cis*- and *trans*-isomers of **2-3a,b** in the IR spectra are in the range 3146-3384 cm^{-1} and correspond to the asymmetrical and symmetrical stretching vibrations $\nu_{as}(NH_2)$ and $\nu_s(NH_2)$ (Table 1). These stretching vibrations allow to define the coordination of amino group to ion of Cu(II). However, unambiguous criteria for the identification of isomers in this area are not detected but for just visible minor broadening and splitting of the absorption bands for the *cis*-isomers.

In addition, in accordance with the literature data, the characteristic stretching vibrations of carboxylate ion ν(COO) for complexes **1-5a,b** corresponds to the frequency range 1580-1651 cm^{-1} for asymmetric ν_{as}(COO) and 1373-1404 cm^{-1} symmetric stretching vibrations ν_s(COO) (Table 1). It was found that the absorption bands of the complexes **1-5a,b** are shifted to shorter region compared with the original α-amino acids (Fig. 1) and corresponds to the literature [22, 26, 28, 30-35].

We have found that stretching vibrations ν_{as}(COO) differ in intensity of peaks for *trans*-(**2-5a**(**a'**)) and *cis*-isomers (**2-5b**(**b'**)). So, the maxima of the absorption bands for **2-5a**(**a'**) are fixed at shorter waves (Fig. 1, Table 1). For complexes **2-5b**(**b'**) low intensity of peaks and a slight shift of the maxima to longer wavelengths of region relative to the *trans*-isomer are characteristic.

The symmetric stretching vibrations of carboxylate ion ν_s(COO) were more sensitive to lateral interactions chelate compounds [36-37], that influence their intensity and the shift of the absorption bands in the region 1373-1394 cm^{-1} with respect to the original amino acid. For example, in the IR spectra of *trans*-isomer **3a** observed intense absorption band in the region 1389(vs) band and in the infrared spectra of a mixture of **3a**+**3b** isomer with predominance **3b** *cis*-isomer observed two absorption 1387(m) 1373(s) band cm^{-1}, and the second one 1373 cm^{-1} was more intense than the first (Fig. 1).

Such differences in the IR spectra allow to identify geometric isomers **3a,b** by the characteristic value $\Delta\nu_{as,s}$(COO) [38], which has a greater value for *cis*- isomer **3b** as compared to *trans*-isomer **3a**. So, for *cis*-isomer (**3b)** $\Delta\nu_{as,s}$(COO) of 242 cm^{-1} and *trans*-isomer (**3a)** of 229 cm^{-1} (Table 1).

3.3. Identification of structural isomers 1-5a(a'),b(b') by XDR

IR data for geometric isomers of **1-5** were confirmed by XDR. For example, in the mixture of geometric isomers **3a+3b** *cis*- and *trans*-isomers were identified in a ratio of 5:1 by XRD method and comply for literature data [29] (Fig. 2).

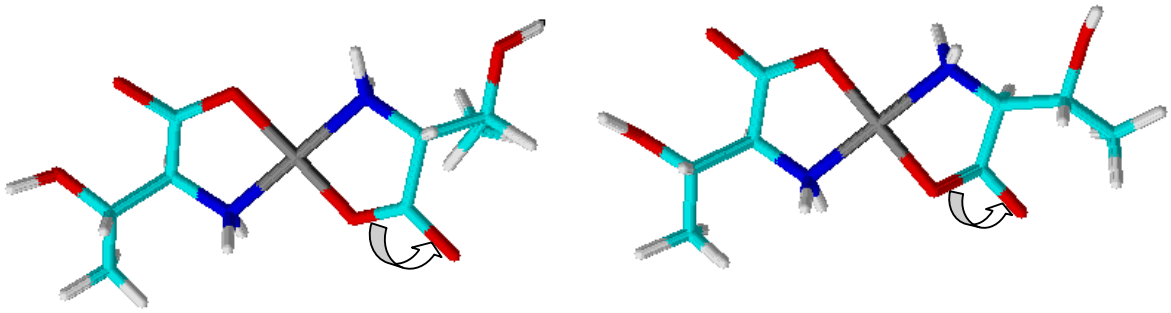
An additional criterion for classifying geometric isomers in medium IR spectra are X-rays of the complexes **3a,b** [25, 39-40]. Thus, for *cis*-isomer **3b** voltage carboxylate moiety will be much greater compared to the *trans*-isomer **3a**. For example, in crystalline samples of *cis*-isomer **3b** the bond C=O is smaller, but *O-C*O bond is longer compared to the similar bonds of *trans*-isomer **3a** [39-40] (Table 2), allowing to make the assumption about the tendency of the "twist" on carboxylate ion of the *cis*-isomer **3b** as compared to the *trans*-isomer **3a**. Apparently, this is due to the peculiarities of crystal packing of geometrical isomers in accordance with the

type of crystal lattice monoclinic ($P2_1$) for *trans*-isomer [41] и orthorhombic ($P2_12_12_1$) for *cis*-isomer [42]). A similar trend changes in bond lengths is observed for geometrical isomers **1-2a,b** [11, 43-44] (Table 2) and other chelate complexes of Cu(II) [45] and amino acid Pt(II) complex [46-47].

3.4. Identification of diastereomers 4a(a'),b(b')

The diastereomers of bis-complexes of Cu(II), containing in their composition fragments (±)-threonine (**4aa'**) were obtained as *trans*-isomer (>90%), consistent with the literature data [48]. The broadening of the band of the asymmetric stretching vibration ν_{as}(COO) as compared to the original amino acid and splitting lanes symmetric stretching vibrations carboxy ν_s(COO) in the IR spectra of **4** leads to the assumption about formation of diastereomeric pairs **4aa'** complexes at a ratio of ~ 1:1. [25]. In this case, $\Delta\nu_{as,s}$(COO) for **4a** was 219 cm^{-1} and for **4a'** 225 cm^{-1} (Table 1). Such value ν_s(COO) in amino acid complexes that do not contain a composition of compounds with two chiral centers is not detected.

Tentative assignment of diastereomers **4aa'** is also based on the phenomenon of a "tightening" of the carboxyl group to the rest of the molecule. Apparently, this trend will continue in the case of diastereomers, because one of them has more hindered geometry relatively to the other one.



***trans*-[Cu(*S*-thr)$_2$] - 4a;** **1:1** ***trans*-[Cu(*S*-thr)(*R*-thr)] - 4a';**

***trans*-[Cu(*R*-thr)$_2$] - 4a** ***trans*-[Cu(*R*-thr)(*S*-thr)] - 4a'**

Since the *R,S*-isomer (**4a**) has a constrained geometry because of the mutual influence of $CH(CH_3)OH$ groups, the conjugate structure will be created in this isomer. This apparently results in the shift of the absorption band maximum ν_s(COO) in a short wave region [37] , which is manifested in the IR spectrum as cleavage of the absorption bands 1395 and 1387 cm^{-1} for *trans*-(**4a**) and 1381 and 1373 for *cis*-isomers (**4b**).

4. Conclusion

Thus, by method of ATR-FTIR characteristic symmetric ν_{as}(COO) and symmetric ν_{s}(COO) stretching vibrations of carboxylic group of *cis*- and *trans*-isomers of amino acid complexes **1-5a(a'), b(b')** were studied.

Established, that ν_{as}(COO) and ν_{s}(COO) stretching vibrations of carboxylic groups of **1-5** have a different maxima for the *trans*(**a**)- and *cis*(**b**)-isomers. In particular, asymmetric stretching vibrations ν_{as}(COO) are different for *trans*-**3a** (1618vs) and *cis*-isomers **3b** (1615vs). The symmetric stretching vibrations ν_{s}(COO) are at 1389s for *trans*-(**3a**) and 1387m, 1373s for *cis*-isomers (**3b**). So, differences in the IR spectra of geometric isomers **3a,b** allow identify them by value $\Delta\nu_{as,s}$(COO), which for *cis*-isomer **3b** (242 cm^{-1}) has a greater value as compared to *trans*-isomer **3a** (229 cm^{-1}). In case formation of diastereomers **4a**(**a´**) two shoulders at 1395 and 1387 cm^{-1} in ratio of 1:1 were observed for ν_{s}(COO).

Shown that in crystalline *cis*-isomer **3b** the bond length *C=O* is smaller, but *O-C*O bond is longer compared to the similar bonds of *trans*-isomer **3a**. Apparently, this fact may be due to the influence of crystal packing of geometrical isomers. According to the literature [43-47], a similar changes in bond length of carboxylic group is observed for *trans*- and *cis*-isomers **1-2a,b** and other chelate complexes of Cu(II) and Pt(II).

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Table1

Important Characteristic ATR-FTIR data (cm^{-1}) of the α-amino acids and bis-*cis*- and *trans*-complexes of Cu(II) 1-5a(a'),b(b')

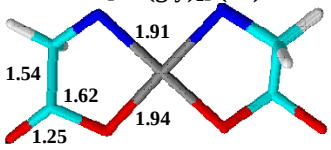
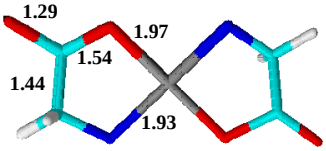
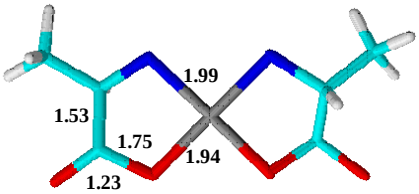
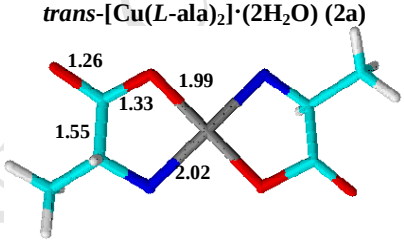
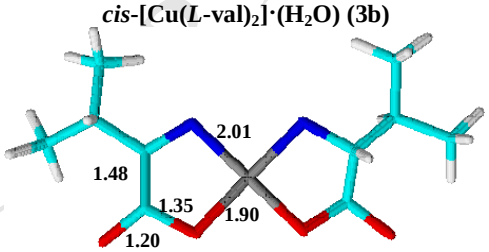
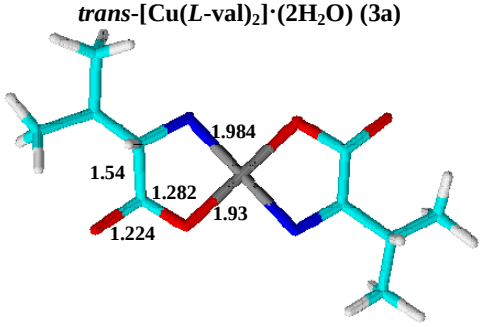
Compound	Color	Yield, %	Characteristic IR spectra						Ref
			ν(COO)		$\Delta\nu_{as,s}$ (COO)	δ (H_2O)	ν(NH_3, NH_2)		
			as	*s*			*as*	*s*	
Glycine (glyH)			1595, 1608vs	1412s	190		3163		
			1593vs	1410s	183		3078		
S-alanine (*S*-alaH)			1590vs	1412s	178				30
			1588vs	1409s	179				31
			1595vs	1416s	179		3133		
R,*S*-valine (*R*,*S*-valH)			1570vs	1362s	208		3114, 3215		32
			1626vs	1417s	209		3030, 3173		
(±)-threonine ((±)-thrH)			1626vs	1418s	210		3026, 3169	2978, 2998	34
			1587vs	1414s	173		3033, 3065		
R,*S*-phenylalanine (*R*,*S*-pheH)			1581vs	1411s	170		3012, 3076		35
cis-[Cu(gly)$_2$] **(1b)**	blue	75-91	1580, 1593, 1605vs	1404s, 1392m	201		3331, 3289	3268	
cis-[Cu(gly)$_2$]·H_2O			1580vs	1390s	202		3335, 3265		23
			1580, 1594, 1606vs	1403s,1389m	198	1676m	3333, 3262	3162	28
trans-[Cu(gly)$_2$]·2H_2O			1589, 1609vs	1389s	210		3315, 3244	3176	28
trans-[Cu(*S*-ala)$_2$] (**2a**)	blue	87	1620vs	1396s	224	-	3306	3250	
cis-[Cu(*S*-ala)$_2$] (**2b**)	violet	71	1616vs	1385s	231	-	3309	3267	
trans-[Cu(*S*-ala)$_2$]			1620vs	1400s, 1394m	222		3293, 3245		23
			1619vs	1400s	219		-		28
cis-[Cu(*S*-ala)$_2$]		55	1624vs	-	-		-	-	28
trans-[Cu(*R*,*S*-val)$_2$] (**3a**)	blue	87	1618vs	1389s, 1373m	**229**, 245	-	3300	3254	
cis-[Cu(*R*,*S*-val)$_2$] (**3b**)	violet	54	1615vs	1387m, 1373s	228, **242**	-	3304	3240	
trans-[Cu(*R*,*S*-val)$_2$]·2H_2O (**3a**·2H_2O)	light blue	98	1618vs	1389s, 1373m	**229**, 245	1651m	3300	3254	
cis-[Cu(*R*,*S*-val)$_2$]·H_2O (**3b**·H_2O)	light violet	58	1614vs	1387m, 1373s	227, **241**	1649m	3301	3255	
trans-[Cu(*S*-val)$_2$]			1584vs	1390s	225		3300, 3272		23
trans-[Cu(*R*,*S*-val)$_2$]			1623, 1595vs	-	-		3291, 3158		26
cis-[Cu(*R*,*S*-val)$_2$]		75	1627, 1585vs	-	-		3284, 3159		26
trans-[Cu(*S*-thr)$_2$]; [Cu(*R*-thr)$_2$] **(4a)**			1614vs	1395m	219				
trans-[Cu(*R*-thr)(*S*-thr)]; [Cu(*S*-thr)(*R*-thr)]**(4a´)**	bright	51-66	1612vs	1387m	225		3307, 3294	3208, 3232	
cis-[Cu(*S*-thr)$_2$], [Cu(*R*-thr)$_2$] **(4b)**	blue-violet		1610vs	1381m	229		3307, 3294	3208, 3232	
cis-[Cu(*R*-thr)(*S*-thr)], [Cu(*S*-thr)(*R*-thr)]**(4b′)**				1373m	237				
trans-+ *cis*-[Cu(*R*,*S*-phe)$_2$] (**5a+5b**)	light violet	59	1651, 1647vs	1397s, 1388s	254, 259		3342	3269	
cis-[Cu(*R*,*S*-phe)$_2$] (**5b**)	light violet	46	1647vs	1388	259		3342	3269	
trans-[Cu(*R*,*S*-phe)$_2$]			1625vs	1398, 1393	223		3315, 3235		23

trans- + *cis*-[Cu(*R*,*S*-(phe)$_2$]·H$_2$O	1627vs 1614s	1377s ~1377s	250 ~237	3320, 3254, 3146	35

[a] *R(S)* – The absolute configuration of asymmetric carbon atom at the COO- and NH_2-groups

Table 2

X-ray Crystal Bond Distances (Å) and Valence Angles (deg) of **1-3a,b**

	***cis*-[Cu(gly)$_2$] (1b)**	***trans*-[Cu(gly)$_2$] (1a)**
Bond Distances		
C=O	1.09(7)/1.40(5) [11]	1.29(2) [11]
***O*-*C*O**	1.62(7) [11]	1.54(3) [11]
***C*(H)-*C*O**	1.36(8)/1.71(7) [11]	1.44(3) [11]
Cu-O	1.83(4)/1.95(4) [11]	1.97(2) [11]
Cu-N	1.94(3)/1.94(3) [11]	1.93(2) [11]
	***cis*-[Cu(*L*-ala)$_2$] (2b)**	***trans*-[Cu(*L*-ala)$_2$]·(2H$_2$O) (2a)**
		
C=O	1.239(2)/1.227(2) [43]	1.25/1.28 [44]
***O*-*C*O**	1.275(2)/1.275(2) [43]	1.29/1.37 [44]
***C*(H)-*C*O**	1.534(2)/1.538(2) [43]	1.55/1.56 [44]
Cu-O	1.947(2)/1.937(2) [43]	1.97/1.95 [44]
Cu-N	1.990(2)/1.993(2) [43]	2.01/2.02 [44]
Valence Angles		
O*-*C*-*O		122/116 [44]
***O*-*C*-*C*(H)**		116/119 [44]
	***cis*-[Cu(*L*-val)$_2$]·(H$_2$O) (3b)**	***trans*-[Cu(*L*-val)$_2$]·(2H$_2$O) (3a)**
		
C=O	1.20(3)/1.25(4) [39]	1.224/1.250 [40]
***O*-*C*O**	1.35(4)/1.36(3) [39]	1.282/1.292 [40]
***C*(H)-*C*O**	1.48(4)/1.54(4) [39]	1.540/1.552 [40]
Cu-O	1.90(2)/1.90(2) [39]	1.93/1.948 [40]
Cu-N	2.010(2)/2.030(2) [39]	1.984/2.010 [40]
Valence Angles		

O*-*C*-*O	122(1)/122(1) [39]	122.9/124.6 [40]
***O*-*C*-*C*(H)**	117(1)/119(1) [39]	120.8/121.5 [40]

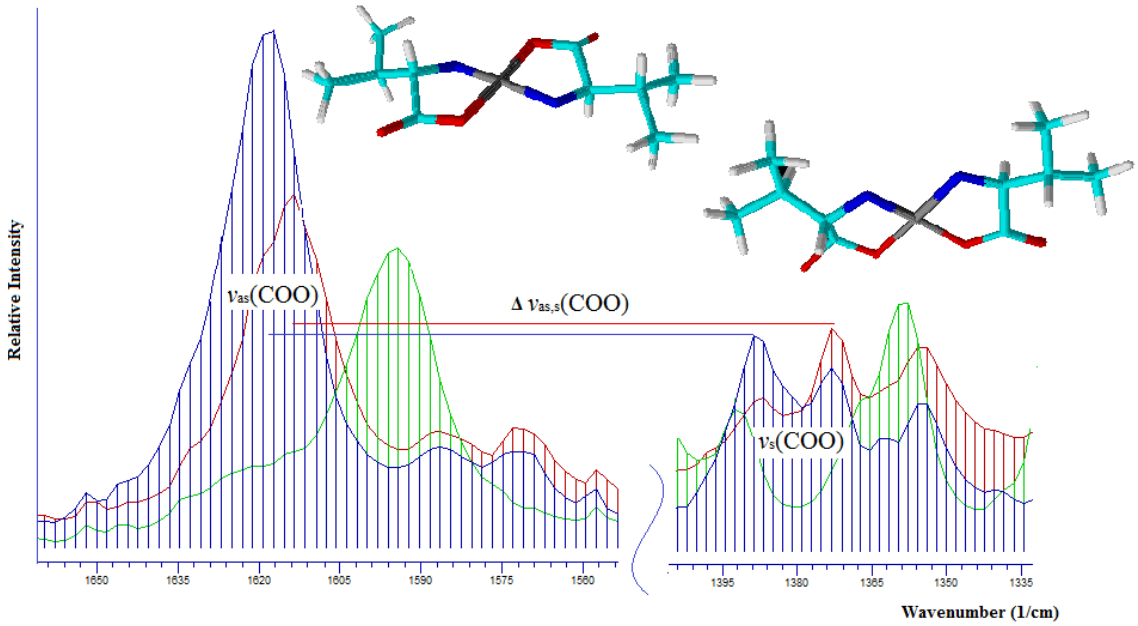


Fig. 1. Fragments of the FTIR spectrum of *trans*-isomers bis-[Cu(*R*,*S*-val)$_2$] (**3a**), *cis*- -isomers bis-[Cu(*R*,*S*-val)$_2$] (**3b**) and *R*,*S*-valH

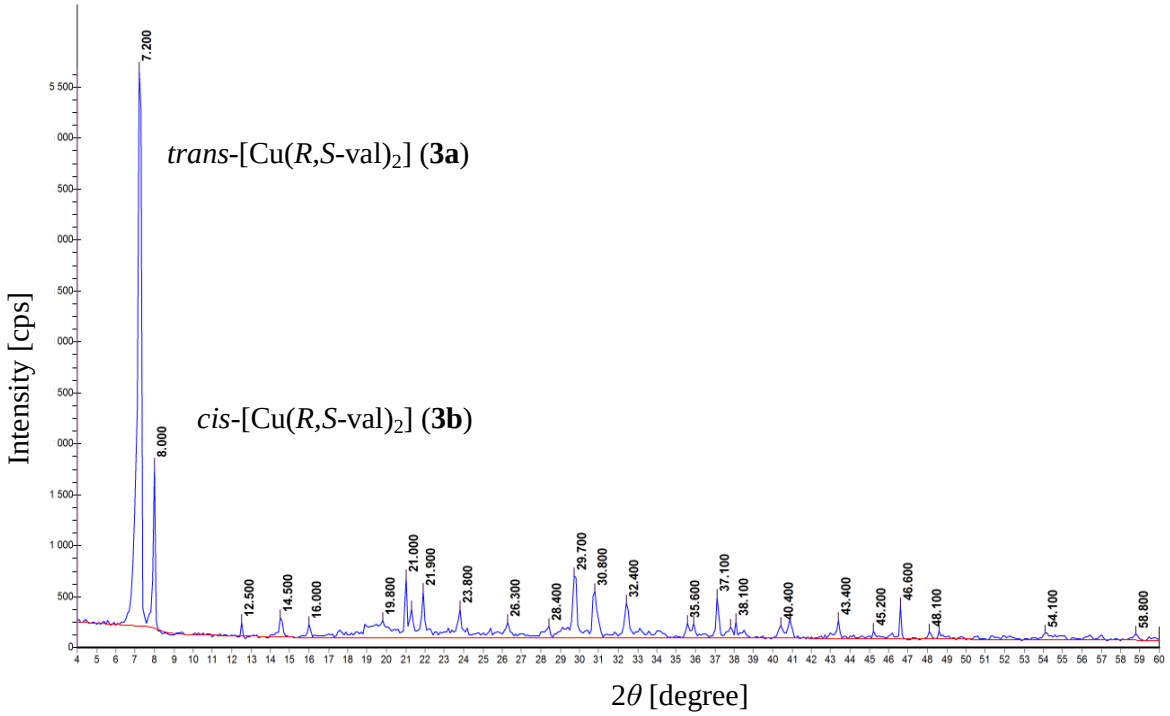


Fig. 2. Powder XRD patterns of *trans*-[Cu(*R*,*S*-val)$_2$] (**3a**) (major) + *cis*-[Cu(*R*,*S*-val)$_2$] (**3b**) (minor)