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Characteristic Raman and IR bands of 3,3'-benzylidenebis(4-hydroxycoumarin) and its La(III), Ce(III) and Nd(III) complexes

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In the present paper we perform a detailed vibrational study of 3,3'-benzylidenebis(4-hydroxycoumarin) (phenyldicoumarol, PhDC) based on both experimental (IR and Raman) and calculated (DFT) vibrational spectra. To help the assignment of the PhDC vibrational modes, the vibrational spectrum of the monomeric building block, 4-hydroxycoumarin (4-HC), was also considered. The PhDC and 4-HC vibrational spectra were calculated and assigned at the B3LYP/6-31G* optimized geometries. The vibrational spectra of the La(III), Ce(III) and Nd(III) complexes with PhDC are discussed in a comparative study with the vibrational spectrum of the free PhDC ligand. The $\delta(\text{CCH})_{\text{ip}}$, $\delta(\text{CCH})_{\text{op}}$ and $\delta(\text{COH})_{\text{ip}}$ vibrational modes as well as in-plane phenyl- and in-plane coumarin rings deformations were observed as strong bands in the Raman spectrum of PhDC and can be considered as a characteristic for the compound. Because of the very low IR intensity, these modes were not detected in the IR spectrum. Informative ligand vibrational modes were selected and their behaviors in the Ln(III) complexes were further studied to suggest the type of the PhDC binding mode to Ln(III) ions. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: La(III); Ce(III) and Nd(III); 3,3'-benzylidenebis(4-hydroxycoumarin); cytotoxic activity; vibrational spectra; DFT

INTRODUCTION

A large number of structurally novel coumarin derivatives have been reported to show substantial cytotoxic and anti-HIV activity *in vitro* and *in vivo*. Further, it was found that lanthanide complexes with selected active hydroxycoumarin ligands retain or even improve their biological activity.^{1–8} The complexes of La(III), Ce(III) and Nd(III) with 3,3'-benzylidenebis(4-hydroxycoumarin) (PhDC) have shown strong cell-proliferation-inhibiting effects.^{7,8} The evaluation of the cytotoxic activity of the novel lanthanide complexes on HL-60 myeloid cells revealed that they are potent cytotoxic agents. The complexes were also tested on HL-60/Dox and SKW-3 cell lines. The overall results from the preliminary screening program showed that the new

Ln(III) complexes achieve 50% inhibition of the malignant cell proliferation and thus could be considered as biologically active. These findings, as well as the practical lack of cross-resistance to these agents in HL-60/Dox, motivated us to perform further pharmacological and toxicological investigations. At the same time, the promising biological activity of the compounds prompted us to perform detailed spectroscopic and theoretical investigations on their molecular and vibrational properties.

Although 3,3'-benzylidenebis(4-hydroxycoumarin) (PhDC) was reported in the literature for a long time and its crystal and molecular structures are known,⁹ there is a lack of data on its vibrational behavior. It is important to undertake a reliable vibrational assignment of PhDC to have a good basis for its comparison with the vibrational spectra of lanthanide(III) complexes with PhDC. In our previous study, we selectively discussed the vibrational spectrum of PhDC to include those vibrational modes that are sensitive to the intramolecular hydrogen bonding in the molecule.^{10,11}

In the present vibrational study we intend to gain a deeper insight into the vibrational behavior of PhDC

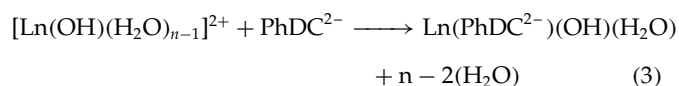
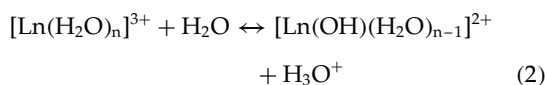
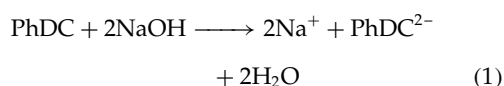
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by studying its vibrational spectra both theoretically and experimentally. A reliable assignment of the ligand vibrational modes is essential for the vibrational analysis of lanthanide(III) complexes. Informative ligand vibrational modes were selected and were further used to suggest the type of the PhDC binding mode in the Ln(III) complexes studied. A detailed interpretation of the vibrational spectrum of PhDC was done on the basis of its crystal and molecular structures.⁹ The vibrational spectrum of PhDC was calculated at B3LYP/6-31G* optimized geometry. To help the assignment of PhDC vibrational modes, the vibrational spectrum of the monomeric building block, 4-hydroxycoumarin (4-HC), was used for comparison. The vibrational spectra of La(III), Ce(III) and Nd(III) complexes were analyzed and discussed in a comparative study with the PhDC vibrational spectrum.

EXPERIMENTAL

Synthesis and analysis of the Ln(III) complexes

The lanthanide(III) complexes with PhDC were synthesized^{5,8} by the reaction of lanthanide(III) nitrate and the ligand in aqueous solution in amounts equal to a metal : ligand molar ratio of 1 : 2. As described previously, the formation of the complex may be represented by the following equations:



where Ln = La(III), Ce(III) and Nd(III), PhDC = C₂₅H₁₆O₆ and PhDC²⁻ = C₂₅H₁₄O₆²⁻.

The elemental analysis data of the Ln(III) complexes suggested the formula, Ln(PhDC²⁻)(OH)(H₂O). The formula was further confirmed by mass spectral fragmentation analysis, NMR, IR and Raman data. The results obtained were in agreement with the metal : ligand ratio of 1 : 1.

The Raman spectra of the compounds were measured in the solid state with a SPEX-Ramalog spectrometer (double monochromator with 1152 × 298 pixel CCD-camera detector) in the 4000–200 cm⁻¹ range. An argon ion laser (514.5 nm) was used for excitation. 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 an FT-IR 113 V Bruker spectrometer. For comparison, the IR spectra were also recorded 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 the cases the resolution was 1 cm⁻¹.

Computational procedure

PhDC is not a small molecule, and post Hartree-Fock methods like MP2 or higher levels could not be applied within a reasonable time. Large biomolecules require the application of less time-consuming methods. The gradient-corrected functionals with partial inclusion of the Hartree-Fock exact exchange are among the DFT methods that have reached a level of reliability, and are competitive with the most sophisticated post Hartree-Fock approaches for a number of properties. In our previous study,¹⁰ we had tested several levels of calculations for PhDC and related coumarin derivatives. The availability of X-ray diffraction data about the crystal and molecular structure of PhDC gave us the opportunity to select a reliable method for the description of its properties. Our DFT calculations were performed with Becke's three-parameter hybrid method using the correlation functional of Lee, Yang and Parr (B3LYP) (with 20% HF exact exchange mixing).^{12,13} Different basis sets were tested in the calculations: 6-31G*, 6-31+G** (Basis 1) and 6-311G* (Basis 2). The geometry analysis based on the X-ray geometry parameters of PhDC and 4-HC showed that the calculated structural parameters of the systems studied are in good agreement with the experiment even when the 6-31G* basis set was used. The average deviations of the calculated bond lengths and bond angles were: at B3LYP/6-31G*, 0.81% and 0.39%; at B3LYP with Basis1, 0.75% and 0.38%; and at B3LYP with Basis2, 0.80% and 0.39%.¹⁰ It should be mentioned that the geometry optimization with the larger basis sets for PhDC (Basis 1 and Basis 2) took very long, but the results were not much better. Therefore, taking into account the size of the PhDC molecule, the B3LYP/6-31G* level was accepted as a good compromise. Moreover, the lower computational cost of B3LYP compared with other correlated methods allowed us to calculate the harmonic vibrational wavenumbers of the large systems studied. Since the method systematically underestimates the calculated wavenumbers, scaling factors are required to improve the coincidence with the experimental values. To assign the calculated wavenumbers to the approximate vibrational descriptor, the vibrational modes were analyzed by means of the atom movements calculated in Cartesian coordinates. To help the assignment, visualization of the vibrational modes was performed using the ChemCraft program. The scale factors used were 0.956 for PhDC and 0.972 for 4-HC. All calculations were performed using the GAUSSIAN98 program package.¹⁴

RESULTS AND DISCUSSION

Geometry optimization

The PhDC and 4-HC optimized geometries calculated at B3LYP/6-31G* level of the theory¹⁰ are shown in Fig. 1. Selected structural parameters for PhDC compared with those of 4-HC are given in Table 1. The molecular asymmetry of PhDC obtained from X-ray diffraction analysis was

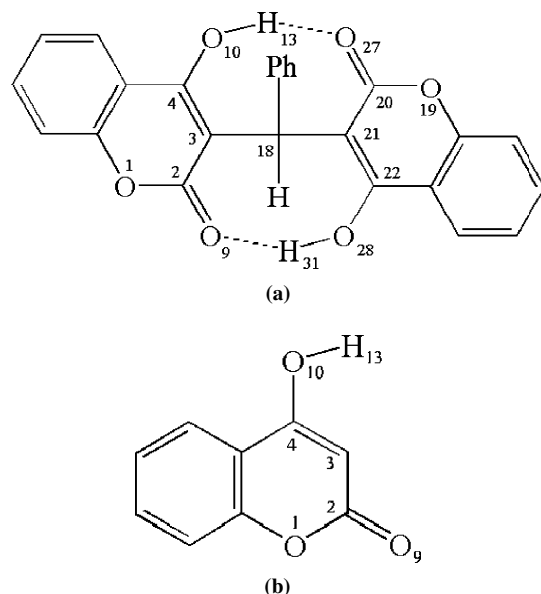


Figure 1. Optimized geometries of 3,3'-benzylidenebis(4-hydroxycoumarin) (PhDC) (a) and of 4-hydroxycoumarin (HC) (b).

Table 1. Selected calculated and experimental bond distances (Å) for PhDC and 4-HC

Name definition ^a	PhDC		4-HC	
	Calcd. B3LYP/ 6-31G*	Exptl ⁹	Calcd. B3LYP/ 6-31G*	Exptl ¹⁵
O ₁₀ ... O ₂₇	2.638	2.624	–	–
O ₉ ... O ₂₈	2.696	2.720	–	–
C ₂₀ =O ₂₇	1.229	1.221	1.208	1.20
C ₂ =O ₉	1.234	1.222	1.208	1.20
O ₁₀ –H ₁₃	1.002	–	0.971	–
O ₂₈ –H ₃₁	1.000	–	0.971	–
(C ₂ –O ₁)	1.373	1.366	1.402	1.37
(C ₁₂ –O ₁)	1.366	1.384	1.362	1.37
(C ₂₀ –O ₁₉)	1.377	1.368	1.402	1.37
(C ₃₀ –O ₁₉)	1.367	1.379	1.362	1.37
C ₄ –O ₁₀ (–H ₁₃)	1.327	1.333	1.353	1.35
C ₂₂ –O ₂₈ (–H ₃₁)	1.330	1.339	1.353	1.35

^a The atom numbering is given in Fig. 1.

reproduced surprisingly well despite the large size of the molecule. The O ... O distances in PhDC were calculated¹⁰ with comparatively low deviations from experiment, 0.014 and 0.026 Å. The comparison of the calculated structural parameters for PhDC and 4-HC showed that in PhDC the differences were obtained in O–H, C=O and C–O bond length distances. Because of participation in hydrogen bonding, both hydroxyl and carbonyl groups in PhDC showed longer O–H (0.971 Å → 1.002/1.000 Å) and C=O

(1.208 Å → 1.229/1.234 Å) bond lengths and shorter C–O (1.353 Å → 1.327/1.330 Å) bond length (Table 1). The differences in the bond lengths of PhDC and 4-HC produced differences in the wavenumbers of the corresponding vibrational modes and the informative ones are discussed below.

Vibrational analysis

The IR spectra of PhDC and its La(III) and Ce(III) complexes are presented in Fig. 2. The Raman spectrum of PhDC (in selected regions) compared with the Raman spectra of La(III), Ce(III) and Nd(III) complexes are shown in Fig. 3. It should be mentioned that the Raman spectra of the Ln(III) complex measured with argon ion laser (514.5 nm laser line) were very poor in quality with strong backgrounds. Unfortunately, the same quality of the spectra was obtained with a krypton ion laser (647.1 nm laser line) also. The reason for obtaining poor Raman spectra of the complexes is that the Ln(III) complexes based on PhDC reveal high luminescence. The lanthanide trivalent cations have electronic configuration (Xe)4f^{*n*}, where *n* varies from 1 (Ce³⁺) to 14 (Lu³⁺). The f–f electron transitions that are responsible for the luminescence properties of the lanthanide ions are not allowed. However, the PhDC ligand is an organic chromophore acting like some sort of 'antenna' that efficiently absorbs and transfers light to the encapsulated lanthanide ion, which is then able to emit its characteristic luminescence. Thus, despite the ligand in the lanthanide complexes behaving independently like the inherent coumarin derivative and the ground state of the lanthanide ion in the complex not being perturbed by the ligand, the Ln(III) complexes of PhDC revealed high luminescence and, therefore, poor Raman spectra. Therefore, the vibrational analysis of the La(III), Ce(III) and Nd(III) complexes was based mainly on their IR spectra.

In contrast, the Raman spectrum of PhDC was of good quality and hence its comparison with the IR spectrum of PhDC was feasible. Comparison of the IR and the Raman spectra of PhDC showed that additional bands appeared in the Raman spectrum and they revealed very high intensities. Thus, by additionally studying the Raman spectrum, we were able to perform a reliable assignment of the vibrational modes of PhDC. The analysis further helped the assignment of the IR and Raman spectra of La(III), Ce(III) and Nd(III) complexes with PhDC. Selected bands that showed different band intensities in the IR and Raman spectra of PhDC, compared with the calculated ones as well as with the corresponding IR and Raman bands of La(III), Ce(III) and Nd(III) complexes, are given in Table 2. The full list of the calculated (unscaled/scaled) vibrational wavenumbers and their assignment, as well as the available experimental IR and Raman spectra of PhDC, La(III), Ce(III) and Nd(III) complexes, are available on request.

To give reliable assignments of the ν(O–H) and ν(C=O) vibrational modes of PhDC at the starting point, we used

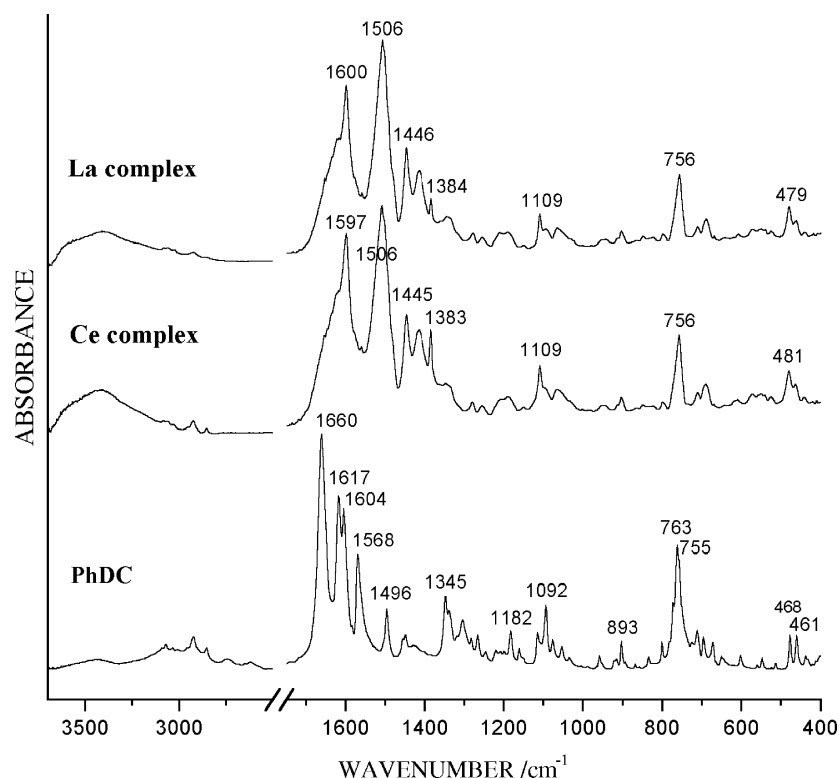


Figure 2. IR spectra of PhDC and its Ce(III) and La(III) complexes.

results from the vibrational analysis of 4-HC at B3LYP/6-31G* optimized geometry.¹⁰ The O–H and C=O group in 4-HC are free, and the experimental (gas-phase)¹⁶ and calculated IR spectrum of 4-HC supplied information about the $\nu(\text{O–H})$ and $\nu(\text{C=O})$ positions when the (O–H) and (C=O) groups were not involved in hydrogen bonding interactions: 3633 cm^{-1} and 1814 cm^{-1} , respectively. In PhDC, both O–H and C=O groups are hydrogen bonded, and the experimental and calculated $\nu(\text{O–H})$ and $\nu(\text{C=O})$ modes showed negative (red) wavenumber shifts; they were observed at 3074 and 3032 cm^{-1} in the IR spectrum and at 3073 and 3012 cm^{-1} in the Raman spectrum (Table 2). The two bands were calculated at 3074 and 3023 cm^{-1} (scaled values in Table 2). The lower wavenumber band of $\nu(\text{O}_{10}\text{–H}_{13})$ at 3023 cm^{-1} was calculated with lower intensity (378.1) as compared with the $\nu(\text{O}_{28}\text{–H}_{31})$ band at 3074 cm^{-1} (1076.8). As can be seen, both the experiment and the calculations showed larger negative (red) shift of the $\nu(\text{O}_{10}\text{–H}_{13})$ mode (-601 cm^{-1} , exptl value, -602 cm^{-1}) as compared to $\nu(\text{O}_{28}\text{–H}_{31})$ (-559 cm^{-1} , exptl value, -560 cm^{-1}).¹⁰ The larger red shift of $\nu(\text{O}_{10}\text{–H}_{13})$ in comparison with that of $\nu(\text{O}_{28}\text{–H}_{31})$ was in line with the higher lengthening of the $r(\text{O}_{10}\text{–H}_{13})$, $+0.0306\text{ \AA}$, in comparison with that of $r(\text{O}_{28}\text{–H}_{31})$, 0.0286 \AA (as compared to $r(\text{O–H})$ in 4-HC), Table 1. The results obtained correlated with the experimental and calculated $\text{O}\cdots\text{O}$ distances and predicted stronger $\text{O}_{10}\text{–H}_{13}\cdots\text{O}_{27}$ hydrogen bond interaction in comparison with that of the $\text{O}_{28}\text{–H}_{31}\cdots\text{O}_9$.¹⁰ In agreement with the stronger $\text{O}_{10}\text{–H}_{13}\cdots\text{O}_{27}$ hydrogen bonding, both

the in-plane $\delta(\text{COH})$ modes in PhDC, $\delta(\text{C}_4\text{O}_{10}\text{H}_{13})_{\text{ip}}$ and $\delta(\text{C}_{22}\text{O}_{28}\text{H}_{31})_{\text{ip}}$ were observed and calculated to be higher as compared to the corresponding experimental (1213 cm^{-1}) and calculated (1203 cm^{-1}) values in 4-HC; they appeared at 1345 and 1336 cm^{-1} in IR and at 1346 and 1336 cm^{-1} in Raman, the calculated values (scaled) being 1309 and 1297 cm^{-1} (Table 2).

The carbonyl stretching vibrational mode, $\nu(\text{CO})$, revealed two components with different intensities in the IR and Raman spectra of PhDC (Table 2). The first component was observed with high intensity in the IR spectrum (1660 cm^{-1}) but was not detected in the Raman spectrum. Conversely, the second component was not observed in the IR spectrum (or it was overlapped because of the strong $\nu(\text{CC})$ absorption in this region) but revealed significant intensity in the Raman spectrum at 1646 cm^{-1} .

In La(III), Ce(III) and Nd(III) Raman spectra, the first component of the carbonyl stretching vibration at 1660 cm^{-1} was not detected. In the IR spectra of the complexes it was shifted to lower wavenumbers and appeared as shoulders at 1621 , 1619 , 1625 cm^{-1} for the three complexes, respectively. The second component of the carbonyl stretching vibration (observed in the PhDC Raman spectrum at 1646 cm^{-1}) was detected only as a shoulder in the IR spectrum (at 1640 cm^{-1}). The second component, however, revealed a strong intensity in the IR spectra of the complexes; it shifted by 40 cm^{-1} to lower wavenumbers (at about $1597\text{--}1600\text{ cm}^{-1}$) and could be considered as the characteristic band for the complexes

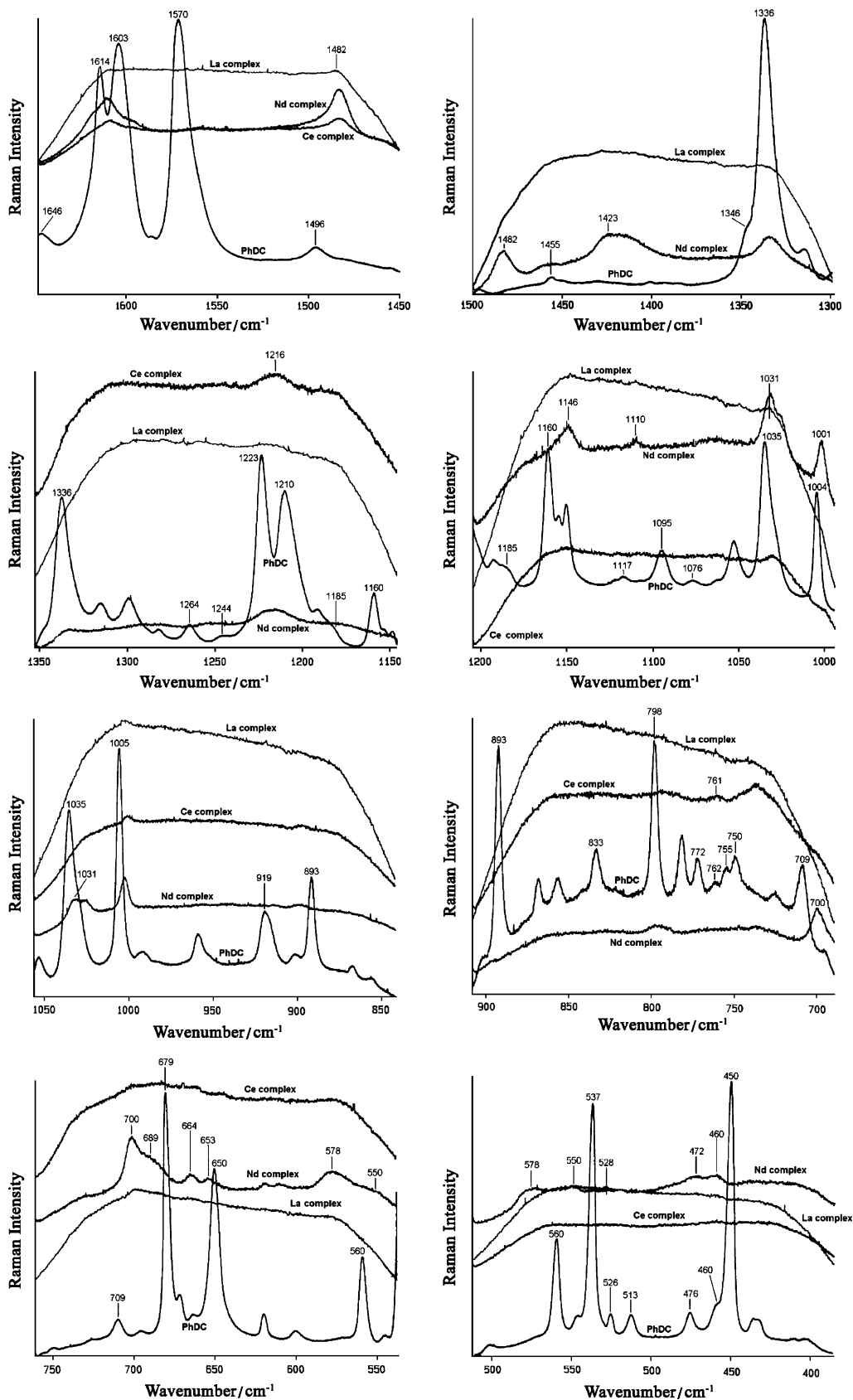


Figure 3. Raman spectra of PhDC and its Ce(III), La(III) and Nd(III) complexes in selected regions.

Table 2. Selected calculated and experimental wavenumbers (cm^{-1}) of PhDC and its La(III), Ce(III) and Nd(III) complexes

Calcd unscaled/ scaled ^a (cm ⁻¹)	PhDC		La complex		Ce complex		Nd complex		Assignment
	Exptl		Exptl		Exptl		Exptl		
	$\nu_{\text{IR}}(\text{cm}^{-1})$	$\nu_{\text{R}}(\text{cm}^{-1})$	$\nu_{\text{IR}}(\text{cm}^{-1})$	$\nu_{\text{R}}(\text{cm}^{-1})$	$\nu_{\text{IR}}(\text{cm}^{-1})$	$\nu_{\text{R}}(\text{cm}^{-1})$	$\nu_{\text{IR}}(\text{cm}^{-1})$	$\nu_{\text{R}}(\text{cm}^{-1})$	
3216/3074	3074 m	3073 vs	3061 w	–	3059 w	–	3055 w	–	$\nu(\text{OH}_{31})$
3162/3023	3032 w	3012 w	3026 w	–	3026 w	–	3024 w	–	$\nu(\text{OH}_{13})$
1742/1665	1660 vs	1661 vw	1619 sh	–	1621 sh	–	1625 sh	–	$\nu_{\text{as}}(\text{C}=\text{O})$
1715/1640	1640 sh	1646 m	1600 s	–	1597 s	–	1598 s	–	$\nu_{\text{s}}(\text{C}=\text{O})$
1670/1596	1617 s	1614 vs	1619 sh	1617 sh	1621 sh	1617 sh	1620 sh	1617 sh	$\nu(\text{CC})_{\text{c}}$
1666/1593	1604 s	1603 vs	1600 s	1610 m	–	1608 m	–	1610	$\nu(\text{CC})_{\text{c}}$
1653/1580	1568 s	1570 vs	1576 sh	–	–	–	–	–	$\nu(\text{CC})_{\text{c}}$
1612/1541	–	–	1508 vs	–	1506 vs	–	1504 vs	–	$\nu(\text{CC})_{\text{c}} + \delta(\text{CCH})_{\text{ip(c)}}$
1544/1476	1496 m	1496 w	–	1482 m	–	1482 m	–	1482 m	$\nu(\text{CC})_{\text{Ph}} + \delta(\text{CCH})_{\text{ip}}$
1506/1439	1456 w	1455 w	1446 s	–	1445 s	–	1448 s	–	$\nu(\text{CO}) + \delta(\text{COH})_{\text{ip(c)}}$
1493/1427	1429 w	1430 w	1423 m	–	–	–	1428 w	1423 m	$\nu(\text{CO}) + \delta(\text{COH})_{\text{ip(c)}}$
1388/1327	1386 vw	1385 w	1384 s	–	1383 s	–	1377 s	–	$\delta(\text{CCH})_{\text{met}} + \nu(\text{CC})$
1369/1309	1345 s	1346 w	–	–	–	–	–	–	$\delta(\text{COH})_{\text{ip(c)}} + \nu(\text{CO})$
1357/1297	1336 m	1336 vs	–	–	–	–	–	–	$\delta(\text{COH})_{\text{ip(c)}} + \nu(\text{CO})$
1325/1267	1265 m	1264 m	–	1264 w	–	1260 w	–	1264 w	$\delta(\text{CCH})_{\text{ip(Ph)}}$
1317/1259	1247 w	1244 w	1253 m	–	1253 m	–	1255	–	$\delta(\text{CCH})_{\text{ip(Ph)}}$
1297/1240	1218 w	1223 vs	–	–	–	–	–	–	$\delta(\text{CCH})_{\text{ip(Ph)}}$
1286/1229	1210 w	1210 vs	1210 m	1216 br	1206 m	1216 br	1216 m	1216 br	$\delta(\text{CCH})_{\text{ip(Ph)}}$
1254/1199	1182 m	1185 w	1191 m	1189 vw	1188 m	1189 vw	1182 m	–	$\nu(\text{CO})_{\text{lac}} + \delta(\text{CCH})_{\text{ip(c)}}$
1241/1186	1160 w	1160 s	1150 w	1146 vw	1150 w	1150 vw	1159 w	1148 w	$\nu(\text{CO})_{\text{lac}} + \delta(\text{CCH})_{\text{ip(c)}}$
1183/1133	1114 m	1117 w	–	–	–	–	–	–	$\delta(\text{CCH})_{\text{ip(c)}}$
1101/1052	1092 s	1095 m	1109 s	1110 w	1109 s	–	1108 s	1110 w	$\nu(\text{CO})_{\text{lac}} + \nu(\text{CC})_{\text{met}}$
1075/1028	1073 w	1076 w	1065 br	1063 w	1066 br	1063 w	1065 br	1064 w	$\nu(\text{CO})_{\text{lac}} + \nu(\text{CC})_{\text{met}}$
1061/1013	1034 w	1035 vs	1029 w	1031 m	1031 w	1030 m	1036 m	1031 m	$\delta(\text{CCH})_{\text{ip(c)}}$
1019/974	1000 w	1005 vs	1001 vw	1001 m	1004 vw	1000 m	–	1001 m	Ring _{ip(Ph)}
965/922	922 w	919 s	–	–	–	–	–	–	$\delta(\text{CCH})_{\text{op(c)}}$
933/892	893 w	893 vs	–	898 w	–	898 w	–	898 w	Ring _{ip(c)}
882/843	834 w	833 s	849 w	–	846 w	–	855 w	–	$\delta(\text{CCH})_{\text{op(c)}}$
863/825	801 m	798 vs	823 w	–	823 w	–	824 w	–	$\delta(\text{CCH})_{\text{op(Ph)}}$
835/798	772 m, sh	772 m	–	–	–	–	–	–	$\delta(\text{COH})_{\text{op}}$
823/787	763 s	762 w	–	–	–	–	–	–	$\delta(\text{COH})_{\text{op}}$
798/763	755 s	755 m	756 s	761 w	756 s	761 w	757 s	–	Ring _{op(c)}
784/750	750 sh	750 m	–	–	–	–	–	–	$\delta(\text{CCH})_{\text{op(c)}}$
743/710	711 m	709 m	711 m	700 w	709 m	700 w	712 m	700 m	Ring _{op(c)}
709/678	–	679 vs	690 m	–	689 m	664 vw	691 m	664 vwm	Ring _{op(Ph)}
668/639	650 w	650 vs	642 w	–	642 vw	–	651 w	653 w	Ring _{ip(c)}
616/589	560 w	560 s	572 w	578 m	572 w	578 w	572 m	578 m	Ring _{ip(ph)}
561/536	530 vw	537 vs	549 w	550 w	549 w	550 w	541 w	550 w	Ring _{ip(c)}
551/526	525 vw	526 m	539 w	537 vw	537 w	537 vw	541 w	537 w	Ring _{ip(c)}
540/516	514 w	513 m	525 w	528 w	525 w	528 w	523 w	528 w	Ring _{op(c)}
522/499	478 s	476 m	479 m	472 w	481 m	–	480 m	472 w	t(CCC(H)C)
489/468	461 s	460 sh	462 m, sh	460 w	461 m, sh	460 w	466 m, sh	460 w	t(CCC(H)C)
470/449	450 sh	450 vs	–	–	–	–	–	–	t(CCC(H)C)
379/362	–	372 s	–	–	–	–	–	–	t(CCCC)
299/286	–	293 m	–	–	–	–	–	–	Ring _{ip(c)}

br, broad; ip, in-plane; op, out-of-plane; Ph, Phenyl; (c), coumarin; t, torsion; s, strong; vs, very strong; w, weak; vw, very weak; sh, shoulder; m, medium.

^a scaled IR wavenumbers, scaling factor 0.956.

studied. The behavior of this component confirmed the formation of the La(III), Ce(III) and Nd(III) complexes with PhDC through the carbonyl oxygen.

The $\nu(\text{CC})_{\text{c}}$ modes give rise to strong absorptions in IR (1617, 1604 and 1568 cm^{-1}) and to very strong bands in the Raman (1614, 1603 and 1570 cm^{-1}) spectrum (Table 2). These bands slightly changed their positions in the spectra of the complexes and were very weak. The $\nu(\text{CC})_{\text{Ph}}$ mode coupled with $\delta(\text{CCH})_{\text{ip}}$ was observed as a weak band in the IR and Raman spectra of PhDC but with medium intensity in the Raman spectra of the La(III), Ce(III) and Nd(III) complexes. No components were observed in the IR spectra of the complexes.

The $\nu(\text{CO})$ vibrational modes in PhDC coupled with $\delta(\text{COH})_{\text{ip(c)}}$ were assigned to the weak bands at 1456 and 1429 cm^{-1} . The first component revealed strong absorption in the IR spectra of La(III), Ce(III) and Nd(III) complexes, which could be explained with $\nu(\text{CO})$ contribution. Two bands due to $\delta(\text{COH})_{\text{ip(c)}}$ were observed at 1345 and 1336 cm^{-1} in the IR spectrum and at 1346 and 1336 cm^{-1} in the Raman spectrum. It should be mentioned that the bands showed completely different intensities in the IR and Raman spectra; the first component produced a strong absorption in the IR spectrum (1345 cm^{-1}), and the second one was found to be very strong and hence a characteristic band in the Raman spectrum (1336 cm^{-1}). Since PhDC acts as a deprotonated ligand in La(III), Ce(III) and Nd(III) complexes, these two bands were not observed in the metal complex spectra, and this finding confirmed their assignment.

The stretching lactone $\nu(\text{CO})$ vibrations give rise to four bands both in the Raman and IR spectra. Only one mode appeared in the Raman spectrum as a strong band (at 1160 cm^{-1}), and it can be considered as another characteristic band for PhDC. The second stretching lactone $\nu(\text{CO})$ component appeared as a strong IR band (at 1092 cm^{-1}). The other two components were observed with moderate intensity in the Raman and IR spectra. In La(III), Ce(III) and Nd(III) complexes, the lactone $\nu(\text{CO})$ modes showed shifts and confirmed the coordination of the metal ion through the oxygen of the neighboring carbonylic group.

The $\delta(\text{CCH})_{\text{ip}}$ and $\delta(\text{CCH})_{\text{op}}$ modes are very weak in the IR spectrum of PhDC and hence their assignment is not reliable enough if we consider only the IR spectrum. However, these modes exhibited strong or medium intensity in the PhDC Raman spectrum. Strong Raman bands due to $\delta(\text{CCH})_{\text{ip}}$ of the phenyl ring were observed at 1223 and 1210 cm^{-1} . However, these bands do not retain their activity in the complex spectra. The $\delta(\text{CCH})_{\text{ip}}$ modes of the coumarin fragment give rise to a medium IR band at 1114 cm^{-1} and to a strong Raman band at 1035 cm^{-1} . In agreement with the literature data for *p*-substituted benzene, the very strong Raman band at about 1000 cm^{-1} is a phenyl ring deformation mode known as 'the star of David'.¹⁷ The coumarin ring deformation mode, $\text{Ring}_{\text{ip(c)}}$, was detected as a strong Raman and weak IR band at 893 cm^{-1} . Further, the

$\delta(\text{CCH})_{\text{op(c)}}$ and $\delta(\text{CCH})_{\text{op(Ph)}}$ modes were observed as strong bands in the Raman spectrum at 919, 833 and 798 cm^{-1} .¹⁸ Owing to the high intensity of these bands in the Raman spectrum they could be considered as characteristic for PhDC. Strong and characteristic Raman bands were detected in the 679–526 cm^{-1} region (679, 650, 560, 537, 526 and 513 cm^{-1}), and on the basis of vibrational analysis they were assigned to in-plane or out-of-plane ring deformations of the phenyl- and coumarin moieties, Fig. 3 and Table 2. It should be mentioned that all of them were obtained as weak or very weak bands in the IR spectrum of PhDC and could have been omitted from being considered if the PhDC Raman spectrum was not measured and interpreted.

As seen from Fig. 2, La(III) and Ce(III) complexes of PhDC showed very similar IR spectra. The same holds for the Raman spectra although they are very weak and not very informative (with the exception of Nd(III) spectrum), Fig. 3. The similarity in the vibrational spectra of the complexes studied is in agreement with the suggestion that the complexes probably have a similar coordination polyhedron and molecular structure.

Unfortunately, we were not able to obtain single crystals with diffraction power for the determination of the crystal and molecular structure of the complexes. Therefore, the molecular polyhedron of the lanthanide (III) complexes was suggested on the basis of the vibrational analysis of the free ligand (including DFT calculations) and molecular modeling of the complex fragment. Firstly, the binding sites in PhDC were predicted on the basis of the behavior of selected vibrational modes, as described above. Further, theoretical estimation of the binding sites was performed with calculations of Fukui functions and molecular electrostatic potential both for the neutral (PhDC) and for the deprotonated (PhDC^{2-}) ligand species.⁸ The calculations predicted that the most probable reactive sites for electrophilic attack (in particular for metal binding) are the carbonylic (O_{27} , O_9) and the deprotonated hydroxylic oxygen atoms (O_{10} , O_{28}).⁸ The theoretical predictions were in agreement with NMR, IR and Raman spectral data, which also predicted that the carbonylic and deprotonated hydroxylic oxygen atoms are involved in the metal binding. As was mentioned in the Experimental section, the variety of data, such as elemental analysis, conductivity measurement, IR, Raman, NMR and mass spectra, has shown that the metal:ligand ratio is 1:1 and hence the suggested formula unit is $\text{Ln}(\text{PhDC}^{2-})(\text{OH})(\text{H}_2\text{O})$.^{5,8} We further assume that in the Ln(III) complexes with PhDC one metal ion coordinates to the carbonylic (O_9) and deprotonated hydroxylic oxygen atoms (O_{28}) of one ligand. The same ligand further binds to other Ln(III) ions, forming the structure shown in Fig. 4. The other two coordination sites of Ln(III) are occupied by hydroxylic oxygen (OH) and water oxygen (H_2O). Thus, in agreement with the theory and experiment, PhDC acts as a tetradentate ligand in the complexes with Ln(III) ions (one

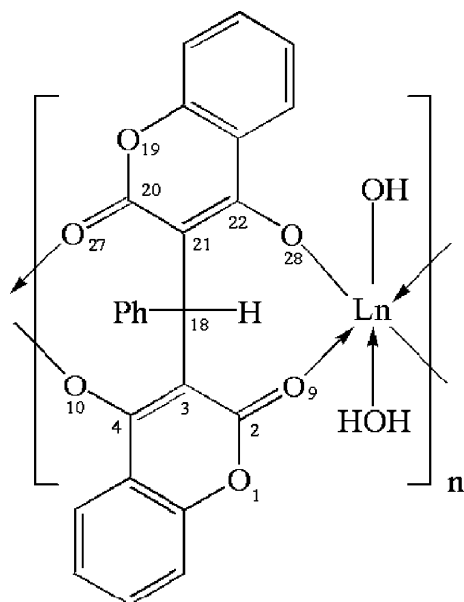


Figure 4. Suggested PhDC binding mode in Ce(III), La(III) and Nd(III) complexes.

ligand binds two different Ln(III) like a bridge), the metal ion is six coordinate and the metal:ligand ratio is 1:1.

CONCLUSIONS

Both Raman and IR spectra of PhDC have shown strong bands due to a number of characteristic modes and are very informative for studying the coordination behavior of PhDC. These are: the second Raman $\nu(\text{C}=\text{O})$ component at 1646 cm^{-1} ; three $\nu(\text{CC})$ components at 1614 , 1603 and 1570 cm^{-1} ; one $\delta(\text{COH})_{\text{ip(c)}}$ component at 1336 cm^{-1} ; two $\delta(\text{COH})_{\text{ip(Ph)}}$ components at 1223 and 1210 cm^{-1} ; one lactone $\nu(\text{CO})$ mode at 1160 cm^{-1} ; one $\delta(\text{CCH})_{\text{ip(c)}}$ at 1035 cm^{-1} ; two $\delta(\text{COH})_{\text{op(c)}}$ at 919 and 833 cm^{-1} ; one $\text{ring}_{\text{ip(c)}}$ at 893 cm^{-1} ; two $\delta(\text{COH})_{\text{op(Ph)}}$ at 798 and 679 cm^{-1} ; two $\text{ring}_{\text{ip(c)}}$ at 650 and 537 cm^{-1} ; two $\delta(\text{COH})_{\text{ip(Ph)}}$ at 1005 and 560 cm^{-1} . The bands mentioned above, however, do not retain their intensity in La(III), Ce(III) and Nd(III) complexes and could not serve as characteristic for these complexes. In the Raman spectra of the complexes studied the following bands were detected: $\nu(\text{CC})$ at $1608\text{--}1610\text{ cm}^{-1}$; $\nu(\text{CC})_{\text{Ph}}$ at 1482 cm^{-1} ; $\delta(\text{CCH})_{\text{ip(c)}}$ at 1030 cm^{-1} ; $\delta(\text{COH})_{\text{ip(Ph)}}$ at 1000 cm^{-1} ; $\text{ring}_{\text{op(Ph)}}$ at 689 cm^{-1} and a torsion at 476 cm^{-1} . The weak Raman bands, however, revealed significant intensity in the IR spectrum. Therefore, PhDC and its La(III), Ce(III) and Nd(III) complexes should be characterized both with IR and Raman spectra. The vibrational study of PhDC and its lanthanide(III) complexes

based on both Raman and IR spectral data is informative and useful for arriving at the metal–ligand binding mode.

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