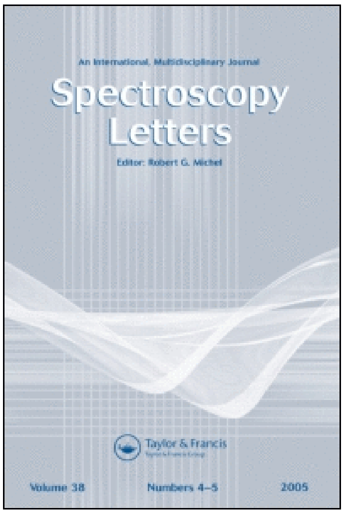

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Spectroscopic and Theoretical Studies of a New Cerium (III) Complex with 3,3'-(*ortho*-Pyridinomethylene)di-[4-hydroxycoumarin]

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Spectroscopic and Theoretical Studies of a New Cerium (III) Complex with 3,3′-(*ortho*-Pyridinomethylene) di-[4-hydroxycoumarin]

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Abstract: A new cerium (III) complex with 3,3′-(*ortho*-pyridinomethylene)di-[4-hydroxycoumarin] (*o*-PyDC) was synthesized and characterized by various spectroscopic methods: mass spectrometry, ^{1}H NMR, ^{13}C NMR, IR, and Raman spectroscopy. The experimental IR and Raman spectra of *o*-PyDC were assigned to the corresponding normal modes on the basis of density functional theory calculations at B3LYP/6-31G(d) optimized geometry. The NMR, Raman, and IR spectra of the Ce(III) complex were interpreted on the basis of comparison with those of the free ligand. The vibrational analysis and the NMR data give evidence that in the Ce(III) complex, the ligand coordinates with the metal ion through both the deprotonated hydroxyl groups and through the carbonyl groups. The spectroscopic data indicates that the pyridine nitrogen is also involved in coordination with Ce(III). Density functional calculations of a complex fragment structure were performed to elucidate further the binding mode of *o*-PyDC to Ce(III) and to explain the NMR and vibrational spectroscopic results.

Keywords: Cerium (III) complex, DFT, 4-hydroxycoumarins, IR spectra, NMR spectra, Raman spectra

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INTRODUCTION

Coumarin (1,2-benzopyrone; 2H-1-benzopyran-2-one; *cis*-*o*-coumarinic acid lactone; coumarinic anhydride) consists of an aromatic ring fused to a condensed lactone ring. Because of certain of its biochemical properties, coumarin has been proposed for use in clinical medicine.[1–5] Coumarin is a naturally occurring compound, being present in a wide variety of plants, microorganisms, and in some animal species. The metabolism, toxicity, and results of tests for carcinogenicity have recently been reviewed with respect to the safety for humans of coumarin present in foodstuffs and for fragrance use in cosmetic products.[6] In many studies, coumarin has been reported to reduce the incidence of tumors produced by genotoxic carcinogens.[7]

Also, coumarins and their derivatives have been studied for their complexation with metal ions.[8–11] Lanthanide ions are subjects of increasing interest in bioinorganic and coordination chemistry.[12,13]

Our previous investigations[14–20] give us reason to suppose that complexes of coumarins with lanthanides could provide interesting compounds with antitumor activity. As a result of our earlier work, the cytotoxic profile of some complexes of coumarin derivatives with lanthanides against different tumor cell lines was proved. It is noteworthy that the lanthanide complexes with coumarins exert pronounced cytotoxic effects. The corresponding lanthanide salts are found to be of very low or missing activity. So far, we can conclude that the metal–ligand binding character determines the antitumor spectrum of the new complexes. The study of *in vitro* effects of the new lanthanide complexes is of interest in connection with other cell lines and tumors in order to find out the differences in their spectrum of activity.

Little is known about the coordination ability of di-[4-hydroxycoumarin]s with cerium (III). A survey of the literature reveals that no work has been done on the reactions of lanthanides with 3,3′-(*ortho*-pyridinomethylene)di-[4-hydroxycoumarin] (*o*-PyDC). It was, therefore, interesting to study the complexation of Ce(III) with *o*-PyDC.

In the current study, we perform the synthesis, spectroscopic and theoretical studies of the new Ce(III) complex 3,3′-(*ortho*-pyridinomethylene) di-[4-hydroxycoumarin]. The spectroscopic characteristics of the free ligand and the complex were derived from ^{1}H NMR, ^{13}C NMR, IR, and Raman spectra. Detailed vibrational analysis based on calculated and experimental (Raman and IR) spectra of *o*-PyDC and the corresponding Ce(III) complex spectra helped to determine the most sensitive vibrational modes of *o*-PyDC upon coordination with Ce(III) and to suggest the metal–ligand binding mode. Model calculations on the fragment complex structure were performed to elucidate the binding type of Ce(III) complex with *o*-PyDC.

MATERIALS AND METHODS

Chemistry

Synthesis of Ce(III) Complex with 3,3′-(ortho-Pyridinomethylene)di-[4-hydroxycoumarin]

The compounds used for preparation of the solutions were Merck products, pure analytical-grade: $Ce(NO_3)_3 \cdot 6H_2O$. For the preparation of the Ce(III) complex, 3,3′-(*ortho*-pyridinomethylene)di-[4-hydroxycoumarin] (*o*-PyDC) ($C_{24}H_{15}NO_6$, H_2L) was used as a ligand (Fig. 1).[20]

The complex of Ce(III) with 3,3′-(*ortho*-pyridinomethylene)di-[4-hydroxycoumarin] was synthesized by reaction of Ce(III) salt and the ligand in amounts equal to metal:ligand molar ratio of 1:2. The ligand is insoluble in water. On raising the pH by the dropwise addition of a dilute solution of sodium hydroxide (0.1 mol L^{-1}), the ligand was dissolved. The complex was prepared by adding aqueous solution of Ce(III) salt (1 mmol) to the solution of the ligand (2 mmol). The reaction mixture was stirred with an electromagnetic stirrer at 25°C. At the moment of solution mixing, a precipitate was obtained. The precipitate was filtered (pH of the filtrates was 5.0) and washed several times with water and dried in a desiccator to a constant weight. The complex is insoluble in water, slightly soluble in methanol and ethanol, and very soluble in DMSO.

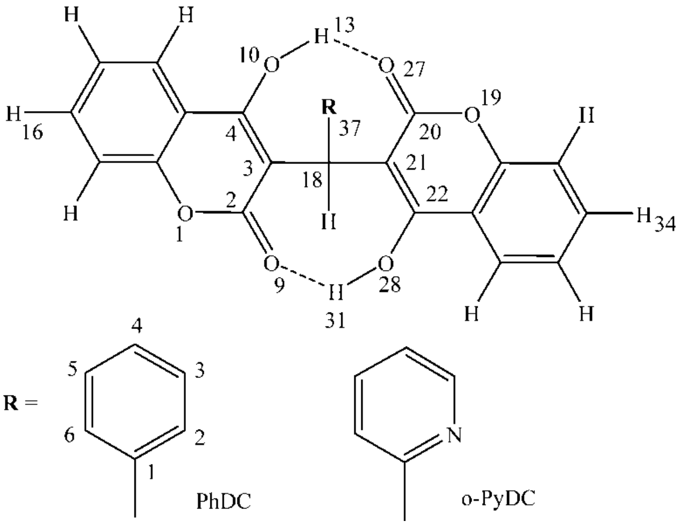


Figure 1. Schematic presentation of phenyl (PhDC) and pyridyl (*o*-PyDC) substituted bis-(4-hydroxycoumarin).

Spectroscopic Measurements

The elemental analyses for C, H, Ce, and H_2O were performed according to standard microanalytical procedures.

The ^1H NMR spectra were recorded at room temperature on a Brucker WP 250 (250 MHz) spectrometer (Germany) in DMSO-d_6.

The ^{13}C NMR spectra were recorded at ambient temperature on a Brucker 250 WM (62.9 MHz) spectrometer (Germany) in DMSO-d_6. Chemical shifts are given in ppm, downfield from TMS.

The mass spectra were recorded on a Jeol JMS D 300 (Japan) double focusing mass spectrometer coupled to a JMA 2000 data system. The compounds were introduced by direct inlet probe, heated from 50°C to 400°C at a rate of 100°C/min. The ionization current was 300 mA, the accelerating voltage 3 kV, and the chamber temperature 150°C.

The solid-state infrared spectra of *o*-PyDC ligand and its Ce(III) complex were recorded in KBr in the 4000–400 cm^{-1} frequency range by an FTIR 113V Bruker spectrometer (Germany). The Raman spectra of the compounds were recorded with a Dilor Labram spectrometer (Horiba Jobin Yvon, Inc.) using the 785-nm excitation line from a Spectra Physics argon ion laser. The Labram integrated system is coupled through an Olympus LMPlanFL 100× objective to the optical microscope. The spectra were collected in the backscattering geometry with a resolution of 2 cm^{-1}. The detection of Raman signal was carried out with a CCD camera (Photometric model 9000). The laser power varied from 100 to 250 mW and is indicated in each figure legend.

RESULTS AND DISCUSSION

Chemistry

Coordination Ability of 3,3′-(*ortho*-Pyridinomethylene)di-[4-hydroxycoumarin] with Ce(III)

The elemental analysis data of the Ce(III) complex with 3,3′-(*ortho*-pyridinomethylene)di-[4-hydroxycoumarin] were in agreement with metal : ligand-ratio of 1 : 1 and Ce(*o*-PyDC^{2-})(OH)(H_2O) formula was suggested, where *o*-PyDC^{2-} $= L{=}C_{24}H_{13}NO_6^{2-}$.

Elemental analysis data for Ce(III) complex with *o*-PyDC: Found/calculated: % C, 49.55/49.14; % H, 3.12/2.73; % N, 2.77/2.39; % H_2O, 3.44/3.07; % Ce, 23.56/23.89.

The suggested formula was further confirmed by mass-spectral fragmentation analysis. The characteristic peaks were observed in the mass spectrum of the ligand and its metal complex, which followed the similar fragmentation pattern as reported earlier.[20,21] The fragmentation of ligand showed molecular ion peak (M + 1) at 413 and occurs via cleavage of organic moiety giving respective peaks to produce 4-hydroxycoumarin at m/z 162. As it is seen in Table 1, the mass spectrum of the metal complex shows molecular ion peak (M + 1) at m/z 589, confirming its molecular weight. Elimination of Ce metal and water molecules was observed at m/z 410, and further fragmentation followed a similar pathway as ligand. In the complex, elimination of one 4-hydroxycoumarin radical and a pyridyl radical gives rise to the formation of 3-methyl-4-hydroxycoumarin at m/z 176, which was observed as a base peak. Although of low intensity, the peak at m/z 589 in the Ce(III) complex spectrum corresponds with the mass weight of the complex formation. The results thus obtained suggest metal:ligand ratio of 1:1 and they are in agreement with the data of the elemental analysis.

^{1}H NMR and ^{13}C NMR Study of 3,3′-(*ortho*-Pyridinomethylene)di-[4-hydroxycoumarin] and its Ce(III) Complex

The Ce(III) complex and the ligand, 3,3′-(*ortho*-pyridinomethylene)di-[4-hydroxycoumarin] were further studied by their ^{1}H NMR and ^{13}C NMR spectra. In the ^{1}H NMR spectrum of the Ce(III) complex, changes of the chemical shifts were observed and they were attributed to coordination of the ligand with Ce(III) (Table 2). Changes in the chemical shifts were observed for the neighboring C-4, C-3, and C-2 carbon atoms of the complex, and they confirmed the expected coordination of the ligand through both deprotonated hydroxyl and carbonyl oxygen atoms (Table 3). In the ^{13}C NMR spectrum of the complex, the signals of the pyridine carbons (C-3′ to C-6′) are significantly shifted to downfield in comparison with those of the free ligand. This fact indicates that the pyridine nitrogen is also a suitable site for coordination with Ce(III). The other carbon atoms were only slightly affected upon the metal binding.

Comparison of the NMR spectra of the complex with those of the ligand reveals that the resonances of the ligand are considerably broadened and also shifted indicating complexation. We considered these shifts as valuable and we used them to confirm the coordination. NMR shifts of this order are typical for coordination compounds of lanthanides. As previously reported,

Table 1. Mass spectral data of 3,3′-(*ortho*-pyridinomethylene)di-[4-hydroxycoumarin] and its Ce(III) complex

Ligand	m/z	Percent (%)	Complex	m/z	Percent (%)
$H_2L{=}C_{24}H_{15}NO_6$	413	7	$Ce(L)(OH) \cdot H_2O$	589	1
	395	2		490	3
	252	7		460	5
	162	30		410	2
	120	28		307	40
	92	38		176	100

Table 2. ^{1}H NMR spectral shifts of 3,3′-(*ortho*-pyridinomethylene)di-[4-hydroxycoumarin] and its Ce(III) complex (250 MHz, DMSO-d_6), δ (ppm)

	δ (ppm)		
Compound	H_5–H_8[a]	H_9[a]	$H_{3'}$–$H_{6'}$[a]
$H_2L{=}C_{24}H_{15}NO_6$	7.24–7.58	6.54	7.80–8.64
$Ce(L)(OH) \cdot H_2O$	7.17–7.78	6.30	8.29–8.64

[a] Atom numbering is given in the structure.

such $\Delta\delta$ values are indicative of the coordinating mode of the coumarin system [14–21]. A similar feature has been observed for coordination compounds of other lanthanides with similar coumarin ligands and has been reported by us recently.[20,21]

FTIR and Raman Spectra of *o*-PyDC and its Ce(III) Complex

The binding mode of *o*-PyDC to Ce(III) ion was further elucidated by analysis of the IR and Raman spectra of the ligand and the corresponding Ce(III)

Table 3. ^{13}C NMR spectral shifts of 3,3′-(*ortho*-pyridinomethylene)di-[4-hydroxycoumarin] and its Ce(III) complex (62.9 MHz, DMSO-d_6), δ (ppm)

	δ (ppm)	
Atom	$H_2L{=}C_{24}H_{15}NO_6$	$Ce(L)(OH) \cdot H_2O$
C-2	168.6	164.9
C-4	164.0	162.0
C-8a	157.6	156.6
C-1′	152.9	152.7
C-7	146.5	148.5
C-3′	141.9	136.0
C-5′	141.9	131.1
C-4′	131.9	126.3
C-6′	125.9	123.1
C-2′	—	—
C-5	124.4	121.1
C-6	123.4	120.2
C-4a	119.3	116.9
C-8	115.9	115.6
C-3	100.5	103.6
C-9	36.7	38.6

complex. Geometry optimization of *o*-PyDC neutral and dianion forms was performed using density functional theory (DFT) method with nonlocal three-parameter hybrid exchange B3LYP density functional and 6-31G(d) basis set.[21–23] The optimization was done without symmetry constraint. The adequacy of B3LYP method for studying conformational behavior, hydrogen-bonding strength, and gas-phase basicity of many systems has been proved in many investigations.[24–29] Our DFT study of phenyl- and pyridyl-substituted bis-4-hydroxycoumarins showed that B3LYP functional (20% HF exchange mixing) with 6-31G(d) basis set is a suitable method for geometry prediction and conformational stability.[21,30] The method used reproduced the experimental geometry parameters of phenyl-substituted bis-4-hydroxycoumarin (PhDC) as well as the intramolecular O-H...O hydrogen bonds in it as obtained from X-ray diffraction analysis.[31] The inclusion of diffuse functions on carbon and oxygen atoms as well as polarization functions on the hydrogen atoms [6-31 + G(d,p) basis set] do not improve the geometry parameters. The average deviations of the calculated bond lengths and bond angles for PhDC and 4-HC were as follows: at B3LYP/6-31G(d), 0.81% and 0.39% and at B3LYP/6-31 + G(d,p), 0.75% and 0.38%, respectively. *o*-PyDC is an analogue of 3,3′-benzylidenebis(4-hydroxycoumarin) (PhDC) the only difference being the type of the substituent: in *o*-PyDC it is pyridyl, in PhDC it is phenyl (Fig. 1). Therefore, we suggested similar bis(4-hydroxycoumarin) skeleton structure of *o*-PyDC like that of PhDC, stabilized with the same type of intramolecular O-H...O hydrogen bonds (Fig. 1). The molecular modeling of *o*-PyDC isomers confirmed the suggested similarity with PhDC.[21] Thus, the availability of X-ray structure data about PhDC gave us the possibility to select a reliable method for calculations of geometry parameters and vibrational properties of *o*-PyDC. We have used further B3LYP/6-31G(d) level of the theory to calculate the harmonic frequencies of *o*-PyDC. The vibrational spectrum of *o*-PyDC was calculated at the optimized B3LYP/6-31G(d) geometry with the GAUSSIAN98 program package.[32] In order to assign the calculated frequencies to approximate vibrational descriptor, the vibrational modes have been analyzed by means of the atom movements, calculated in Cartesian coordinates. Because the calculated wavenumbers were overestimated, the scaling factor derived by Scott and Radom (0.9614) was used to obtain better coincidence with the experimental Raman and IR spectra.[33]

The IR spectra of *o*-PyDC and its Ce(III) complex are given in Fig. 2, and the corresponding Raman spectra are presented in Fig. 3. Selected calculated and experimental wavenumbers of *o*-PyDC and its Ce(III) complexes are given in Table 4.

ν(C=O) stretching mode

The ν(C=O) stretching mode give rise to the highest absorption in the IR spectrum of *o*-PyDC. The calculated high intensity of the band at 1671 cm^{-1} (scaled) confirmed its assignment to ν(C=O). The second component of

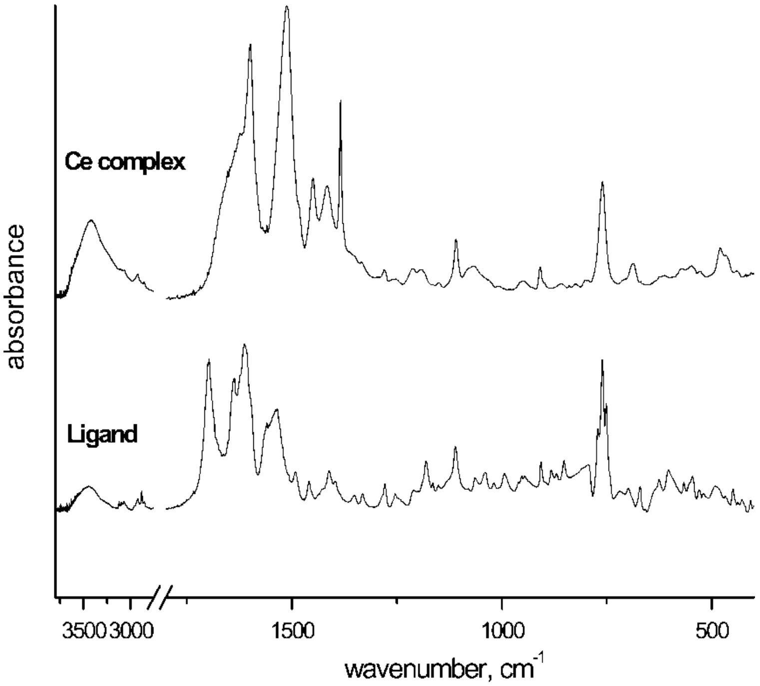


Figure 2. FTIR spectra of *o*-PyDC and its Ce(III) complex in the 4000–400 cm^{-1} frequency range.

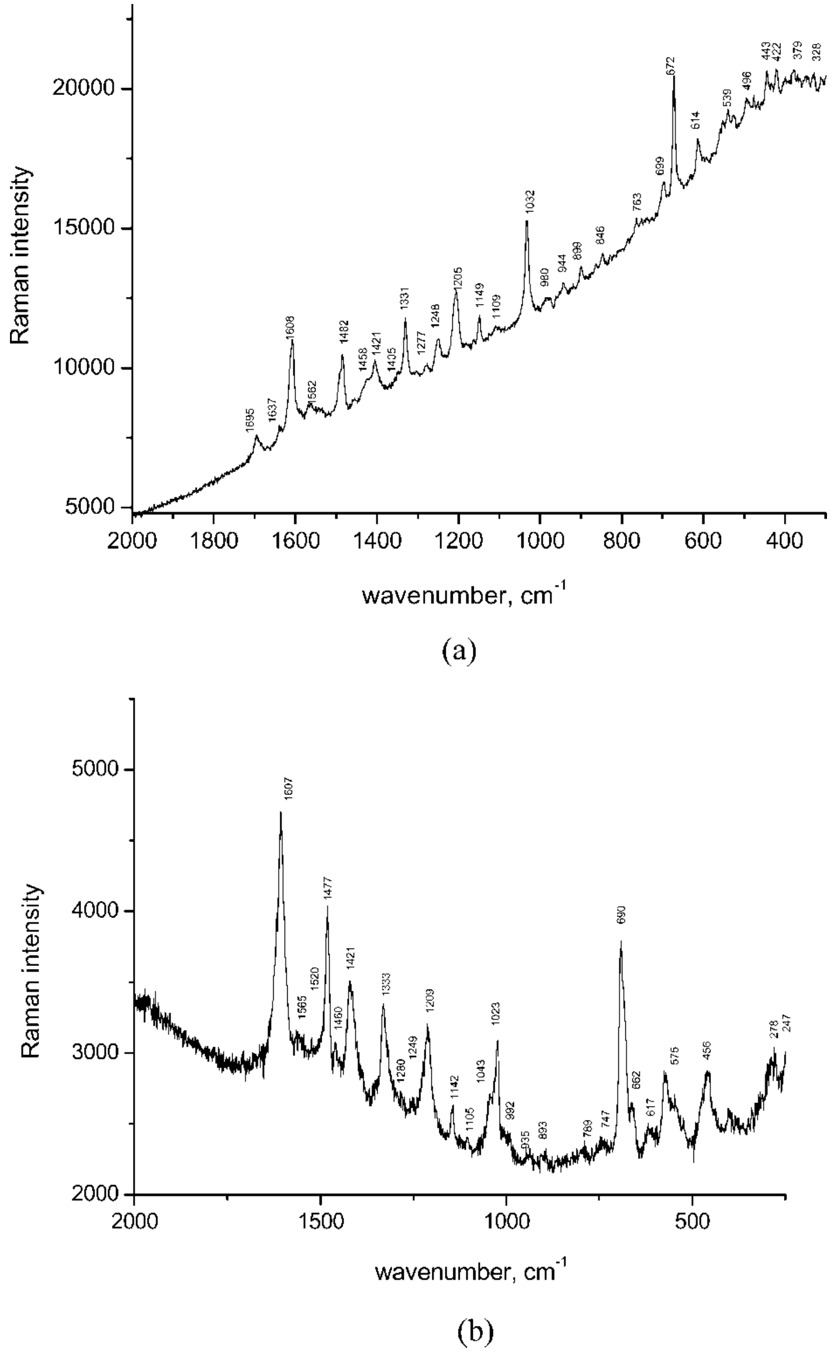
ν(C=O), calculated at 1652 cm^{-1} (scaled), revealed a modest intensity. In the IR spectrum of the Ce(III) complex, the $\nu(C{=}O)_{as}$ band exhibited a redshift of 44 cm^{-1}, 1697 cm^{-1} → 1653 cm^{-1} (observed), and this finding was taken as evidence for participation of the C=O group in coordination with the metal ion. In the Raman Ce(III) complex spectrum, the ν(C=O) modes were not observed. The second ν(C=O) component was observed only in the IR spectrum of the ligand as a shoulder at 1690 cm^{-1}.

$\delta(COH)_{ip}$ Modes

According to our calculations, the $\delta(COH)_{ip}$ modes were assigned to the bands at 1431 and 1349 cm^{-1} in IR (1433 and 1314 cm^{-1} calculated). In the IR spectrum of the Ce(III) complex, these bands were not observed, and thus this finding supported the suggestion that the ligand binds the metal ion through its deprotonated form, *o*-PyDC^{2-}. No bands were detected in the Raman spectrum.

$\delta(COH)_{op}$ Modes

The $\delta(COH)_{op}$ modes of the ligand were assigned to the IR bands at 771 and 761 cm^{-1}, the first band being with medium intensity and the second one



(a)

(b)

Figure 3. Raman spectra of *o*-PyDC (a) and its Ce(III) complex (b) in the 2000–400 cm^{-1} frequency range.

Table 4. Selected calculated [DFT/B3LYP/6-31(d)] and experimental (IR and Raman) wavenumbers of *o*-PyDC compared with IR and Raman wavenumbers of its Ce(III) complex (ν, cm^{-1})

	o-PyDC	Ce(III) complex			
Calculated ν_{IR}	Experimental ν_{IR}	Experimental ν_{R}	Experimental ν_{IR}	Experimental ν_{R}	Approximate description
	3441		3390br		
3271 (3144)[a]	3124m				$\nu(\mathrm{OH})$
3082 (2963)	2877m				$\nu(\mathrm{OH})$
3063 (2945)	2846w		2724vw		$\nu(\mathrm{CH})_{\mathrm{met}}$
1738 (1671)	1697vs	1695m	1653sh		$\nu(\mathrm{C{=}O})_{\mathrm{as}}$
1718 (1652)	1690sh				$\nu(\mathrm{C{=}O})_{\mathrm{s}}$
1670 (1606)	1639s	1637w			$\nu(\mathrm{CC})$
1665 (1601)	1623s		1621s	1607vs	$\nu(\mathrm{CC})$
1656 (1592)	1610vs	1608s			$\nu(\mathrm{CC})$
1654 (1590)	1594s		1599s		$\nu(\mathrm{CC})$
1647 (1583)	1570s				$\nu(\mathrm{CC})_{\mathrm{py}}$
1632 (1590)	1560s	1562w		1565w	$\nu(\mathrm{CC})_{\mathrm{py}} + \nu(\mathrm{CN})_{\mathrm{py}}$
1614 (1552)	1539m,d		1511vs	1520w	$\nu(\mathrm{CC}) + \delta(\mathrm{COH})_{\mathrm{ip}}$
1611 (1549)	1533m				$\nu(\mathrm{CC}) + \delta(\mathrm{COH})_{\mathrm{ip}}$
1517 (1458)	1488m	1482s		1477s	$\nu(\mathrm{CC})_{\mathrm{py}} + \nu(\mathrm{CN})$
1498 (1440)	1457m	1458sh	1452s	1460w	$\nu(\mathrm{CC}) + \delta(\mathrm{CCH})_{\mathrm{ip}}$
1491 (1433)	1431m				$\delta(\mathrm{COH})_{\mathrm{ip}}$
1477 (1420)	1412m	1421m	1417m	1421s	$\nu(\mathrm{CC})_{\mathrm{py}} + \delta(\mathrm{CCH})_{\mathrm{ip(py)}}$
1395 (1341)	1393m	1405w			$\nu(\mathrm{CC}) + \delta(\mathrm{CCH})_{\mathrm{ip}}$
1367 (1314)	1349m				$\nu(\mathrm{CO}) + \delta(\mathrm{COH})_{\mathrm{ip}}$
1354 (1302)					$\nu(\mathrm{CO}) + \delta(\mathrm{COH})$
1338 (1286)	1330m	1331s		1333s	$\delta(\mathrm{CCH})_{\mathrm{ip(py)}}$
1329 (1278)	1288sh	1304vw		1280w	$\nu(\mathrm{CN})_{\mathrm{py}} + \delta(\mathrm{CCH})_{\mathrm{ip(py)}}$
1312 (1261)	1275m	1277w	1280m		$\nu(\mathrm{CC})_{\mathrm{py}} + \nu(\mathrm{CN})_{\mathrm{py}}$
1296 (1246)	1254w	1248m		1249sh	$\delta(\mathrm{CCH})_{\mathrm{ip}}$
1259 (1210)	1212m	1205s	1211m,d	1209s	$\nu(\mathrm{CO})_{\mathrm{lactone}}$
1219 (1172)	1180m	1149m		1142m	$\delta(\mathrm{CCH})_{\mathrm{ip}}$
1140 (1096)	1111s	1109w	1108m	1105w	$\delta(\mathrm{CCH})_{\mathrm{ip(py)}}$
1111 (1068)	1064m	1055vw	1062m	1043sh	$\nu(\mathrm{CO})_{\mathrm{lactone}} + \nu(\mathrm{CC})_{\mathrm{met}}$
1072 (1031)	1040m	1032s	1024sh	1023s	$\nu(\mathrm{CO})_{\mathrm{lactone}} + \delta(\mathrm{CCH})_{\mathrm{ip}}$
1013 (974)	1017w		1012w		$\delta(\mathrm{CCC})_{\mathrm{ip(py)\ star\ of\ David}}$
1006 (967)	995m	980w		992w	$\delta(\mathrm{CCH})_{\mathrm{op(py)}}$
981 (943)	945m	944w	950m	935w	$\delta(\mathrm{CCH})_{\mathrm{op(py)}}$
962 (925)	907m	899w	908m	893w	$\delta(\mathrm{CCH})_{\mathrm{op}}$
923 (887)	883m				$\delta(\mathrm{CCC})_{\mathrm{ip\ star\ of\ David}}$
912 (877)	869m	861vw			$\delta(\mathrm{CCH})_{\mathrm{op(py)}}$
907 (872)	851m	846w	858w		$\delta(\mathrm{CCC})_{\mathrm{ip\ star\ of\ David}}$
881 (847)	791m		800w	789w	$\delta(\mathrm{CCH})_{\mathrm{op}}$
866 (833)	771m				$\delta(\mathrm{COH})_{\mathrm{op}}$
814 (783)	761vs	763w			$\delta(\mathrm{COH})_{\mathrm{op}}$
784 (754)	750s		759vs	747w	$\delta(\mathrm{CCH})_{\mathrm{op}}$
773 (743)	734m,sh				$\delta(\mathrm{CCH})_{\mathrm{op(py)}}$
718 (690)	688sh	699w	687m	690s	$\mathrm{ring}_{\mathrm{op}}$

(*continued*)

Table 4. Continued

	o-PyDC	Ce(III) complex			
Calculated ν_{IR}	Experimental ν_{IR}	Experimental ν_{R}	Experimental ν_{IR}	Experimental ν_{R}	Approximate description
692 (665)	672m	672s		662sh	$ring_{ip}$
662 (636)	624m	630vw			$ring_{op}$
637 (612)	602m	614m	613w	617w	$ring_{ip(py)}$
551 (530)	546m	539m	547w	575m	$\delta(CC_{18}C) + ring_{ip}$
541 (520)	526w	523w	527w		$ring_{op}$
490 (471)	482m	496w	479m		$\delta(CC_{18}C) + ring_{op(py)}$
458 (440)	447m	443m	440w	456m	$ring_{ip}$
449 (432)	437sh	422m		402w	$ring_{op}$

ip, in-plane; op, out-of-plane; py, pyridyl; s, strong; vs, very strong; w, weak; vw, very weak; sh, shoulder; m, medium.

[a]Values in parentheses are scaled with scaling factor 0.9614.

being very strong. Because the ligand participates in the Ce(III) complex with its deprotonated form, these bands were not detected in both IR and Raman spectra of the complex.

ν(CC) Stretching Vibrations

Several bands due to the ν(CC) stretching vibrations of the coumarin and pyridine rings appeared in the IR and Raman spectra. The IR bands at 1639, 1623, 1610, 1594 cm^{-1} are strong, and the main contribution to them is the ν(CC) mode of the coumarin moiety. In the Raman spectrum, only two of them appeared with very low intensity: 1637 and 1608 cm^{-1}. The ν(CC) stretching vibrations of the pyridine ring appeared as strong bands at lower wavenumbers, 1570, 1560, and 1488 cm^{-1} in the IR spectrum and at 1562 and 1482 cm^{-1} in the Raman, and they are coupled with ν(CN). The ν(CC) stretching band positions are not significantly changed in the Ce(III) complex spectrum. The ν(CN) mode observed at 1304 cm^{-1} in the Raman spectrum of *o*-PyDC is slightly shifted to 1280 cm^{-1} in the Ce(III) complex. The low frequency shift could be used to suggest a participation of the nitrogen atom in metal coordination. However, the ν(CN) vibration appears in the Raman spectra with low intensity and hence its behavior should be used with caution for prediction of *o*-PyDC coordination through the N atom.

A broad band, characteristic for ν(O-H) of a coordinated water, was observed in the spectra of the complex at about 3400 cm^{-1} giving confirmation for the presence of water in the general complex formula, as suggested from the physicochemical measurements and elemental analysis, $Ce(L)(OH)(H_2O)$. According to the calculations, the medium IR bands at

3124 and 2877 cm^{-1} of *o*-PyDC ligand were assigned to the O-H stretching modes. The bands were not observed in the Raman spectrum of *o*-PyDC. Due to the intramolecular O...H-O bonds, the O-H stretching modes appeared at lower wavenumbers in the IR spectrum in comparison with the free ν(OH) vibrations at 3634 cm^{-1} in 4-HC.[34] In agreement with the asymmetric intramolecular H-bonds in *o*-PyDC, different ν(OH) shifts were observed for the O-H groups. The shifts are larger compared with those of PhDC and predicted stronger hydrogen bonds in *o*-PyDC.[21] The comparison between the IR spectra of *o*-PyDC and its Ce(III) complex revealed that the absorption bands associated with the stretching ν(O-H) of the phenolic groups (observed at 3124 cm^{-1} and 2877 cm^{-1} in the free ligand) disappeared in the Ce(III) complex IR spectrum, indicating a loss of phenolic protons upon complexation and thus forming metal–oxygen bonds.

C-H Stretching Modes, ν(CH)

According to literature data, the bands due to the C-H stretching vibrations of coumarin and pyridine rings appeared in the 3260–2850 cm^{-1} region.[35] The IR band at 2846 cm^{-1} in *o*-PyDC was assigned to the C-H stretching mode of the methylene group. In the Ce(III) complex IR spectrum, this band was slightly shifted to the lower frequencies and it was observed with low intensity.

CH In-Plane Bending Modes, $\delta(CCH)_{ip}$

The CH in-plane bending modes of *o*-PyDC, $\delta(CCH)_{ip}$, were observed at their usual positions in the 1330–1070 cm^{-1} IR region.[35] The IR bands due to in-plane bending modes are with medium to strong intensity: 1330, 1254, 1180, and 1111 cm^{-1} (Table 4). The corresponding Raman bands are with medium or low intensity. Only the pyridyl $\delta(CCH)_{ip}$ band at 1331 cm^{-1} revealed high Raman activity.

$\nu(C\text{-}O)_{lactone}$ Stretching Modes

The calculations suggested that two bands (assigned to the stretching modes of the shorter lactone C_{12}-O_1 and C_{30}-O_{19} bonds) and two bands (due to the stretching vibrations of the longer lactone C_2-O_1 and C_{20}-O_{19} bonds) appeared in the 1330–1070 cm^{-1} frequency region. The medium IR band at 1212 cm^{-1} (strong in Raman 1205 cm^{-1}) for *o*-PyDC was assigned to the first lactone ν(C-O) modes (the second band, however, is weak and overlapped). The medium IR bands at 1064 and 1040 cm^{-1} were assigned to the second two lactone ν(C-O) modes. With the exception of the Raman band at 1055 cm^{-1} (which was detected with low intensity) in the Raman spectra of the ligand, the $\nu(C\text{-}O)_{lactone}$ modes appeared as strong bands. In the IR and Raman Ce(III) complex spectra, the $\nu(C\text{-}O)_{lactone}$ modes appeared with different intensities and without significant changes in their positions. This finding confirmed the suggestion that no interaction with the metal occurred through the lactone oxygen atoms.

CH Out-of-Plane Bending Modes, δ(CCH)$_{op}$

In the 995–750 cm^{-1} IR frequency region, the out-of-plane deformation vibrations of the hydrogen atoms of the rings were observed. It should be mentioned that in general, the CH out-of-plane bending modes are medium in IR spectra and weak in the Raman spectra of the ligand and its Ce complex. The strong IR band at 750 cm^{-1} of the ligand was assigned to the CH out-of-plane bending vibration of the coumarin ring, including simultaneous movement of four adjacent ring hydrogen atoms, whereas the medium IR band at 734 cm^{-1} is due to the same type vibration of *o*-pyridine ring. Because these modes showed unchanged positions in both IR and Raman spectra, they could not be considered as informative and suitable for virational analysis of the Ce(III) complex.

In comparison with the free ligand, the Ce(III) complex IR spectrum showed new bands in the range 550–400 cm^{-1}, and they were assigned to the metal–oxygen stretching vibrations, in agreement with literature data.[36]

Computational Modeling of Ce(III) Complex with *o*-PyDC

On the basis of NMR and vibrational data, we suggested that the *o*-PyDC binds to the Ce(III) through both deprotonated hydroxyl oxygens and both carbonyl oxygens. Further, NMR results of the complex showed significantly shifted signals of the pyridine carbons (protons) to downfield in relation to the free ligand. At the same time, the vibrational spectra revealed that the ν(CN) mode in the complex was shifted to low frequencies compared with the ligand. These facts could indicate that the pyridine nitrogen is involved in Ce(III) coordination. To investigate the binding mode of the ligand to the Ce(III), we undertook computational modeling of the complex fragment. The model calculations revealed that it is unfavorable for the four oxygen atoms of one *o*-PyDC ligand to bind to one Ce(III). Therefore, we suggest that the ligand gives one deprotonated hydroxyl oxygen and one carbonyl oxygen for coordination with one Ce(III). The second deprotonated hydroxyl oxygen and carbonyl oxygen are bound to other Ce(III) and the metal : ligand ratio is 1:1, as the experimental results showed, and thus a polymeric structure seems very likely (Fig. 4). A fragment of such a structure was modeled at B3LYP/6-31G(d) level, and the core electrons of Ce(III) were described with the quasi-relativistic effective core potential (RECP) optimized by the Stuttgard–Dresden group.[37–39] Large core ECP for Ce(III) treating the 5*s*, 5*p*, 5*d*, and 6*s* electrons in the valence shell was applied. The reliability of large core ECP to reproduce the ground state geometry of lanthanide complexes was demonstrated elsewhere.[40] The geometry optimization of the fragment was performed without symmetry constraint. The structure obtained is a global minimum structure without imaginary frequency. In the initial fragment geometry, we suggested binding only through the oxygen atoms. During the optimization procedure, however, binding to the nitrogen atom of the pyridyl substituent occurred, as shown in Fig. 4. Such a binding

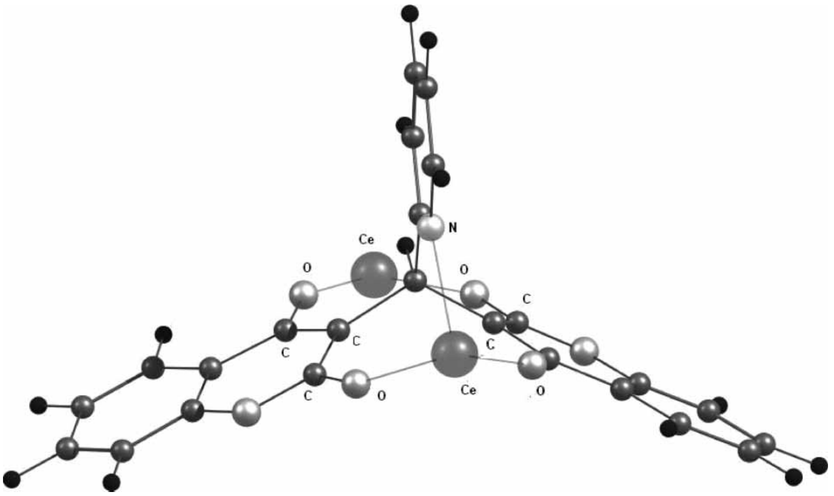


Figure 4. Model Ce(III) complex fragment, $[Ce_2(o\text{-}PyDC^{2-})]^{4+}$, optimized at B3LYP/6-31G(d) level, offering the binding mode of o-PyDC^{2-} to Ce(III) ions in the suggested polymeric structure of the complex.

explains the significant NMR shifts observed for the pyridine carbons of Ce(III) complex, as well as the low frequency shift of the ν(CN) mode in the complex Raman spectrum.

CONCLUSIONS

The coordination ability of 3,3′-(*ortho*-pyridinomethylene)di-[4-hydroxycoumarin] was proved in complexation reaction with Ce(III). The binding of *o*-PyDC to Ce(III) is realized through its deprotonated form, o-PyDC^{2-}. ^{1}H NMR, ^{13}C NMR, IR, and Raman spectroscopic data of the free ligand and its Ce(III) complex revealed that both deprotonated hydroxyl oxygen atoms and both carbonyl oxygen atoms take part in Ce(III) complex formation. The model calculations of the complex formation suggested that one deprotonated hydroxyl oxygen and one carbonyl oxygen atom of the ligand bind to one Ce(III) atom, the other hydroxyl and carbonyl oxygen atoms bind to a next Ce(III) atom forming a polymeric structure. The other coordination sites of Ce(III) are occupied from one OH and one water molecule in agreement with the general formula Ce(o-PyDC)(OH)(H_2O). The model calculations suggested further that a coordination of Ce(III) with the nitrogen atom of the pyridyl substituent is also possible due to the immediate proximity of the nitrogen atom in *ortho* position to the other coordination centers of the ligand.

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