The FT-IR, FT-Raman, ^1H and ^{13}C NMR study on molecular structure of sodium(I), calcium(II), lanthanum(III) and thorium(IV) cinnamates

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Abstract. In this work the effect of sodium(I), calcium(II), lanthanum(III) and thorium(IV) ions on the electronic structure of cinnamic acid (phenylacrylic acid) was studied. In this research: infrared (FT-IR), Raman (FT-Raman), nuclear magnetic resonance (^1H , ^{13}C NMR) were used. In the series of $\text{Na(I)} \rightarrow \text{Ca(II)} \rightarrow \text{La(III)} \rightarrow \text{Th(IV)}$ cinnamates: (1) systematic shifts of several bands in the FT-IR and FT-Raman spectra, and (2) regular chemical shifts of protons ^1H and ^{13}C nuclei were observed.

Keywords: Sodium, calcium, lanthanum and thorium cinnamates, FT-IR, FT-Raman, NMR

1. Introduction

In this work we studied the effect of $\text{Na(I)} \rightarrow \text{Ca(II)} \rightarrow \text{La(III)} \rightarrow \text{Th(IV)}$ cations on the electronic system of cinnamic acid by means of many complementary methods: infrared (FT-IR), Raman (FT-Raman), nuclear magnetic resonance (^1H , ^{13}C NMR). In the chosen series of metals the oxidation state changes whereas the ionic radius remains almost the same. Previously we studied the effect of $\text{Li} \rightarrow \text{Na} \rightarrow \text{K} \rightarrow \text{Rb} \rightarrow \text{Cs}$ on the molecular structure of cinnamic acid (in this series of metals the oxidation state is the same, but the ionic radius increases) [4]. Application different and specially selected metal ions allows to study the spectroscopic properties of complexes depending on the metal parameters. The participation of double bond in cinnamic acid molecule on the influence of metals on the electronic system of ligand was discussed as well.

2. Experimental

The preparation of metal complexes was described previously [4–6]. The elementary and thermogravimetric analyses showed that obtained complexes were anhydrous, the metal:ligand ratio was 1:1 in case of Na cinnamate, 1:2 in case of Ca cinnamate, 1:3 – La complex and 1:4 – Th complex. The IR spectra

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were recorded with the EQUINOX 55, BRUKER FT-IR spectrometer within the range 4000–400 cm^{-1} . Samples in the solid state were measured: (1) in KBr matrix and (2) by the use of ATR technique. Pellets were obtained with a hydraulic press under 739 MPa pressure. Raman spectra of solid samples in capillary tubes were recorded in the range of 4000–400 cm^{-1} with a FT-Raman accessory of the Perkin Elmer System 2000. The resolution of spectrometer was 1 cm^{-1} . The NMR spectra of DMSO solution were recorded with the Bruker Avance II 400 MHz unit at room temperature. TMS was used as an internal reference

3. Results and discussion

In Table 1 wavenumbers of selected bands from the FT-IR, FT-Raman spectra of Na(I), Ca(II), La(III) and Th(IV) cinnamates were collected. The spectral assignments were done on the basis of the literature data [3,4,8]. The change of metal cation in the carboxylic group of cinnamic acid did not evoke serious changes in the wavenumbers of bands from the IR and Raman spectra of cinnamates. Only bands: $\gamma(\text{CCH})_{\text{C}=\text{C}}$ ($\sim 980 \text{ cm}^{-1}$), $\alpha(\text{C}=\text{C}-\text{C})_{\text{C}=\text{C}}$ ($\sim 540 \text{ cm}^{-1}$), band no. 4 and bands assigned to carboxylate anion vibrations undergo distinct displacements along the metal series of $\text{Na} \rightarrow \text{Ca} \rightarrow \text{La} \rightarrow \text{Th}$. The regular displacement of bands suggests that the influence of metal ions on the electronic charge distribution in the ligand depends on selected metal parameters. In this study the analysis for linear correlation between selected metal ions parameters (ionic potential, ionic radius, reverse of atomic mass) and wavenumbers of bands from FT-IR and FT-Raman spectra was done. Among studied parameters the highest correlation coefficients were in most cases obtained for ionic radii of metal ions. The difference between wavenumbers of bands from FT-IR spectra assigned to asymmetric and symmetric stretching vibrations of carboxylate anion [$\Delta\nu(\text{COO}^-)$] reveals the type of metal coordination [1,2]. The values of $\Delta\nu(\text{COO}^-)$ were following: 136 cm^{-1} for sodium cinnamate, 125 and 104 cm^{-1} for calcium complex, 125 and 106 cm^{-1} for lanthanum complex, 133 and 102 cm^{-1} for thorium cinnamate. Comparing the values of $\Delta\nu(\text{COO}^-)$ and the location of $\nu_{\text{as}}(\text{COO}^-)$ and $\nu_{\text{s}}(\text{COO}^-)$ in the FT-IR of complexes the following type of coordination was suggested: bidentate chelating, bidentate bridging or tridentate bridging–chelating. The metal complex formation caused the biggest changes in the FT-IR and FT-Raman spectra in the region of carboxylic anion and double bond vibrations.

The location of selected bands from the FT-IR and FT-Raman spectra of cinnamic and benzoic acids [7] as well as Na, Ca, La, Th cinnamates and benzoates [5,6] were compared. More significant changes in the displacement of appropriate bands from the spectra of acid and complexes were visible after the substitution of metal in the carboxylic group of benzoic acid than cinnamic acid. In the spectra of $\text{Na(I)} \rightarrow \text{Ca(II)} \rightarrow \text{La(III)} \rightarrow \text{Th(IV)}$ complexes bigger differences were observed in the spectra of benzoates than cinnamates.

In the ^1H NMR spectra of cinnamates all signals were shifted downfield compared with signals from the spectra of acid (Table 2). The biggest differences in the location of appropriate signals were noticeable between the spectra of sodium cinnamate and the rest of studied cinnamates. This may be caused by different type of bonding, i.e. ionic in the case of sodium salt and covalent in the structure of calcium, lanthanum and thorium cinnamates. The ^{13}C NMR spectra of studied compounds showed an increased in the electronic charge density around the carbon atom no. 9 and a decrease around the carbon atoms nos 7 and 8 in the structure of cinnamates compared with the structure of acid (Fig. 1). In the series of $\text{Ca(II)} \rightarrow \text{La(III)} \rightarrow \text{Th(IV)}$ complexes an increase in the values of chemical shifts assigned to carbon atoms nos 2, 4, 6, 9 and a decrease in the values of chemical shifts derived from the carbon atoms nos 1, 3, 5 and 8 were observed.

Table 1
Wavenumbers, intensities and assignments of bands occurring in the FT-IR

Sodium(I) cinnamate		Calcium(II) cinnamate				Lanthanum(III) cinnamate				Thorium(IV) cinnamate				Assignments		Aromatic ring vibrations					
IR KBr		IR KBr		IR ATR _{solid}		Raman		IR KBr		IR ATR _{solid}		Raman		IR KBr		IR ATR _{solid}		Raman			
1640	m*	1641	s	1641	m	1645	vs	1640	s	1640	m	1642	vs	1638	s	1638	w	1640	vs	$\nu(\text{C}=\text{C})_{-\text{C}=\text{C}-}$	
1599	vw					1602	s					1602	s					1602	s	$\nu(\text{CC})_{\text{ar}}^{**}$	8a
1577	m	1579	s			1580	vw	1578	s	1578	w	1580	vw	1578	m			1579	w	$\nu(\text{CC})_{\text{ar}}$	8b
1548	vs	1545	s					1531	s	1532	m			1545	sh	1506	m			$\nu_{\text{as}}(\text{COO}^-)$	
		1524	sh	1520	s			1516	s	1516	m			1514	s						
1495	m	1496	m					1497	s	1495	m			1497	s					$\nu(\text{CC})_{\text{ar}}$	19a
1451	m	1452	s	1450	m	1458	w	1450	s	1450	m	1456	vw	1450	s	1450	w	1461	w	$\nu(\text{CC})_{\text{ar}}$	19b
1412	s	1420	vs	1410	vs	1419	vw	1410	vs	1408	vs			1412	vs	1406	vs			$\nu_{\text{s}}(\text{COO}^-)$	
1392	m											1398	vw					1401	w	$\beta(\text{CH})_{\text{ar}}$	3
1244	w	1252	m	1250	w	1255	m	1250	m	1250	w	1253	m	1250	m			1253	m	$\beta(\text{CH})_{-\text{C}=\text{C}-}$	
970	m	977	m	978	m			980	m	978	w			980	w	984	w			$\gamma(\text{CCH})_{-\text{C}=\text{C}-}$	
852	vw	852	vw	850	vw	852	vw	851	w			851	vw	853	w	841	vw	852	vw	$\beta_{\text{s}}(\text{COO}^-)$	
728	m	737	w					737	m	739	w			745	w	741	vw			$\varphi(\text{CCC})$	4
713	w	717	w	718	m			718	m	714	w			716	w	716	w	717	vw	$\gamma_{\text{s}}(\text{COO}^-)$	
586	w	590	w	590	m			588	m	590	m			590	m	590	m			$\beta_{\text{as}}(\text{COO}^-)$	
530	w	539	w					540	w	567	vw			548	w					$\alpha(\text{C}=\text{C}-\text{C})_{-\text{C}=\text{C}-}$	
486	w	485	w					484	w					484	w					$\varphi(\text{CCC})$	16b

Notes: KBr – sample registered in KBr matrix, ATR_{solid} – sample registered in solid state by the use of ATR technique) and the FT-Raman spectra of sodium, calcium, lanthanum and thorium cinnamates ($_{-\text{C}=\text{C}-}$ – double bond vibrations, _{ar} – aromatic ring vibrations. *s – strong; m – medium; w – weak; v – very; sh – shoulder, ** ν – stretching vibrations, β – in-plane bending modes, γ – out-of-plane bending modes; $\varphi(\text{CCC})$ – the aromatic ring out-of-plane bending modes; $\alpha(\text{CCC})$ – aromatic ring in-plane bending modes.

Table 2

The experimental chemical shifts of protons in the ^1H NMR and carbons in the ^{13}C NMR spectra of DMSO solution of cinnamic acid and sodium, calcium, lanthanum and thorium cinnamates (atom numbering in Fig. 1)

Cinnamic acid		Cinnamates			
		Na(I)	Ca(II)	La(III)	Th(IV)
Proton position					
A	12.40	–	–	–	–
C	7.68	7.44	7.49	7.49	7.58
D, H	7.67	7.32	7.44	7.44	7.53
F	7.60	7.24	7.26	7.30	7.31
E, G	7.41	7.06	7.26	7.30	7.31
B	6.53	6.36	6.51	6.49	6.45
Carbon position					
7	167.61	169.84	173.16	176.62	173.30
9	143.95	136.93	139.61	139.95	141.69
1	134.27	134.76	135.75	135.32	134.91
4	130.23	130.93	128.75	129.01	129.56
3, 5	128.92	128.59	128.66	128.65	128.56
2, 6	128.22	127.72	127.34	127.47	127.83
8	119.27	126.81	126.41	125.59	124.92

Fig. 1. Atom numbering for cinnamic acid molecule and cinnamates.

4. Conclusions

Na(I), Ca(II), La(III) and Th(IV) metal ions affect the molecular structure of cinnamic acid. The metal ions mostly influence the electronic charge distribution in carboxylate anion and double bond between aromatic ring and carboxylate group of ligand. The effect of metals depends mainly on the ionic radii of metals and the type of metal coordination.

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