

## Vibrational spectral characterization of new La(III) and Dy(III) complexes

I. KOSTOVA<sup>A\*</sup>, I. HUBERT JOE<sup>B</sup>, S. CÎNTĂ PÎNZARU<sup>C</sup>

<sup>a</sup>*Department of Chemistry, Faculty of Pharmacy, Medical University, 2 Dunav St., Sofia 1000, Bulgaria*

<sup>b</sup>*Center for Molecular and Biophysics Research, Department of Physics, Mar Ivanios College, Thiruvananthapuram - 695015, Kerala, India.*

<sup>c</sup>*Babes-Bolyai University, Molecular Spectroscopy Department, Cluj-Napoca, Romania*

New La(III) and Dy(III) complexes of 4-hydroxy-3[1-(4-nitrophenyl)-3-oxobutyl]-2H-1-benzopyran-2-one (Acenocoumarol) were characterized using FT-IR, FT-Raman spectral analyses. The infrared and Raman spectra of the ligand were predicted theoretically from the calculated intensities using B3LYP density functional theory (DFT) methods. The DFT calculated harmonic vibrational wavenumbers including IR and Raman scattering activities for the ligand were in good agreement with the experimental data, a complete vibrational assignment being proposed. Significant differences in the IR spectra of the complexes were observed as compared to the spectrum of the ligand. A comparative analysis of the Raman spectra of the complexes with that of the free ligand allowed a straightforward assignment of the vibrations of the ligand groups involved in coordination. The detailed vibrational study gave evidence for the bidentate binding mode of the ligand to lanthanide ions.

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### 1. Introduction

Coumarin derivatives are of great interest owing to their vital and diverse role in the fields of biology, medicine, industry, botany and chemistry [1-5]. Comprehensive reviews on the pharmacological activity of a large variety of coumarin derivatives have been recently reported, pointing out the importance of structure-activity relationship [6-9]. Many naturally occurring coumarin derivatives have considerable interest in terms of biological and potential drugs. The pharmacological activity of lots of coumarin derivatives has been extensively investigated. Some coumarin derivatives are found to have antimicrobial, antifungal, antitubercular activities and antitumor promoting effect. Thus, coumarin derivatives are the subject of considerable pharmaceutical and chemical interest.

In recent years considerable interest has arisen in the chemistry of coordination complexes of coumarins [10-13]. The ability of coumarin derivatives to bind metal ions has reached an increasing interest, since their pharmacological response was found to be improved upon complexation. Much of the attention has been focused mainly on the synthesis and identification of such complexes, whereas spectroscopic and structural studies are limited. To evaluate the relationship between the biological activity and molecular structure, the knowledge of their electronic structure and spectral properties are particularly important. An adequate understanding of the vibrational fundamentals of coumarin derivatives may provide help in the study of biological activities. Systematic studies reflecting the fundamental vibrations of coumarin derivatives and their metal complexes are lacking.

As a part of our continuing work on the synthesis, characterization and applications of lanthanide(III) complexes [14-21], it was observed that changes in ligands, lanthanides and reaction conditions had profound effects on selectivity and activity of the products obtained.

Considering the biological and commercial implications of the compound Acenocoumarol (4-hydroxy-3-[1-(4-nitrophenyl)-3-oxobutyl]-2H-1-benzopyran-2-one), we analyzed the fundamental vibrations of this ligand and its lanthanide complexes in detail using the FTIR and FT-Raman spectra.

Acenocoumarol (4-hydroxy-3-[1-(4-nitrophenyl)-3-oxobutyl]-2H-1-benzopyran-2-one), Warfarin (4-hydroxy-3-(3-oxo-1-phenylbutyl)-2H-1-benzopyran-2-one) and Coumachlor (4-hydroxy-3-[1-(4-chlorophenyl)-3-oxobutyl]-2H-1-benzopyran-2-one) as well as other 4-hydroxycoumarin derivatives possess anticoagulant, anticancer and anti-HIV activities. Nowadays, many studies report coumarin derivatives and their complexes with rare earth metals, which possess biological activity. Due to their high sensitivity to the structural changes, the FT-Raman and FT-IR spectroscopy were employed for a complete vibrational characterization of the Acenocoumarol sodium structure as well as of the newly synthesized lanthanide complexes. The recorded spectra and the marker bands of characteristic functional groups are identified, in order to use them as data bank for further application in trace analysis of rare-earth complexes of Acenocoumarol, synthesized by us. 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. To the best of our knowledge, no detailed vibrational analysis data for Acenocoumarol sodium were yet published. With this study we intend to gain a deeper insight into the vibrational spectra and to suggest further the type of binding mode of this biologically active molecule in complex formation.

In the present study we performed the investigation of the coordination ability of 4-hydroxy-3-[1-(4-nitrophenyl)-3-oxobutyl]-2H-1-benzopyran-2-one in complexation reaction with lanthanum(III) and dysprosium(III), characterized by IR- and Raman spectroscopy. The most sensitive to coordination modes of the ligand have been assigned, discussed and compared with those of the lanthanide complexes. The synthesis of lanthanide(III) complexes with 4-hydroxy-3-[1-(4-nitrophenyl)-3-oxobutyl]-2H-1-benzopyran-2-one is taken into consideration with cytotoxic screening and further pharmacological study.

## 2. Experimental

### *Computational details*

Quantum chemical calculations were used for the Acenocoumarol sodium salt to carried out the vibrational wavenumbers with the 2003 version of the Gaussian suite of program [22] using the B3LYP functional [23,24] supplemented with the standard 6-31G\* basis set (referred to as DFT calculations). The calculated vibrational frequencies were scaled down by using the scaling factor 0.9613 to offset the systematic error caused by neglecting anharmonicity and electron density.

### *Chemistry*

The compounds used for preparing the solutions were Merck (Germany) products, p.a. grade:  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Dy}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  and 4-hydroxy-3-[1-(4-nitrophenyl)-3-oxobutyl]-2H-1-benzopyran-2-one (Acenocoumarol), Fig. 1. 4-Hydroxy-3-[1-(4-nitrophenyl)-3-oxobutyl]-2H-1-benzopyran-2-one sodium salt (Acenocoumarol sodium) was used as a ligand for the preparation of metal complexes.

The synthesis, analytical and spectral procedures for the characterization of sodium salt of the ligand 4-hydroxy-3-[1-(4-nitrophenyl)-3-oxobutyl]-2H-1-benzopyran-2-one (Acenocoumarol sodium salt) have been presented by us earlier [25]. The compound has been characterized and identified on the basis of elemental analysis, conductivities, and NMR-spectroscopy.

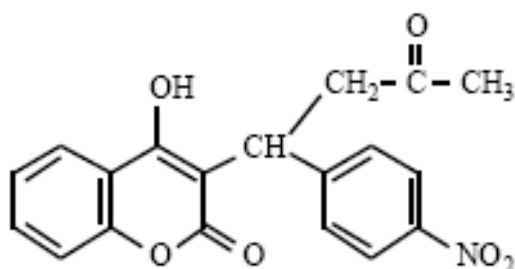


Fig. 1. The molecular structure of Acenocoumarol ( $C_{19}H_{15}NO_6$ ).

The complexes were synthesized by mixing water solutions of the respective Ln(III) salts and the ligand, in amounts equal to metal: ligand molar ratio of 1: 3. At the moment of mixing of the solutions, precipitates were obtained. The precipitates were filtered, washed several times with water and dried in a desiccator to constant weight. The complexes were insoluble in water, slightly soluble in methanol and ethanol and well soluble in DMSO.

#### *Analytical and spectral methods and instruments*

The carbon, hydrogen and nitrogen were determined by elemental analysis. The water content was determined by Metron Herizall E55 Karl Fisher Titrator and thermogravimetrically. The metal ion was determined after mineralisation and thermogravimetrically. The presence of sodium ion was checked up by means of flame photometry.

FT-IR spectra of the powder samples of Acenocoumarol sodium salt and its complexes were recorded using a FT-IR Equinox 55 Bruker spectrometer with an attenuated total reflectance (ATR) module.

An integrated FRA-106 S Raman module was employed for recording the FT-Raman spectra, using a Nd:YAG laser operating at 1064 nm line for excitation. The laser power was 300 mW and 50 scans were collected for each spectrum. The detection of the Raman signal was carried out with nitrogen cooled Ge detector. The spectral resolution was  $2\text{ cm}^{-1}$ .

### **3. Results and discussion**

#### **3.1. Coordination ability of 4-hydroxy-3-[1-(4-nitrophenyl)-3-oxobutyl]-2H-1-benzopyran-2-one to Ln(III)**

Reaction of Ln(III) and 4-hydroxy-3-[1-(4-nitrophenyl)-3-oxobutyl]-2H-1-benzopyran-2-one afforded complexes which were found to be quite stable both in solid state and in solution. They are insoluble in water and most of the common organic solvents and slightly soluble in dimethylsulfoxide. Elemental analysis data for the La(III) and Dy(III) complexes of Acenocoumarol: Found/calculated (%): La(L)<sub>3</sub>.6H<sub>2</sub>O: C- 52.40/52.49; H- 4.28/4.14; N- 3.38/3.22; H<sub>2</sub>O- 8.33/8.29; Ln- 10.82/10.67; Dy(L)<sub>3</sub>.6H<sub>2</sub>O: C- 51.89/51.54; H- 4.30/4.07; N- 2.90/3.16; H<sub>2</sub>O- 8.19/8.14; Ln- 11.93/12.21. The elemental analysis data of the Ln(III) complexes obtained are in agreement with the formula, Ln(L)<sub>3</sub>.nH<sub>2</sub>O, where L = C<sub>19</sub>H<sub>14</sub>NO<sub>6</sub><sup>-</sup>. The analytical data observed for the new complexes support the stoichiometry.

#### **3.2. Vibrational spectral analysis**

The vibrational spectral analysis of Acenocoumarol sodium salt was performed on the basis of the characteristic vibrations of the phenyl ring, carbonyl group, methyl group and nitro group. The computed vibrational wavenumbers, their IR intensities and Raman activities as well as the atomic displacements corresponding to the different normal modes were employed to identify

the vibrational modes unambiguously. The calculated vibrational wavenumbers, measured infrared and Raman band positions and their tentative assignments for Acenocoumarol sodium and its La(III) and Dy(III) complexes are presented in Tables 1 and 2. The different regions of the FT-IR and FT-Raman spectra are given in Figs. 2-7, respectively.

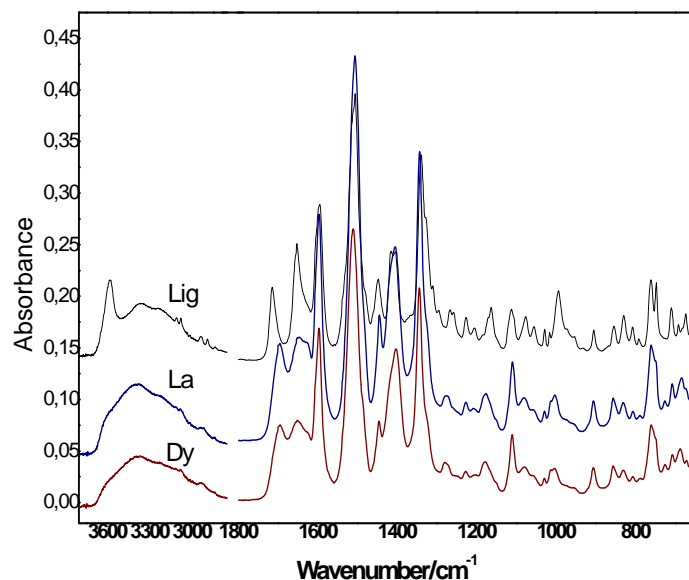


Fig. 2. FT-IR spectra of Acenocoumarol sodium salt and its La(III) and Dy(III) complexes.

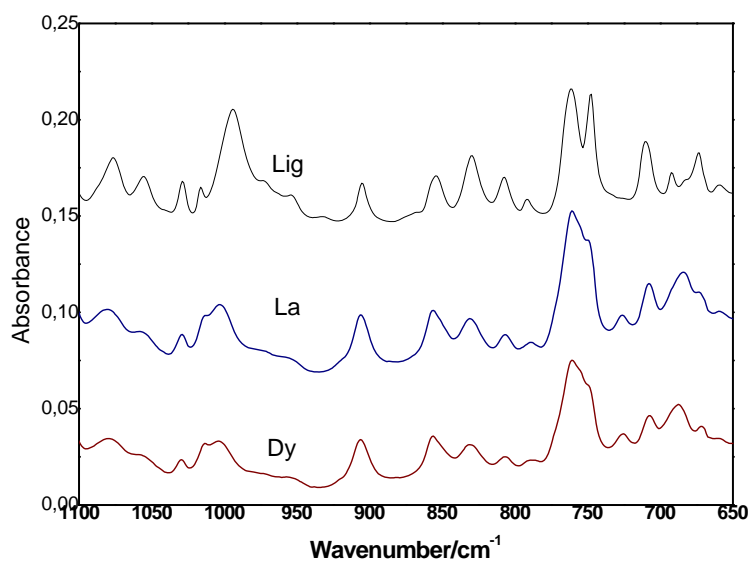


Fig. 3. Low wavenumber region of the ATR/FT-IR spectra of Acenocoumarol sodium salt and its corresponding La(III) and Dy(III) complexes.

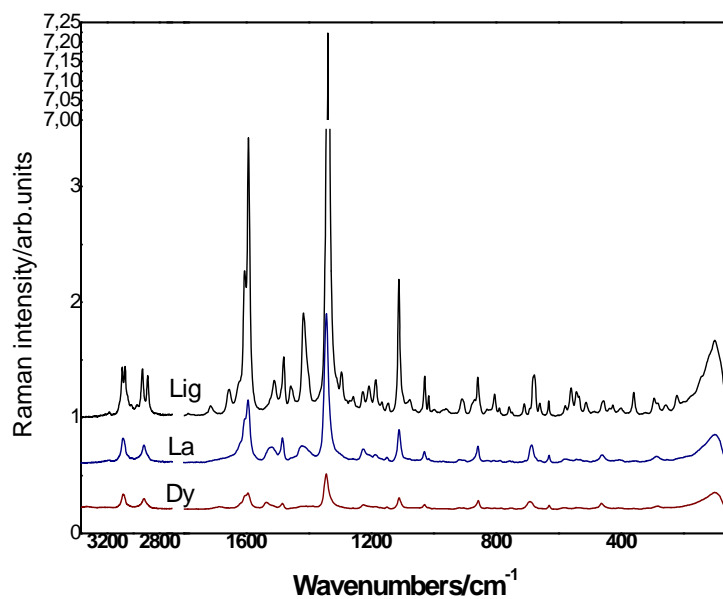


Fig. 4. FT-Raman spectra of Acenocoumarol sodium salt and its corresponding La(III) and Dy(III) complexes. Excitation: 1064 nm, 200 mW.

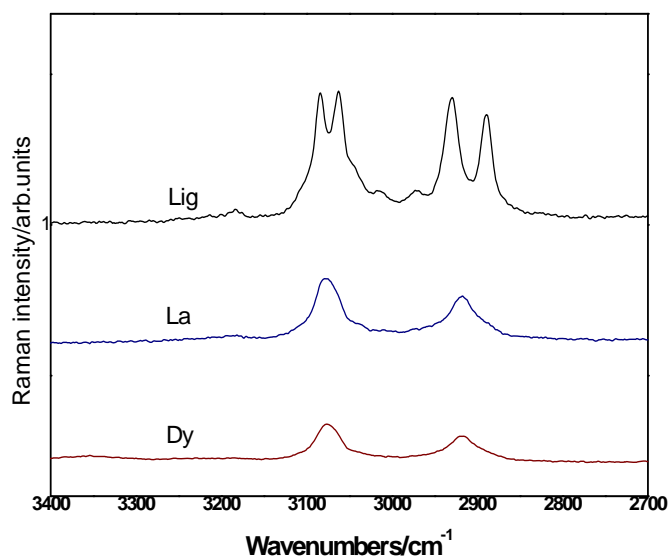


Fig. 5. High wavenumber region of the FT-Raman spectra of Acenocoumarol sodium salt and its corresponding La(III) and Dy(III) complexes.

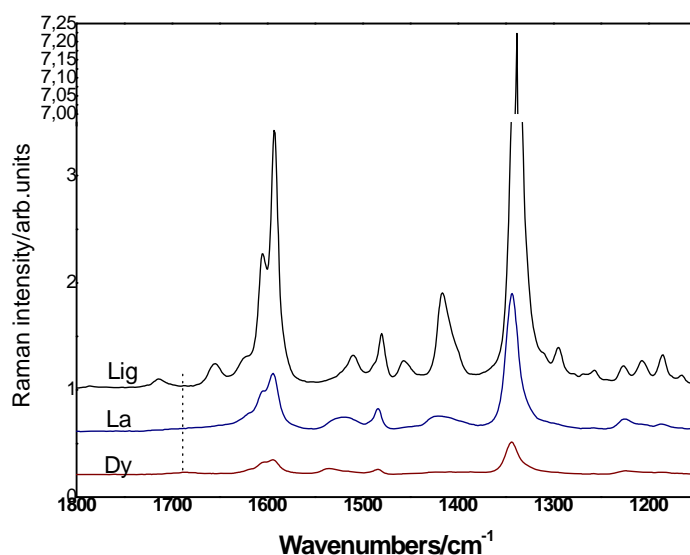


Fig. 6. The 1800-1150 cm<sup>-1</sup> spectral range of the FT-Raman spectra of Acenocoumarol sodium salt and its corresponding La(III) and Dy(III) complexes.

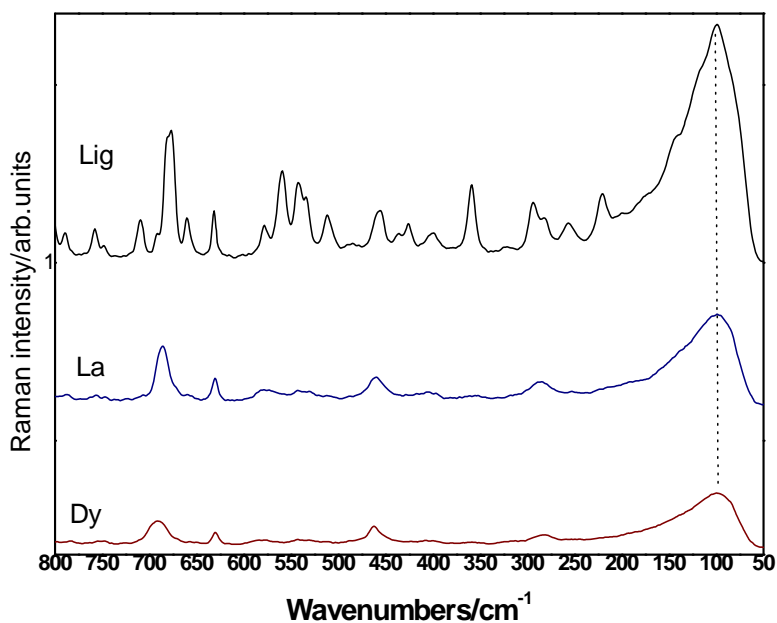


Fig. 7. Low wavenumber region of the FT-Raman spectra of Acenocoumarol sodium salt and its corresponding La(III) and Dy(III) complexes.

The mode of bonding of the ligand to La(III) and Dy(III) was elucidated by the experimental IR and Raman spectra of the complexes as compared with the spectra of the free ligand. The weak band observed at 3577 cm<sup>-1</sup> in the IR spectrum of the free ligand shifted to a lower wavenumber in the complexes. A broad band characteristic of  $\nu(\text{OH})$  of crystalline or coordinated water was observed at about 3400 cm<sup>-1</sup> in the IR spectra of the complexes and had

higher intensity than the one of the free ligand. This was attributed to the presence of crystalline water.

#### *Phenyl ring vibration*

Vibrational spectral behavior of the di-substituted benzene derivatives have been extensively studied by adopting Wilson's scheme [26]. The phenyl ring Ph1 is asymmetric ortho-disubstitution and Ph2 possesses the para-disubstitution, where Ph1 is phenyl of the coumarin structure and Ph2 is phenyl of the side chain. The ring C-H stretching vibration modes are observed as a medium intensity band at  $3118\text{ cm}^{-1}$  and a weak band at  $3079\text{ cm}^{-1}$  in the IR spectrum of the ligand as well as a weak band at  $3062\text{ cm}^{-1}$  in the Raman spectrum of the ligand for Ph2 which were changed in the respective spectra of the complexes because of the coordination. The weak band in Raman at  $3083\text{ cm}^{-1}$  for Ph1 was not changed considerably in the spectra of the complexes. The decrease in intensity of all these C-H stretching modes is due to the steric interaction that induces effective conjugation and charge carrier localization [27].

The selection rule for the di-substituted phenyl ring allows some C-C stretching modes. In the Raman spectrum of Acenocoumarol sodium salt a medium intense band at  $1605\text{ cm}^{-1}$ , a weak band at  $1533\text{ cm}^{-1}$  and a weak band at  $1512\text{ cm}^{-1}$  for Ph1 ring were observed. The same modes appear in IR at  $1505\text{ cm}^{-1}$  for Ph1 ring and at  $1596\text{ cm}^{-1}$  (IR) as a medium intensity, at  $1593\text{ cm}^{-1}$  (Raman) as a strong intensity and a weak band in Raman at  $1482\text{ cm}^{-1}$  for the Ph2 ring. The tangential pairs C-C stretching vibrational modes in IR and Raman, respectively are mixed with the C-H stretching.

The C-H in plane bending mode of Ph2 is observed at  $1256\text{ cm}^{-1}$  as medium shoulder intensity in IR and at  $1294\text{ cm}^{-1}$  in Raman, and the same mode is assigned at  $1231\text{ cm}^{-1}$  in the Raman spectrum for Ph1. Another normal vibration is found at  $1201\text{ cm}^{-1}$  and  $1206\text{ cm}^{-1}$  as a weak intensity in IR and Raman, respectively mixed with C-H in-plane bending vibration for Ph1. The weak bands in IR at  $1112\text{ cm}^{-1}$  and at  $1165\text{ cm}^{-1}$  are assigned to vibrations of Ph1 and Ph2, respectively. The observed C-H out of plane bending mode is the weak band in IR at  $947\text{ cm}^{-1}$  assigned to the normal mode of Ph2. The modes of Ph1 appear at  $903$  and  $910\text{ cm}^{-1}$  in IR and Raman as weak bands. Some of these bands are combined with methyl asymmetric bending and  $\text{CH}_2$  twisting. The radial skeletal modes of Ph1 are observed as very weak bands in Raman at  $715$  and  $559\text{ cm}^{-1}$ ; the same mode of ph2 is observed at  $637\text{ cm}^{-1}$  in Raman as a weak band.

The positions of the above discussed bands remain almost the same or are slightly changed in the respective spectra of the complexes.

#### *Methyl group and O-Na group vibrations*

Methyl groups are generally referred to as electron-donating substitution in the aromatic ring system [28]. The asymmetric stretching mode of  $\text{CH}_3$  is expected in the region around  $2980\text{ cm}^{-1}$  and symmetric one around  $2870\text{ cm}^{-1}$  [29,30]. The asymmetric stretching of  $\text{CH}_3$  appears as a weak band in Raman spectrum at  $3013\text{ cm}^{-1}$ . The methyl symmetric stretching is observed as a weak band in IR at  $2932\text{ cm}^{-1}$  and in Raman at  $2931\text{ cm}^{-1}$  combined with  $\text{CH}_2$  symmetric stretching. The symmetric and asymmetric bending modes of methyl group are normally expected in the region  $1465\text{-}1440\text{ cm}^{-1}$  and  $1390\text{-}1370\text{ cm}^{-1}$  respectively. The asymmetric bending of  $\text{CH}_3$  is observed at  $1445\text{ cm}^{-1}$  as a medium band in IR. The lowering of the methyl bending and the enhancement in the methyl stretching wavenumber is due to the presence of C=O adjacent to the  $\text{CH}_3$  group.

The O-Na stretch of Acenocoumarol sodium appears at  $357\text{ cm}^{-1}$  as a weak intense band in Raman and the DFT level computed wavenumber is  $347\text{ cm}^{-1}$ . This band was not observed in the spectra of the complexes and hence bidentate binding of the carboxylic group of the side chain and deprotonated hydroxyl in the complexes could be suggested.

Our previous calculations for similar complexes predicted that the bands due to  $\nu(\text{Ln-O})_{\text{water}}$  modes should appear at about  $250\text{ cm}^{-1}$ . At similar positions appear the corresponding vibrational modes in La(III) and Dy(III) complexes, observed in their Raman spectra. Obviously, the assignment of the Ln-O bands is uncertain and they cannot be used for reliable prediction of the ligand binding mode.

Table 1. Calculated vibrational wavenumbers at B3LYP/6-31G\* level and measured FT-IR band positions and assignments of Acenocoumarol sodium and its La(III) and Dy(III) complexes.

$\nu_{\text{calc}}, \text{cm}^{-1}$		$\nu_{\text{IR}}, \text{cm}^{-1}$		IR Int.	Assignments
Acenocoum. sodium	Acenocoum. sodium	La(III) complex	Dy(III) complex		
3122	3118 m	3224	3217	1.2	C-H stretch of ph2 <sup>a</sup>
3095	3079 w	3082 w	3083w	7.4	C-H stretch of ph2
2934	2932 w	2915	2923	5.5	CH <sub>3</sub> sym. stretch + CH <sub>2</sub> sym. stretch
2927	2902 vw	2900 vw	2900 vw	8	CH <sub>3</sub> sym. stretch + CH <sub>2</sub> sym. stretch
1727	1713 m	1695	1694	124.1	C=O (keto) stretch
1686	1648 m	1646	1651	456.5	C=O (lacton) stretch
1598	1596 m	1595	1595	140.3	C-C stretch of ph2 + NO <sub>2</sub> asym. stretching
1508	1505 s	1510	1511	379.3	C-C stretch of ph1 <sup>b</sup> + C-C stretch of lacton ring
1446	1445 m	1444 m	1446 m	10.5	CH <sub>3</sub> asym. bending
1407	1407 m	1404 m	1403 m	27.3	C-C stretch of ph2 + CH <sub>2</sub> scissoring + C-H in plane bending
1340	1338 m	1342	1344	454.1	NO <sub>2</sub> sym. stretching + C-H in plane bending
1330	1311 msh	1312 msh	1312 msh	10.6	CH <sub>2</sub> wagging + C-H in plane bending
1270	1275 w	1277 w	1279 w	30	C-C stretch of ph2 + CH <sub>2</sub> twisting + C-H in plane bending
1260	1256 wsh	1260 wsh	1261 wsh	77.5	C-H in plane bending of ph2 + CH <sub>2</sub> wag + C-H in plane bending
1208	1201 vw	1205 vw	1203 vw	19	C-H in plane bending of ph1 + C-H in plane bending
1166	1165 w	1176 w	1177 w	2.4	C-H stretch of ph2
1134	1112 w	1110 w	1111 w	3.8	C-H in plane bending of ph1
1087	1074 w	1081 w	1080 w	32.2	C-H in plane bending of ph2
1052	1057 w	1059 w	1062 w	6.6	radial skeletal of ph1 + CH <sub>2</sub> wagging + CH <sub>3</sub> asym. bending
1021	1032 w	1029 w	1029 w	87.8	C-H in plane bending of ph1
996	993 m	1003	1004	3.5	radial skeletal of ph2
948	947 w	960 w	957 w	0.6	C-H out of plane vibration of ph2
922	903 w	906 w	906 w	2.3	C-H out of plane vibration of ph1
867	859 w	856 w	856 w	13.1	C-H out of plane of ph2
840	832 w	831 w	830 w	9.5	C-H out of plane of ph2 +



					CH <sub>2</sub> twisting + CH <sub>3</sub> asym. bending
819	801 w	807 w	807 w	24	CH <sub>2</sub> wagging + CH <sub>3</sub> asym. bending
762	790 vw	789 vw	788vw	1.4	C-H out of plane of ph1
750	755 m (Splitting)	761	761	44	C-H out of plane of ph1
737	746 m	749 m	748 m	8.9	CH <sub>2</sub> wagging + CH <sub>3</sub> asym. bending
714	707w	708w	706w	25.7	C-H out of plane of ph2
689	685 w	684 w	687 w	11.3	C-H out of plane of ph1
669	672 w	674 w	673 w	2	C-H out of plane of ph2
621	631 w	630 w	629 w	6.8	radial skeletal vibration of ph2

<sup>a</sup> ph2 is phenyl of the side chain

<sup>b</sup> ph1 is phenyl of the coumarin structure

#### Carbonyl vibration

The characteristic infrared absorption frequencies of carbonyl group in cyclic ketones have been extensively investigated and reported earlier [31]. The C=O stretching vibration band can be easily identified from the IR and Raman spectra, and because of the degree of conjugation the strength and polarizations are increasing. The carbonyl vibration bands in ketones normally having a strong intensity are expected in the region 1715-1680 cm<sup>-1</sup> [32]. The carbon-oxygen double bond is formed by Pπ-Pπ between carbon and oxygen and the lone pair of electron on oxygen also determines the nature of carbonyl group.

Table 2. Calculated vibrational wavenumbers at B3LYP/6-31G\* level and measured FT-Raman band positions and assignments of Acenocoumarol sodium and its La(III) and Dy(III) complexes

$\nu_{\text{calc}}, \text{cm}^{-1}$		$\nu_{\text{Raman}}, \text{cm}^{-1}$		Raman act.	Assignments
Acenocoum. sodium	Acenocoum. sodium	La(III) complex	Dy(III) complex		
3097	3083 w	3077	3076	250	C-H stretch of ph1 <sup>a</sup>
3062	3062 w			51.1	C-H stretch of ph2 <sup>b</sup>
3043	3013 w	3012 vw	3012 vw	98.7	CH <sub>3</sub> asym. stretch
2954	2969 w	2970 vw	2971 vw	35.31	CH stretch of side chain
2934	2931 w	2916	2920	175.4	CH <sub>3</sub> sym. stretch + CH <sub>2</sub> sym. stretch
2927	2888 w			62.2	
1727	1707 vw	1707 vw	1707 vw	2.1	C=O (keto) stretch
1686	1652 w	1653 vw	1653 vw	97.1	C=O (lacton) stretch
1600	1605 m	1609 m	1603 m	201.1	C-C stretch of ph1
1598	1593 s	1593	1596	11.7	C-C stretch of ph2 + NO <sub>2</sub> asym. stretching
1544	1533 w	1533 vw	1535 w	69.5	C-C stretch of ph1
1508	1512 w	1519 w	1518 vw	157.7	C-C stretch of ph1 + C-C stretch
1471	1482 w	1481	1478	10.8	C-C stretch of ph2
1466	1456 w	1457 vw	1457 vw	126.5	C-C stretch of ph1

1412	1419 m	1422 m	1420 w	9.7	CH <sub>2</sub> scissoring
1348	1342 sh	1343	1344	17.8	C-C stretch of ph2 +
1340	1338 m			1029.2	NO <sub>2</sub> sym. stretching + C-H in plane bending
1300	1294 w	1294 vw	1294 vw	61.4	C-H in plane bending of ph2
1226	1231 w	1226 w	1225 w	1.9	C-H in plane bending of ph1 + C-H in plane bending
1208	1206 w	1210 w	1210 w	68.8	C-H in plane bending of ph1 + C-H in plane bending
1182	1185 w	1191 w	1191 w	27	CH <sub>2</sub> twisting + CH in plane bending of C-H
1134	1117 s	1110	1109	14	C-H in plane bending of ph1
1021	1035 w	1029 w	1027 w	28.3	C-H in plane bending of ph1
1011	1012 w	1012 vw	1012 vw	10.3	C-H in plane bending of ph1
922	910 w	913 w	910 vw	0.7	C-H out of plane vibration of ph1
867	859 w	858 w	857 w	6.9	C-H out of plane of ph2
819	814 vw	813 vw	814 vw	16.4	CH <sub>2</sub> wagging + CH <sub>3</sub> asym. bending
750	755 vw	755 vw	756 vw	15.3	C-H out of plane of ph1
717	715 vw	714 vw	715 vw	9.8	NO <sub>2</sub> wagging + radial skeletal of ph1 + C-C bend. + out of plane of Ph2
714	709 w	710 vw	709 vw	12.8	C-H out of plane of ph2
689	678 w	680 w	679 w	3.5	C-H out of plane of ph1
669	660 w	660 vw	660 vw	1.7	C-H out of plane of ph2
621	637 w	631 w	629 w	12.6	radial skeletal vibration of ph2
577	577 w	577 vw	577 vw	4.9	CH <sub>3</sub> Umbrella mode
551	559 vw	560 vw	561 vw	5.2	radial skeletal vibration of ph1 + dinone ring breathing
535	541 vw	542 vw	540 vw	8.8	radial skeletal of ph1 and ph2
524	515 vw	514 vw	515 vw	1.1	NO <sub>2</sub> twisting
452	452 vw	455 w	457 w	7.9	CH <sub>2</sub> wagging + CH <sub>3</sub> asym. bending
347	357 w	-	-	8.4	O-Na stretch
-	-	284	282	8.4	O-Ln stretch

<sup>a</sup> ph1 is phenyl of the coumarin structure

<sup>b</sup> ph2 is phenyl of the side chain

In Acenocoumarol sodium salt the keto-carbonyl vibration C=O stretch is calculated at 1727 cm<sup>-1</sup> and is observed at  $\nu_{\text{IR}}=1713$  cm<sup>-1</sup> as a medium band and  $\nu_{\text{Raman}}=1707$  cm<sup>-1</sup> as a weak band. The band at 1713 cm<sup>-1</sup> (IR spectrum of the ligand) attributed to the stretching vibrations of the keto-carbonyl group in the side chain was shifted with 20–30 cm<sup>-1</sup> to lower wavenumber values. This might be taken as evidence for the participation of this C=O group in the coordination process.

The C=O stretch corresponding to the carbonyl group in the lacton ring is observed as a medium band in IR at 1648 cm<sup>-1</sup> and in Raman at 1652 cm<sup>-1</sup>. The calculated C=O stretching wavenumber is assigned at 1686 cm<sup>-1</sup>. This band is not changed considerably on complex formation suggesting that this group does not participate in the coordination.

#### *Nitro group vibration*

Generally the asymmetric stretching of aromatic nitro group gives rise to a very strong band between 1560 and 1500  $\text{cm}^{-1}$  [33]. The most intense band measured at 1596  $\text{cm}^{-1}$  and at 1593  $\text{cm}^{-1}$  (as a medium in IR and strong in Raman, respectively) can be described as the asymmetric stretching mode of  $\text{NO}_2$  group. The predicted  $\text{NO}_2$  asymmetric stretching mode (1598  $\text{cm}^{-1}$ ) is very close to the experimental results. The symmetric stretching mode of this vibration usually appears as intense band in IR and Raman spectra between 1390 and 1330  $\text{cm}^{-1}$ , respectively [34]. In Acenocoumarol sodium the  $\text{NO}_2$  symmetric stretching group is identified at 1338  $\text{cm}^{-1}$  as a medium band in IR. The nitro group is capable of bending in a number of different directions and these vibrations give rise to several variable intensity bands at lower wavenumber. The  $\text{NO}_2$  wagging and twisting vibrations are identified as weak bands in Raman at 715 and 515  $\text{cm}^{-1}$ , respectively. All the bands attributed to  $\text{NO}_2$  show insignificant change in the respective spectra of the lanthanide complexes suggesting that this group does not participate in the complex formation.

#### 4. Conclusions

Quantum chemical calculations and vibrational spectral studies have been performed on Acenocoumarol sodium salt in order to identify its structural and characteristic features. The theoretical vibrational analysis confirms the phenyl ring, carbonyl methyl, nitro and the O-Na group vibrations. As one can notice, there is a very good agreement between the experimental vibrational frequencies and theoretically determined values.

The coordination ability of 4-hydroxy-3-[1-(4-nitrophenyl)-3-oxobutyl]-2H-1-benzopyran-2-one was proved in complexation reaction with lanthanide(III) ions. IR and Raman spectral analyses of the ligand and its Ln(III) complexes confirmed the suggested coordination of 4-hydroxy-3-[1-(4-nitrophenyl)-3-oxobutyl]-2H-1-benzopyran-2-one through both the hydroxyl and carbonyl oxygen atoms.

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\*Corresponding author: irenakostova@yahoo.com