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Vibrational spectroscopic investigation on the binding modes in Zr(IV) complexes of coumarins

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The zirconium(IV) complexes with bis-coumarins: bis(4-hydroxy-2-oxo-2H-chromen-3-yl)-piridin-3-yl-methane (m-PyDC) and bis(4-hydroxy-2-oxo-2H-chromen-3-yl)-piridin-4-yl-methane (p-PyDC) have been synthesized and characterized. Vibrational study of meta- and para-pyridinomethylene substituted di(4-hydroxycoumarin)s (m- and p- PyDCs) and their Zr(IV) complexes was performed by Fourier transform infrared (FTIR) and Raman (FTR) spectroscopies. Density functional theory (DFT) at B3LYP/6-31G(d) level was used to determine the vibrational characteristics of the neutral PyDCs isomers. The characteristic IR and Raman bands of m- and p-PyDC and their zirconium(IV) complexes were specified and discussed. The vibrational spectral data of zirconium(IV) complexes were interpreted on the basis of comparison with the spectra of the free ligands. These comparative analyses showed that in the Zr(IV) complexes the ligands coordinated to the metal ion through both deprotonated hydroxyl groups and the carbonyl groups.

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Keywords: Bis-coumarins, Zirconium(IV) complexes, FTIR and FT-Raman spectra

1. Introduction

The widespread application of early transition metal complexes has attracted numerous interests in recent years. The recent publication of articles dealing with early transition metal-coordinate complexes reflects a continuing interest in this subject, especially with regard to their structural aspects [1–4] and possible application of these complexes in medicine and pharmacy. Our current interest is in the development of routes for synthesis and characterization of such complexes and their use as cytotoxic agents.

Currently, a considerable effort was devoted in developing of new chelating ligand systems for group IV metals, since their complexes may lead to active pharmacological agents [5]. The most commercially available entry point for the preparation of zirconium(IV) complexes include zirconium tetrachloride. The number of reported group IV metal complexes with N,O mixed donor chelating ligands has grown quickly in the recent years [6-20]. Investigations on the preparation and reactivity of these complexes generally aim at development of a new generation of coordination complexes. It is of interest to understand the effects of the electronic and steric properties and the coordination geometry of the ligands and their complexes.

The ligands used in this study are bis(4-hydroxy-2-oxo-2H-chromen-3-yl)-piridin-3-yl-methane and bis(4-hydroxy-2-oxo-2H-chromen-3-yl)-piridin-4-yl-methane (Fig. 1). 3,3'-Methylenebis[4-hydroxycoumarin] (dicumarol), the main part of investigated ligands, is a naturally occurring anticoagulant derived from coumarin, which is obtained from sweet clover (*Melilotus alba*) [21, 22]. Coumarin, the parent molecule of dicumarol, and a variety of coumarin compounds have demonstrated numerous antitumor and antiproliferative effects. Coumarin compounds have been shown to inhibit proliferation of particular human malignant cell lines *in vitro* [23– 28], as well as affecting tumor activity against several *in vivo* tumor types [21, 29–33]. In clinical trials, these compounds have also been demonstrated to have some activity against prostate cancer, malignant melanoma, and metastatic renal cell carcinoma [34 –36]. Additionally, dicumarol studies have found decreased metastases in animal models [37]. Recently, it was proved that dicumarol appears to induce oxidative stress and pancreatic cancer cell cytotoxicity, as well as apoptosis in a time-dependent and dose-dependent manner [38]. Although such coumarin compounds as dicumarol have been used in cancer therapy, little is known about the mechanism of action of these drugs.

A number of coumarins have been investigated for complexing ability. A lot of different coordination compounds and the mechanism of cytotoxic action have been discussed with regard to the development of new antitumor agents. It was found that in some cases the metal complexes of coumarins obtained revealed higher biological activity than their ligands [39-49]. The promising results, concerning their significant cytotoxic activity, prompted us to search for new transition metal complexes with coumarin derivatives. The previous data from the literature which are in accordance with our investigations give to us the reason to suppose that complexes of coumarins with zirconium(IV) could present

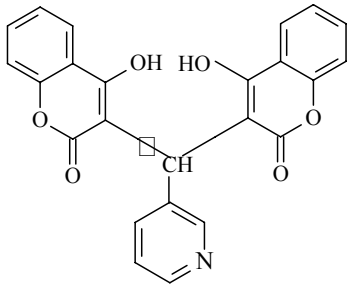
interesting metalorganic compounds with antitumor activity. These compounds are known to form complexes with other transition metals and lanthanides [41, 46-49].

Zirconium complexes of mendiaxon, warfarin, coumachlor, and niffcoumar have been synthesized by us earlier [39] and cytotoxic screening by MTT-assay has been carried out. Among these compounds the zirconium complex of mendiaxon showed highest cytotoxic activity against human promyelocytic leukemic HL-60 cells. It was, therefore, considered worthwhile to study the complexation of bis(4-hydroxy-2-oxo-2H-chromen-3-yl)-piridin-3-yl-methane and bis(4-hydroxy-2-oxo-2H-chromen-3-yl)-piridin-4-yl-methane with zirconium(IV). In a systematic effort aimed at identifying new cytotoxic agents with potent activity against cancer cells, we examined the cytotoxic effects of some zirconium(IV) complexes with coumarins on the human cancer cell lines. Our results presented recently provide evidence that zirconium(IV) complexes with these coumarin ligands possess cytotoxic activity in human chronic myeloid leukemia LAMA-84 and the acute promyelocyte leukemia HL-60 cells. To our knowledge, this was the first report on the antitumor effects of such kind of zirconium(IV) complexes against human cancer cells [50].

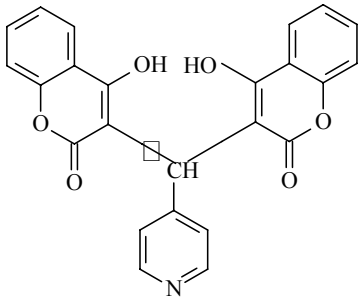
The promising biological activity of these compounds lead us to perform detailed spectroscopic and theoretical investigations on their molecular and vibrational structure. Reliable vibrational assignment of the ligands is important to be done in order to have a good basis for comparison with the vibrational spectra of the complexes with those of the ligands. In our previous study we have selectively discussed both theoretically and experimentally (Raman and IR) the vibrational spectra of the ligands as to those vibrational modes which are sensitive to the intramolecular hydrogen bonding [51]. With the present vibrational study we intend to gain a deeper insight into the vibrational spectra of the new Zr(IV) complexes, studying them comparatively with the ligand vibrational spectra. In this work informative ligand vibrational modes were selected and they were further used to suggest the type of PyDC binding mode in the Zr(IV) complexes studied. The vibrational modes of PyDCs and their Zr(IV) complexes are analyzed and discussed in this comparative study.

2. Experimental

The compounds used for preparing the solutions were Merck products, p.a. grade: $ZrCl_4$. Bis(4-hydroxy-2-oxo-2H-chromen-3-yl)-piridin-3-yl-methane (m-PyDC) and bis(4-hydroxy-2-oxo-2H-chromen-3-yl)-piridin-4-yl-methane (p-PyDC) were used for the preparation of metal complexes as ligands (Fig. 1).



m-PyDC = bis(4-hydroxy-2-oxo-2H-chromen-3-yl)-piridin-3-yl-methane



p-PyDC = bis(4-hydroxy-2-oxo-2H-chromen-3-yl)-piridin-4-yl-methane

Fig. 1. Structures of the ligands.

The solid-state infrared spectra of the compounds were recorded in the 4000-150 cm^{-1} range (in KBr in the 4000-400 cm^{-1} and in CsI in the 400-150 cm^{-1}) by FT-IR 113V Bruker spectrometer. For comparison, the IR spectra were recorded also in Nujol on FTIR-8101M Shimadzu (3800-400 cm^{-1}) and Perkin-Elmer GX Auto image system (700-200 cm^{-1}) IR-spectrometers. In all cases, the resolution was 1 cm^{-1}.

The Raman spectra of the ligands and their new zirconium(IV) complexes were recorded with a Dilor microspectrometer (Horiba-Jobin-Yvon, model LabRam) equipped with a 1800 grooves/mm holographic grating. The 514.5 nm line of an argon ion laser (Spectra Physics, model 2016) was used for the probes excitation. The spectra were collected in a backscattering geometry with a Raman microscope equipped with an Olympus LMPlanFL 50x objective and with a resolution of 2 cm^{-1}. The detection of Raman signal was carried out with a Peltier-cooled CCD camera. The laser output power was 100 mW.

3. Results and discussion

3.1. Chemistry

The complexes of zirconium(IV) with bis(4-hydroxy-2-oxo-2H-chromen-3-yl)-piridin-3-yl-methane (m-PyDC) and bis(4-hydroxy-2-oxo-2H-chromen-3-yl)-piridin-4-yl-methane (p-PyDC) were synthesized by reaction of zirconium(IV) salt and the ligand, in amounts equal to metal: ligand molar ratio of 1: 1. The formation of the complexes may be represented by the following equations:

$$PyDC + 2NaOH \rightarrow 2Na^{+} + PyDC^{2-} + 2H_2O \quad (1)$$

$$[Zr(H_2O)_n]^{4+} + H_2O \leftrightarrow [Zr(OH^{-})_2(H_2O)_{n-2}]^{2+} + 2H_3O^{+} \quad (2)$$

$$[Zr(OH^{-})_2(H_2O)_{n-2}]^{2+} + PyDC^{2-} \rightarrow Zr(PyDC^{2-})(OH^{-})_2(H_2O)_{n-2}\ , \quad (3)$$

where PyDC = $C_{24}H_{15}NO_6$ and $PyDC^{2-}$ = $C_{25}H_{13}O_6^{2-}$.

The elemental analysis data of the zirconium(IV) complexes suggested the formula, $Zr(PyDC^{2-})(OH)_2.nH_2O$, where n=3 for m-PyDC and n=4 for p-PyDC [50]. The formula was further confirmed by mass spectral fragmentation analysis, ^{1}H and ^{13}C NMR data [50]. The results obtained were in agreement with metal : ligand ratio = 1 : 1. However, the experimental data were not enough to suggest the type of the PyDC binding to Zr(IV) and to give idea about the coordination polyhedron of the complexes.

3.2. Vibrational analysis of the m- and p- PyDC and their Zr(IV) complexes

According to the synthesis procedure, the PyDC ligands were firstly deprotonated and the corresponding dianionic species are the active ligand forms in the reaction with Zr(IV) ions. Our previous calculations of molecular electrostatic potential of dianionic PyDCs suggested that among all the possible reactive sites (pyridine N, carbonylic O and hydroxylic O atoms), both hydroxylic oxygens and carbonylic oxygens revealed the most negative molecular electrostatic potential values and thus they appeared to be the most preferred sites for electrophylic attack for reaction with metal ions [49]. Thus, it is expected that the coordination of the ligands to Zr(IV) ions is realized through both the carbonylic oxygens and both the hydroxylic oxygens of the ligand. This suggestion will be checked below on the basis of a detailed and comparative vibrational study of m- and p-PyDC and their Zr(IV) complexes.

Selected calculated and experimental wavenumbers of m-PyDC and p-PyDC and of their Zr(IV) complexes are given in Tables 1 and 2, respectively. All the calculated modes are numbered from the largest to the smallest frequency within each fundamental wavenumber. The observed FTIR and FT Raman frequencies for various modes of vibrations are assigned. The last column in Tables 1-2 shows the approximate description of the normal modes according to the B3LYP/6-31G(d) method [51]. A survey of the last column shows that many vibrations are complex and involve strongly coupled motions.

Table 1. Selected experimental (IR and Raman) and calculated (DFT/B3LYP/6-31(d)) wavenumbers of m-PyDC. Comparison with experimental IR and Raman spectra of its Zr(IV) complex.

m-PyDC			Zr complex		Approximate description
Calculated [51]	Exp.		Exp.		
ν_{IR}	ν_{IR}	ν_{Ra}	ν_{IR}	ν_{Ra}	
	3447br				$\nu(OH)_w$
3219 (3095)[a]	3061w				$\nu(OH)+\nu(CH)_{py}$
3137 (3016)	2919w				$\nu(OH)$
3069 (2951)	2856w				$\nu(CH)_{met}$
1739 (1672)	1687vs		1674sh		$\nu(C=O)_{as}$
1715 (1649)		1671m			$\nu(C=O)_s$
1670 (1606)	1636sh				$\nu(CC)$
1655 (1591)	1615vs	-			$\nu(CC)$
1653 (1589)	-	1607vs	1607s	1607s	$\nu(CC)$
1647 (1583)	1565sh	1554m	1537	1555m	$\nu(CC)_{py}$
1628 (1565)					$\nu(CC)_{py}+\nu(CN)$
1612 (1550)	1539vs	1532m	1507vs	1500w	$\nu(CC)+\delta(COH)_{ip}$
1608 (1546)	1534s	-			$\nu(CC)+\delta(COH)_{ip}$
1526 (1467)	1491w	1479vs		1483s	$\nu(CC)_{py}+\nu(CN)+\delta(CCH)_{ip(py)}$
1497 (1439)	1460m	1457w		1462m	$\nu(CC)+\delta(CCH)_{ip}$
1495 (1437)	1449sh	1444w	1460vs		$\nu(CC)+\delta(CCH)_{ip}$
1493 (1435)		1431sh			$\delta(COH)_{ip}$
1466 (1409)		1409s			$\nu(CC)_{py}+\delta(CCH)_{ip(py)}$
1393 (1339)	1407m				$\nu(CC)_c+\delta(CCH)$
1374 (1321)	1360w			1423m	$\nu(CO)+\delta(COH)_{ip}$

m-PyDC			Zr complex		Approximate description
Calculated [51]	Exp.		Exp.		
ν_{IR}	ν_{IR}	ν_{Ra}	ν_{IR}	ν_{Ra}	
1368 (1315)		1362vw	1408s	1393sh	ν(CO)+δ(COH)
1357 (1305)	1330w	1324s	1331	1330m	$\delta(CCH)_{met}$
1306 (1256)	1277m	1296m	1277w	1311vw	$\nu(CC)_{py}$ +$\nu(CN)_{py}$
1298 (1248)	1254m	1255s	1259w	1251w	$\delta(CCH)_{ip}$
1255 (1207)	1209sh	1207vs	1209m	1209m	$\nu(CO)_{lactone}$
1239 (1191)	1193sh	1195sh			$\nu(CO)_{lactone}$ +$\nu(CC)_{met}$
1224 (1177)	1177m	1171w	1180m	1168vw	$\delta(CCH)_{ip(py)}$ +ν(CO)
1196 (1150)	1148w	1138s		1146w	$\delta(CCH)_{ip}$
1158 (1113)	1119m				$\delta(CCH)_{ip(py)}$
1137 (1093)	1109m	1120w	1109s	1110vw	$\delta(CCH)_{ip}$ +$\delta(CCH)_{ip(py)}$
1132 (1088)	1080w		1049s	1058vw	$\delta(CCH)_{ip}$
1109 (1066)	1050m	1046s			$\nu(CO)_{lactone}$
1071 (1030)	1035m	1026vs	1026	1028m	$\nu(CO)_{lactone}$+$\delta(CCH)_{ip}$
1061 (1020)	1020m				$\delta(CCH)_{ip}$
1039 (999)	1003sh	1010m	1007	1012w	$\delta(CCC)_{ip(py)}$ (Star of David)
994 (956)		951m		951vw	$\delta(CCH)_{op}$
982 (944)	943m	936m	942m	935vw	$\delta(CCH)_{op(py)}$
954 (917)	904m	898m	906s	905w	$\delta(CCH)_{op(py)}$
906 (871)	872m	873vw			$ring_{ip\ star\ of\ David}$
883 (849)	851m	847m	849w	847	$\delta(CCH)_{op}$
883 (849)		829s	824m	825vw	$\delta(CCH)_{op}$
852 (819)	809m	808vw	800m	778m	$ring_{(ip)\ breathing}$
845 (812)	-	781s			$\delta(COH)_{op}$
832 (800)	760s	757sh			$\delta(COH)_{op}$
777 (747)	752sh	743m	760s	743w	$\delta(CCH)_{op}$ +$\delta(CCH)_{op(py)}$
723 (695)	714m	713m			$\delta(OCO)_{op}$
691 (664)	695m	692m		702w	$ring_{ip(py)}$
672 (646)	677m	674s	692m	674sh	$ring_{op}$
637 (612)	630sh	623m			$ring_{ip(py)}$
621 (597)	614m	605m	613w	617m	$ring_{ip(py)}$
570 (548)	565m	576vw	572m	562m	δ(CCC)
551 (530)	552m	557m	553m	526w	$ring_{ip}$
540 (519)	530m	543m			$ring_{op}$
486 (467)	492w	504s	484s		$ring_{op(py)}$
449 (432)	448m	439s		477	$ring_{op}$

[a] values in brackets are scaling with scaling factor 0.9614; ip – in-plane; op – out-of-plane; py – pyridyl; s – strong; vs– very strong; w – weak; vw – very weak; sh shoulder; m – medium.

Table 2. Selected experimental (IR and Raman) and calculated (DFT/B3LYP/6-31(d)) wavenumbers of p-PyDC. Comparison with experimental IR and Raman spectra of its Zr(IV) complex

p-PyDC			Zr complex		Approximate description
Calculated [51]	Exp.		Exp.		
ν_{IR}	ν_{IR}	ν_{Ra}	ν_{IR}	ν_{Ra}	
			3434br		$\nu(OH)_{w}$
3215 (3091)[a]	3141w				ν(OH)
3154 (3032)	2887w	2891w			ν(OH)
3066 (2948)	2846w	-	2855w		$\nu(CH)_{met}$
1740 (1693)	1702,1694s	1695w			$\nu(C=O)_{as}$
1714 (1669)	1686,1683s	1682m	1653br	-	$\nu(C=O)_{s}$
1670 (1606)	1634m	1636w	1623sh	1619w	$\nu(CC)_{c}$
1655 (1591)	1615s,sh	-	-	1607s	$\nu(CC)_{c}$
1653 (1589)	1610s	1607vs	1598vs	1577m	$\nu(CC)_{c}$
1651 (1587)	1565m			1569m	$\nu(CC)_{py}$

p-PyDC			Zr complex		Approximate description
Calculated [51]	Exp.		Exp.		
ν_{IR}	ν_{IR}	ν_{Ra}	ν_{IR}	ν_{Ra}	
1614 (1552)	1557m	1554m	1545	1552m	$\nu(CC)_{py} + \nu(C=N)$
1611 (1549)	1539m	1532w	1500vs	1538	$\nu(CC)_c + \delta(COH)_{ip}$
1608 (1546)	1531d,m			1500	$\nu(CC)_c + \delta(COH)_{ip}$
1543 (1483)	1497s	1479s	1483sh	1483w	$\nu(CC)_{py} + \nu(CN)$
1505 (1448)	1467w				$\delta(COH)_{ip} + \nu(C\text{-}O)$
1497 (1439)	1460w	1463sh,		1462w	$\nu(CC)_c + \delta(CCH)_{ip}$
1495 (1437)	1454w	1445m	1449s	-	$\nu(CC)_c + \delta(CCH)_{ip}$
1494 (1436)		1435m			$\delta(COH)_{ip} + \nu(CO)$
1458 (1402)	1417w	1423m	1423m	1426w	$\nu(CC)_{py}$
1393 (1339)	1407m	1399s			$\nu(CC)c$
1390 (1336)	1400m				$\nu(CC)c$
1369 (1316)	1372w	1386sh	1410m		$\nu(CO) + \delta(COH)_{ip}$
1366 (1313)	1359w	1353w		1407m	$\nu(CO) + \delta(COH)_{ip}$
1302 (1252)	1277m	1250m	1279w	1316	$\nu(CN) + \nu(CC)_{py}$
1254 (1206)	1206m	1202vs	1204m	1209s	$\nu(CO)_{lactone} + \delta(CCH)_{ip}$
1240 (1192)	overlap.	1199m	1199sh		$\nu(CO)_{lactone} + \delta(CCH)_{ip}$
1226 (1179)	1180m	1186w	1180m	-	$\delta(CCH)_{ip(py)} + \nu(CC)_{met}$
1196 (1150)	overlap.	1174s	1148w	1146m	$\delta(CCH)_{ip}$
1185 (1139)	1148w	1143s			$\delta(CCH)_{ip}$
1132 (1088)	1106m	1100m	1109m	1105w	$\delta(CCH)_{ip}$
1108 (1065)	1066m	1061m	1063w	1067w	$\nu(CO)_{lactone} + \delta(CCH)_{ip(py)}$
1103 (1060)	1053m	1043m		1046w	$\delta(CCH)_{ip(py)}$
1076 (1034)	1036m	1031vs	1030w	1037m	$\nu(CO)_{lactone} + \delta(CCH)_{ip}$
1057 (1016)	1011w	1008m		1003w	$\delta(CCH)_{ip}$
1015 (976)	989m	984m			$\delta(CCC)_{ip(py)}$ (S.of David)
983 (946)	949m	969m	945w	940w	$\delta(CCH)_{op(py)}$
974 (937)	940w	948m			$\delta(CCH)_{op(py)}$
965 (928)	904m	898m	907m	905m	$\delta(CCH)_{op}$
896 (862)	853m	850m	858w	858w	$\delta(CCH)_{op(py)}$
883 (849)	807m	814vw	814w		$\delta(CCH)_{op}$
883 (849)	795sh	788m	791w	784w	$\delta(CCH)_{op}$
859 (826)	782sh	776s			$\delta(CCH)_{op(py)}$
840 (808)	763vs				$\delta(COH)_{op(sym)}$
823 (792)	760s	757w			$\delta(COH)_{op(as)} + \delta(CCH)_{op}$
781 (751)	752m	731w	760s	743w	$\delta(CCH)_{op} + \delta(CCH)_{op(py)}$
729 (701)	695w	692w		674s	$\delta(OCO)_{op} + \delta(CCO)_{op}$
681 (655)	676w	674s		647w	$\delta(CCO)_{op(s)}$
502 (483)	481m	477m	480m	474w	$ring_{py(op)}$
445 (428)	422w	445m			$ring_{op}$

[a]values in brackets are scaling with scaled factor 1.9614; $PyDC^{2-}$, ip – in-plane; op – out-of-plane; py – pyridyl; s – strong; vs– very strong; w – weak; vw – very weak; sh shoulder; m – medium.

The Raman spectra of m- and p-PyDC are presented in Fig. 2. The m-PyDC and p-PyDC are isomers and similar vibrational behavior of the dicoumarin fragment has to be expected. Pyridine-ring modes, however, are affected by the position of the acceptor (methylene) substituent in m- and p-positions. Thus, the characteristic modes of m- and p-pyridine substituent could be used to characterize and distinguish the PyDC isomers, which could be considered as di-substituted benzenes with one donor (N) and one acceptor (alkyl, CHR_2) substituents. At the same time, the coumarin ring vibrations (four adjacent ring hydrogen atoms) ought to resemble the vibrational behavior of 1:2 di-substituted benzene. Both the IR and the Raman spectra were considered for full description of the vibrational behavior of PyDC species. Below we discuss characteristic vibrational modes of the ligands that change upon the complexation with Zr(IV) ions.

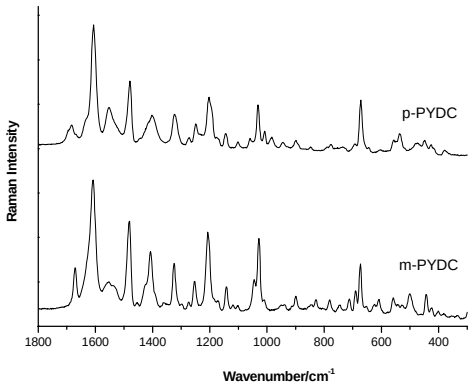


Fig. 2. Raman spectra of the ligands.

In general, the Raman and the IR spectra of Zr(IV) complexes with the ligands studied are very similar. To illustrate the vibrational behavior of PyDCs upon the metal coordination we present the FT-IR spectra of m-PyDC, p-PyDC and their Zr(IV) complexes in the 3600-500 cm^{-1} range in Figs. 3 and 4, as well as the Raman spectra of m-PyDC, p-PyDC and their Zr(IV) complexes in the 1800-200 cm^{-1} range, Figs. 5 and 6.

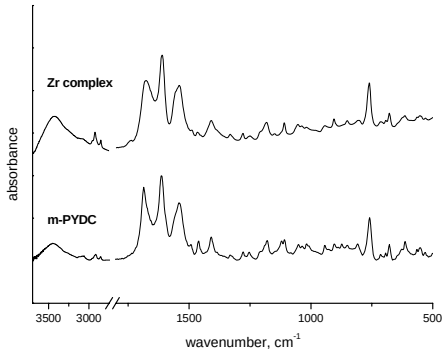


Fig. 3. IR spectra of m-PyDC and its Zr(IV) complex.

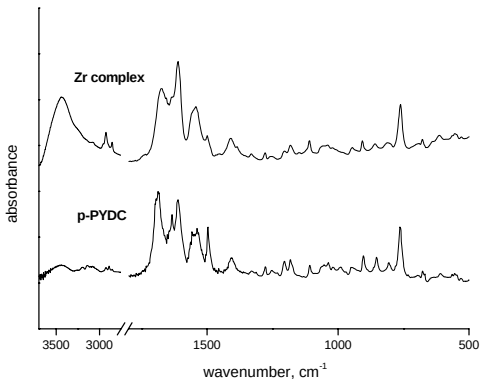


Fig. 4. IR spectra of p-PyDC and its Zr(IV) complex.

O-H stretching modes, ν(OH)

According to the calculations, the weak (to medium) IR bands at 3061 and 2919 cm^{-1} for m-PyDC and at 3141 (IR) and 2887(IR)/2891(Raman) cm^{-1} for p-PyDC are assigned to the O-H stretching mode [51]. Due to the intramolecular O…H-O bonds these modes are shifted to lower wavenumbers in comparison with the free ν(OH) vibrations. In agreement with the asymmetric intramolecular H-bonds in PyDCs, different ν(OH) shifts were observed for the O-H groups in m- and p-PyDC predicting relatively strong HBs. In the vibrational spectra of the Zr(IV) complexes with the PyDCs, the bands corresponding to the ν(OH) modes are not detected and this finding confirms their assignment in the ligands and the suggestion that the deprotonated forms of the ligands participate in the complexes studied.

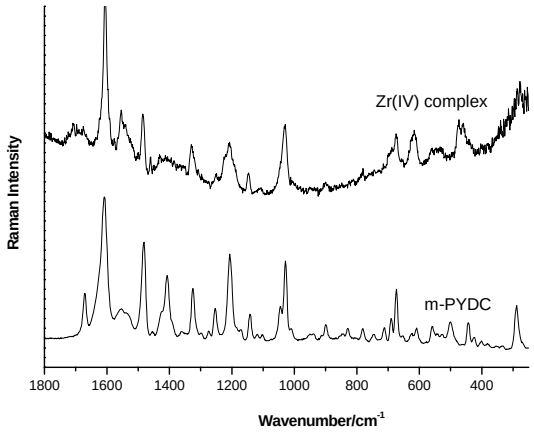


Fig. 5. Raman spectra of m-PyDC and its Zr(IV) complex.

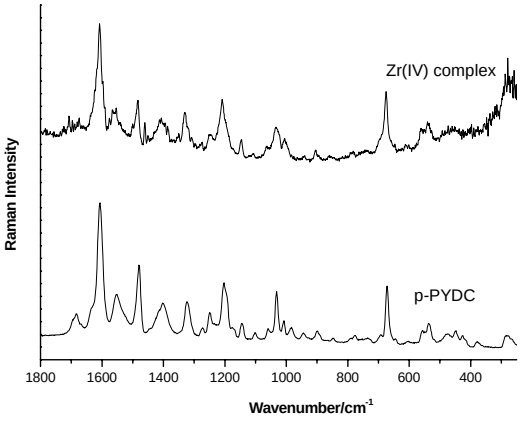


Fig. 6. Raman spectra of p-PyDC and its Zr(IV) complex.

Vibrational modes of the carbonylic C=O and carboxylic COH groups

The most informative for the metal-ligand binding mode in the Zr(IV) complexes studied is the behavior of ν(C=O) mode. According to our DFT calculations [51], the bands in the 1700-1670 cm^{-1} region were assigned to the asymmetric and symmetric stretching vibration of the carbonylic groups. The first component of the carbonylic stretching mode is active in the IR spectra and the second one is active in the Raman spectra of the Zr(IV) complexes. In the ligand IR spectra the ν(C=O) mode appears at 1687 cm^{-1} for m-PyDC, whereas in p-PyDC the band is split to four components, Tables 1, 2. It should be mentioned that due to the intramolecular C=O…H hydrogen bond, this mode appears at lower wavenumbers in PyDCs in comparison with the free C=O vibration.

In the IR spectra of Zr(IV) complexes with m- and p-PyDC, the bands due to ν(C=O) mode appear as shoulders at 1674 (m-PyDC) and 1653 (p-PyDC) cm^{-1}, Tables 1-2, Figs. 3, 4. Hence, as compared to the ligands, in Zr(IV) complexes, the observed ν(C=O) is shifted with ~ 30-40 cm^{-1} to lower wavenumbers, indicating explicitly a coordination of the carbonylic oxygens to the Zr(IV) ions.

The coordination of Zr(IV) to the carbonylic oxygens affected also the IR bands due to the lactone ν(C-O) modes. The IR bands at 1209, 1193 cm^{-1} and Raman bands at 1207, 1195 cm^{-1} for m-PyDC and the IR band at 1206 cm^{-1} (the second one is weak and overlapped) and Raman bands at 1202, 1199 cm^{-1} for p-PyDC were assigned to the first two lactone ν(C-O) modes. The IR bands at 1050 and 1035 cm^{-1} and Raman bands at 1046, 1029 cm^{-1} for m-PyDC and at 1066 and 1036 cm^{-1} (IR) and 1061 and 1031 cm^{-1} (Raman) for p-PyDC were assigned to the second two lactone ν(C-O) modes. In the Raman spectra all $\nu(C\text{-}O)_{lactone}$ modes appeared as strong bands, Figs. 5, 6. The calculated PyDC vibrational spectra and those of the new Zr(IV) complexes, confirmed the suggestions made, Tables 1-2.

In PyDCs, the COH groups are involved in intramolecular H-bonds and the stretching ν(C-O), in-plane deformation, $\delta(COH)_{ip}$ and out-of-plane deformation, $\delta(COH)_{op}$ modes of PyDCs should be affected. According to the calculations [51], both in-plane and out-of-plane δ(COH) modes are shifted to higher wavenumbers due to the intramolecular H-bonds. The bands at 1431 cm^{-1} (Raman) for m-PyDC and at 1467 (IR) and 1435 cm^{-1} (Raman) for p-PyDC were assigned to the in-plane δ(COH) modes. These bands are weak in the IR spectra. The second COH mode appears active in the Raman spectra of m- and p-PyDC. In agreement with experiment the calculations suggested high IR intensities for the out-of-plane δ(COH) modes of PyDCs [51]. Thus, the bands at 760 and 763 cm^{-1} were assigned to the out-of-plane δ(COH) modes in the m- and p-PyDC spectra, respectively. As it is expected the bands assigned to the COH bending modes were not observed in the vibrational spectra of the Zr(IV) complexes since the ligands participate with their deprotonated forms.

The comparative vibrational analysis of the ligands and their Zr(IV) complexes gives also evidence for hydroxylic oxygen coordination to the Zr(IV) ions. According to our calculations [51] the bands observed at 1360 (IR) and 1362 (Raman) cm^{-1} for m-PyDC and at 1372 and 1359 (IR)/(1386, 1353 (Raman)) cm^{-1} for p-PyDC were assigned to the ν(C-O) modes with low intensity in both IR and Raman spectra. The ν(C-O) mode was calculated coupled with in-plane deformation δ(COH) mode. The bands at 1408 (IR) and 1423 (Raman) cm^{-1} in the spectra of the Zr(IV) complex of m-PyDC and the bands at 1410 (IR) and 1407 (Raman) cm^{-1} in the spectra of the Zr(IV) complex of p-PyDC were assigned to the ν(C-O) modes (see Tables 1, 2). In agreement with our suggestion the ν(C-O) band shifts to higher wavenumbers with ~ 50 cm^{-1} in the complexes studied in comparison with that in the neutral PyDCs. At the same time the IR intensity of the band increases.

Ring stretching modes, ν(CC)

The ν(CC) stretching vibrations of the coumarin and pyridine rings are expected to appear in the 1650-1400 cm^{-1} range. Generally, they are detected in four regions: (I) 1650-1585 cm^{-1}, (II) 1588-1540 cm^{-1}, (III) 1525-1460 cm^{-1} and (IV) 1450-1400 cm^{-1} [51]. According to the frequency calculations of m- and p-PyDCs the characteristic bands observed at 1636s (m-PyDCs) and ~1639s (p-PyDCs) (both IR active) (I); ~1610s (IR and Raman active) (I), ~1539 (IR active) (II), ~1460m (IR and Raman active) (III), ~1400 (IV) cm^{-1} were assigned to the coumarin ν(CC) modes, Tables 1-2, Figs.3-6. These modes are slightly affected by coordination of the ligands to the Zr(IV) and in the IR spectra of the Zr(IV) complexes, the coumarin ν(CC) bands appeared at 1607, 1537, 1507, 1460 cm^{-1} for Zr(IV) complex of m-PyDC and at 1623, 1598, 1500, 1449 cm^{-1} for Zr(IV) complex of p-PyDC, Figs. 3, 4. The coumarin ν(CC) bands appeared also in the Raman spectra of the complexes at 1607, 1555, 1500, 1462 cm^{-1} for Zr(IV) complex of m-PyDC and at 1619, 1577, 1500 cm^{-1} for Zr(IV) complex of p-PyDC, Figs. 5, 6. Only the bands at 1610 and 1539 cm^{-1} in the m- and p-PyDCs spectra were shifted to the lower frequency in the spectra of the Zr(IV) complexes due to the Zr(IV) – O interaction and π-conjugation in the coumarin ring after the deprotonation. The increasing IR intensities of these bands in the complexes are also in agreement with our calculations [51].

In agreement with our analysis and with literature data, the bands observed in the 1570-1557 (I), 1507-1497 (II), 1425-1400 (III) cm^{-1} IR regions are assigned to the pyridine stretching modes [51]. The position and the intensity of the bands in the second region (II) is directly related to the position of the methylene substituent meta- and para-, respectively. In full agreement with literature data the band at 1491(IR)/1479(Raman) cm^{-1} for m-PyDC and at 1497(IR)/ 1479(Raman) cm^{-1} for p-PyDC were assigned to ν(CC) of the pyridyl substituent. In the Raman spectra these bands were detected with very high

intensities. On the basis of our calculations the medium peaks at 1277 cm^{-1} in the IR spectra and at 1296 (m-PyDC) and 1250 cm^{-1} (p-PyDC) in the Raman spectra were assigned to C-N and C-C stretching vibrations of pyridine ring. In the vibrational spectra of the Zr(IV) complexes the pyridine stretching modes were almost unchanged, suggesting that the ligands do not coordinate through pyridine N atom.

CH bending modes, δ(CCH)

The CH in-plane bending modes, $\delta(CCH)_{ip}$, were observed at their usual positions for 1:2 (coumarin), 1:3 (m-pyridine) and 1:4 (p-pyridine) di-substituted benzenes in the 1330 – 1070 cm^{-1} region. The most of these bands are stronger in the Raman than in the IR spectra.

Strong IR bands are observed in the 1000-650 cm^{-1} region and they were assigned to out-of-plane deformation vibrations of the hydrogen atoms in the ring, $\delta(CCH)_{op}$. The CH out-of-plane bending modes are more informative to distinguish 1:3-di-substituted (m-pyridine) and 1:4-di-substituted (p-pyridine) aromatic fragment. Our DFT calculations [51] and assignments are in full agreement with the expected positions and intensities of the pyridine $\delta(CCH)_{op}$ bands: 904 cm^{-1} for m-PyDC, 853 cm^{-1} for the p-PyDC in the IR spectra and 898 cm^{-1} for m-PyDC, 850 cm^{-1} for the p-PyDC in the Raman spectra. The medium band at ~752 cm^{-1} in the IR spectra of PyDCs and 743 cm^{-1} for m-PyDC, 731 cm^{-1} for the p-PyDC in the Raman spectra were assigned to the CH out-of-plane bending vibration of coumarin ring, including simultaneous movement of four adjacent ring hydrogen atoms.

Ring in-plane and out-of-plane deformations

There are two ring-in-plane vibrations, the so called "star of David" mode and the "breathing" mode, which appear with different intensity in the Raman and the IR spectra and in a specified vibrational region for m- and p-substituted benzenes. The weak IR band at 1003 cm^{-1} and 1010 cm^{-1} (Raman) for m-PyDC and the medium IR and Raman bands at 989 cm^{-1} and 989 cm^{-1} for p-PyDC, were assigned on the basis of our DFT calculations to the "star of David" mode [51] and this assignment is in full agreement with the experimental data. The "breathing" mode of m- and p-PyDC are observed around 898 cm^{-1} with low intensity and they are not informative. The bands due to the CH bending modes and to the ring deformations are slightly changed in the vibrational spectra of Zr(IV) complexes.

Zr-O stretching and O-Zr-O bending modes

According to our calculations the metal-ligand vibrations appear bellow 600 cm^{-1}. In the IR and Raman spectra of the Zr(IV) complexes with PyDCs the bands are weak. The analysis of the calculated frequencies showed that the weak bands observed in this region in the vibrational spectra of Zr(IV) complexes with m- and p-PyDC are due to the Zr-O stretching modes. The bending O-Zr-O modes were predicted to appear around 400 cm^{-1}. As seen from the vibrational spectra of the studied complexes (Tables 1-2, Figs. 3-6) the stretching and bending modes, including Zr, are weak and thus they are not characteristic and informative. IR-spectra of the compounds were also recorded on solid state in Nujol in the range 700 - 220 cm^{-1}. The spectra of the complexes showed new bands in comparison with those of the free ligands that have been assigned to the rocking, waggling and metal-oxygen stretching vibrations.

On the basis of vibrational analysis we suggest binding of the ligands to the Zr(IV) ions through both the carbonylic and the deprotonated hydroxylic oxygens.

4. Conclusions

The vibrational properties of m- and p-PyDC species and their Zr(IV) complexes have been investigated by FT-Raman and FT-IR spectroscopies and supported by previously published by us B3LYP/6-31G(d) calculations [51]. The difference between observed and calculated wavenumber values of the most of the fundamental modes is very small. Although the PyDCs showed some differences in their vibrational behavior, their complexes revealed very similar vibrational spectra, suggesting that they are isostructural. The vibrational analyses assisted in deeper understanding and explaining the experimental Raman and IR spectra of Zr(IV) complexes with m- and p-PyDC ligands. Vibrational evidence for coordination of both the carbonylic oxygens and both the deprotonated hydroxylic oxygens to the Zr(III) ions was found.

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