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Vibrational spectroscopic investigation on the binding modes in Gd(III) and Dy(III) complexes

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The gadolinium(III) and dysprosium(III) complexes of 3, 5-pyrazoledicarboxylic acid (H_3pdc) were synthesized and characterized. The structures of the final complexes were determined by means of FTIR and FTRaman spectral analyses. To help the binding mode elucidation in the new Gd(III) and Dy(III) complexes of H_3pdc, detailed vibrational analysis was performed on the basis of comparison of experimental vibrational spectra of the ligand and its Ln(III) complexes with theoretically predicted by us earlier as well as with literature data about related compounds. Significant differences in the IR and Raman spectra of the complexes were observed as compared to the spectra of the ligand. Vibrational evidence for bidentate coordination of carboxylic oxygens to the Gd(III) and Dy(III) ions was found.

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1. Introduction

Recent advances in medicinal inorganic chemistry demonstrate significant prospects for the utilization of lanthanides and their coordination complexes as drugs, presenting a flourishing arena for inorganic chemistry. Significant progress in lanthanide-based agents has been achieved, based in part on a mechanistic understanding of the pharmacological effects of classical drugs. Much attention has focused on designing new coordination compounds with improved pharmacological properties and a broader range of activity [1].

Lanthanides constitute an interesting group of elements with similar physicochemical properties, which change periodically with the atomic number. Their unique chemical similarity is due to the shielding of 4f valence electrons by the completely filled $5s^2$ and $5p^6$ orbitals. Although the members are very similar from a chemical point of view, each of them has its own very specific physical properties. The localized 4 *f* shell gives rise to large local magnetic moments in the lanthanide series. The large local moments affect the cohesive properties through local polarization of the valence and conduction bands. The lanthanides are all very reactive electropositive metals. The values of ionic radii of lanthanides are relatively higher than those in other elements with the same oxidation number. Despite the high charge, the large size of the Ln(III) ions results in low charge densities and their compounds are predominately ionic in character. The Ln(III) ions are class-a or hard in character so they tend to bond to O, N and F donors with F preferred to Cl > Br > I. They generally adopt high coordination numbers. The use of lanthanide ions as central atom for the construction of coordination polymers is more difficult than their transition metal analogues for the high and variable coordination number and flexible coordination geometry of lanthanide ions [1].

Recent interest in the development of new metal complexes with 3, 5-pyrazoledicarboxylic acid (H_3pdc) has attracted tremendous attention due to the interesting properties of the ligand. In the 3, 5-pyrazoledicarboxylic acid (H_3pdc) molecules are joined into one-dimensional chains by O-H.O and N-H.O hydrogen bonds. In addition to the potential for forming open-channel frameworks, access to the six coordination atoms of H_3pdc can be directly controlled by varying the pH of the reaction environment, allowing further control over the design and synthesis of novel coordination complexes using various metal centers [2-8]. Our literature survey on 3,5-pyrazoledicarboxylic acid as a multiple dentate ligand has shown that this ligand readily reacts with rare-earth, transition, and posttransition metal ions to yield versatile structures. By adjusting the pH level desired products may be isolated and purified. The syntheses and crystal structures of coordination compounds containing the monoanion of 3,5-pyrazoledicarboxylic acid and ammonium-based counterions were reported recently [2]. A series of M(II) complexes with the ligand 3,5-pyrazoledicarboxylic acid (H_3dcp) has been synthesised mainly *via* hydrothermal reactions and their structures have been characterised recently [3]. Rare-earth metal coordination polymers have been obtained, e.g. ([$Eu_2(Hpdc)_3(H_2O)_6$] [7]. Lanthanide atom sizes (the lanthanide contraction) directly control the type of structure formed by the coordination of a single multidentate ligand, 3,5-pyrazoledicarboxylic acid (H_3pdc) [8].

The ligand, 3,5-pyrazoledicarboxylic acid (H_3pdc), known both as a multiple proton donor and acceptor, can use its carboxylate oxygen and pyrazole nitrogen atoms, which are highly accessible to metals, to form both monodentate and/or multidentate M-O and M-N bonds. The coordinated structural motifs thus generated can then readily form hydrogen-bonded networks [9, 10]. To date, the majority of known supramolecular assemblies are synthesized by direct reactions of metal salts with various ligands. This ligand possesses three different protonated hydrogens (H_a, H_b, and H_c in Fig. 1). The difference in the binding power of these protons allows to deprotonate them at different pH levels. The flexible, multifunctional coordination sites of this ligand also give a high likelihood for generation of coordination polymers with high dimensions. Its functional groups (carboxylate and pyrazole ring) bind to metals selectively. For instance, the 'harder" lanthanide metals coordinate more preferably to oxygen atoms than to the 'softer" nitrogen atoms, while the latter show a strong tendency to bind to transition metals. Cadmium was selected as a metal center in [9] because of its ambi-ability to form bonds with both nitrogen and oxygen atoms with a d^{10} configuration.

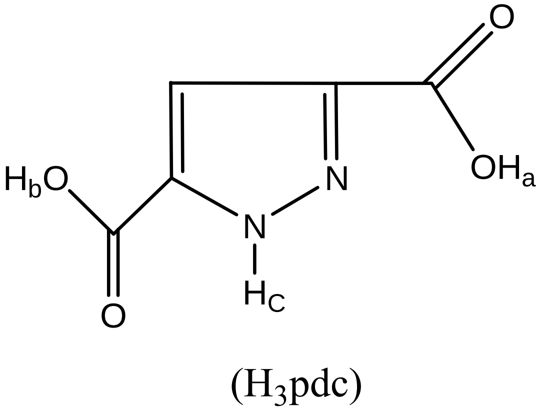

Fig. 1. The structure of the ligand 3,5-pyrazoledicarboxylic acid.

Although a variety of coordination polymers and complexes of H_3dcp containing transition metal elements have been synthesized, very few involve rare-earth metal centers. Our recently published studies on rare-earth metal coordination compounds involving biologically active ligands showed that a number of human tumor cell lines were very sensitive to the lanthanide complexes and these metals had different cytotoxic profile [11-20]. These promising results prompted us to search for new cytotoxic lanthanide complexes with 3,5-pyrazoledicarboxylic acid. Considering versatile coordination modes of the ligand during the formation of numerous coordination frameworks, it was a challenge for us to obtain new lanthanide(III) coordination complexes with 3,5-pyrazoledicarboxylic acid. Thus, the aim of this work was to synthesize and characterize complexes of gadolinium(III) and dysprosium(III) with 3,5-pyrazoledicarboxylic acid and to determine their most probable structure on the basis of the detailed vibrational study. The vibrational FT-IR and FT-Raman spectra of H_3dcp and its Gd(III) and Dy(III) complexes showed that some vibrational modes exhibit different IR intensity and Raman activity, therefore the combination of IR and Raman experimental spectroscopy afforded an opportunity for more precise characterization of the vibrational spectra of the Ln(III) complexes.

2. Experimental

Physical and spectroscopic measurements

The carbon, hydrogen and nitrogen contents of the compounds were determined by elemental analysis. The water content was determined by Metrohn Herizall E55 Karl Fisher Titrator.

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 compounds were recorded with a Dilor Labram 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 confocal 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 power of 100 mW was used in our measurements.

General method of synthesis

The complexes were synthesized by reaction of Gd(III) and Dy(III) nitrates and the ligand, in amounts equal to metal: ligand molar ratio of 1: 2. The complexes were prepared by adding an aqueous solution of the respective lanthanide(III) salt to an aqueous solution of the ligand subsequently raising the pH of the mixture gradually to ca. 5.0 by adding dilute solution of sodium hydroxide. The reaction mixture was stirred with an electromagnetic stirrer at 25 ^{o}C for one hour. At the moment of mixing of the solutions, precipitates were obtained. The precipitates were filtered, washed several times with water and dried in a desicator to constant weight.

Table 1. Selected calculated and experimental IR wavenumbers (cm^{-1}) of H_3pdc and its Gd(III) and Dy(III) complexes and their tentative assignments.

Calculated [22]				Experimental			Vibrational assignment
B3PW91		B3LYP					
LANL2DZ	6-311++G**	LANL2DZ	6-311++G**	H_3pdc	Gd(H_2pdc)	Dy(H_2pdc)	
3347		3331		3353 sh	3406 vs	3404ms	ν (NH)
	3294		3285	3220 s	3228 sh	3230 sh	ν (OH)
				3144 wm	3157 sh	3164 wm	ν (CH)
				3109 w		3093 sh	ν (CH)
				3064 sh	3087 sh		ν (CH)
				3002 w	2962 vw	2983 w	ν (=C-H)
				2920 w	2925wm	2924 w	ν (CH)
				2876 sh	2854 w	2855 w	ν (C-C-H)
				1968 w			ν_{asym} (COO)
1716		1698		1717 vs	1736 vw		ν_{sym} (COO)
1710		1692		1700 vs			ν_{asym} (C=O)
				1633 sh			ν_{sym} (C=O)
1601	1604	1585	1590	1560 m	1588 vs	1597 s	ν_{sym} (ring)
1524	1519		1501	1492 s		1495 w	δ_{ip} (ring)
1459	1476	1507	1457	1460 m	1509 m	1468 m	ν (N=N); ν (ring)
1436	1450	1440	1433			1438 wm	ν (ring)
1375	1383	1420		1395 sh	1439 m		ν (ring)
1332	1350	1357	1363	1357 m	1363 vs	1359 vs	ν (ring); δ (C-OH)
1332		1320	1337	1322 s		1314 s	ν (C-O)
1281	1288	1270	1279	1278 ms	1265 vw	1270 w	δ_{op} (CH)
1222	1244		1225	1244 m			δ_{ip} (CH); ν (COC)
1222	1188	1200	1181	1210 s	1198 w	1218 w	ν_{sym} (C=O)
1158	1168	1153	1152		1126 vw		δ_{ip} NH; ν (ring)
1081	1092	1090	1089	1094 w	1042 w	1101 vw	ν (ring); ν (CH)
1021	1030	1012	1025	1018 m	1019 wm	1017 m	δ_{ip} (CH); δ_{op} (CH); ν (ring)
984	998	976	994	998 m			δ_{ip} (ring)
	884		885	881 wm		872 vw	δ_{op} (CH); δ_{op} (ring)
				852 m	835wm	840 wm	δ_{op} (CH)
794	797	787	792	806 wm		809 sh	δ_{op} (CH)
777	779	766	773	772 ms	791 m	789 m	δ_{op} (CH)
771	733	759	773	747 wm			δ_{op} (CH)
713	716	708	729		626 w		δ (OCO)
585	571	579	609	577 m	579 w	594 w	δ_{op} (ring)
555	552	552	547	522 w	525 w	524 w	δ_{op} (NH)
495	504	492	502		515 sh	516 sh	ν (M-O)
445	460	443	458	499 w	470 sh	457 wv	δ (OCO)

Abbreviations: vw – very weak; w – weak; m – medium; ms – medium strong; s – strong; vs – very strong; sh – shoulder; ν - stretching; δ - bending; sym – symmetric; asym – asymmetric; ip – in-plane; op – out-of-plane; M – metal.

Table 2. Selected calculated and experimental Raman wavenumbers (cm^{-1}) of H_3pdc and its Gd(III) and Dy(III) complexes and their tentative assignments.

Calculated [22]				Experimental			Vibrational assignment
B3PW91		B3LYP		solid			
LANL2DZ	6-311++G**	LANL2DZ	6-311++G**	H_3pdc	Gd(H_2pdc)	Dy(H_2pdc)	
3348		3332				3417 vw	ν (NH)
	3295		3285				ν (OH)
				3137 m	3160 sh	3145 wm	ν (CH)
				3111 w	3142 w		ν (CH)
				3071 w		3071 w	ν (CH)
						1996 sh	ν_{asym} (COO)
1710		1698		1679 vs			ν_{asym} (C=O)
1601		1691		1641 sh	1634 w	1639wm	ν_{sym} (C=O)
1524	1604	1585	1590	1558 w	1598 sh	1553 s	ν_{sym} (ring)
	1476	1507	1501			1489 ms	δ_{ip} (ring)
1459	1450	1440	1457	1464 m		1460 s	ν (N=N); ν (ring)
1436		1420	1433	1436 w/m	1432 s	1429 vs	ν (ring)
1375		1357	1363	1356 vs	1345 m	1342 ms	ν (ring); δ (C-OH)
1332	1350	1320	1337	1316 w	1317 vw	1303 w	ν (C-O)
1280	1288	1270	1279		1275 vw		δ_{op} (CH)
1222	1244		1225	1231 w		1255 w	δ_{ip} (CH); ν (COC)
	1188	1200	1181	1201 w		1209 vw	ν_{sym} (C=O)
1158	1168	1153	1152	1133 vw		1114 vw	δ_{ip} NH; ν (ring)
1081	1092	1090	1089	1090 vw		1088 vw	ν (ring); ν (CH)
1021	1030	1012	1025	1003 s	1007 s	1003 vvs	δ_{ip} (CH); δ_{op} (CH); ν (ring)
984	998	976	994	988 ms			δ_{ip} (ring)
	884		885	897 vw			δ_{op} (CH); δ_{op} (ring)
				844 vw		861 vw	δ_{op} (CH)
	797	787	792			799 wm	δ_{op} (CH)
794	779	766	773	782 vw	808 w		δ_{op} (CH)
771		759		756 sh			δ_{op} (CH)
713	733	708	729	729 w/m	670 vw	645 vw	δ (OCO)
585	571	579	609	605 vw	565vw	571 w	δ_{op} (ring)
555	552	552	547		514 vw	515 w	ν (M-O)
323	328	322	326	366 m	349vw	383 wm	ν (M-O)
217	222	218	224		224 sh	212 sh	ν (O-M-O)

Abbreviations: vw – very weak; w – weak; m – medium; ms – medium strong; s – strong; vs – very strong; sh – shoulder; ν - stretching; δ - bending; sym – symmetric; asym – asymmetric; ip – in-plane; op – out-of-plane; M – metal.

3. Results and discussion

3.1. Chemistry

The compositions of the new complexes were characterized by elemental analysis. The metal ions were determined after mineralization. The water content in the complexes was determined by Karl Fisher analysis. The data of the elemental analysis of the compounds obtained serving as a basis for the determination of their empirical formulas and the results of the Karl Fisher analysis are as follows: Calculated/found: for $Gd(H_2pdc)_2(OH).6H_2O$ C: 19.10/18.64; H: 3.02/2.65; N: 8.92/9.33; H_2O: 17.19/16.89; Gd: 25.00/24.68 and for $Dy(H_2pdc)_2(OH).3H_2O$ C: 20.72/21.03; H: 2.24/2.39; N: 9.67/9.30; H_2O: 9.33/8.89; Dy: 27.98/27.54, where H_2pdc = $C_5H_3N_2O_4^-$. The elemental analysis data of the Ln(III) complexes obtained are in agreement with the presented formulas. According to the synthesis procedure, the ligand was deprotonated by using sodium hydroxide and the corresponding anionic species are the active ligand forms in the reaction with lanthanide ions. As shown in Fig. 1, H_3pdc contains three different hydrogens (H_a, H_b, H_c). The H_c in this ligand is linked to the nitrogen of the pyrazole ring and is more difficult to deprotonate than the two carboxylate hydrogen atoms. Thus, among all the possible reactive sites, carboxylic oxygens revealed the most negative charge and thus they appeared to be the most preferred sites for electrophylic attack in reaction with metal ions and it is expected that the coordination of the ligand to Ln(III) ions is realized through the carboxylic oxygens of the ligand. Although H_a and H_b are both attached to carboxylic oxygen atoms, H_a can be deprotonated more easily, allowing the oxygen initially attached to it to form a chelating bond to a metal center. This suggestion will be checked below on the basis of a detailed and comparative vibrational study of the ligand and its Ln(III) complexes.

3.2. Vibrational analysis of H_3dcp and its Gd(III) and Dy(III) complexes

The mode of bonding of the ligand to Gd(III) and Dy(III) ions was elucidated by recording the IR and Raman spectra of the complexes as compared with those of the free ligand. The vibrational fundamentals from the IR and Raman spectra, presented in Figs. 2 and 3, were analyzed by comparing these modes with those from the literature [21] in combination with the results of our DFT calculations (i.e., harmonic vibrational wavenumbers and their Raman scattering activities) [22]. In the Tables 1 and 2 the selected calculated and experimental IR and Raman data together with their tentative assignments are given. All the calculated modes are numbered from the largest to the smallest frequency within each fundamental wavenumber. The last column in Tables 1 and 2 shows the approximate description of the normal modes according to the B3PW91 and B3LYP methods [22]. A survey of the last column shows that many vibrations are complex and involve strongly coupled motions. The assignments have been given by studying literature reports [23] and comparing the spectra of the ligand and of the metal complexes. As a general remark we must emphasize that some stretching and deformation modes are coupled, so that the proposed assignments should be regarded as approximate descriptions of the vibrations.

To illustrate the vibrational behavior of the ligand upon the metal coordination we present the FT-IR spectra in the 4000-500 cm^{-1} range (Fig. 2), as well as the Raman spectra of the investigated compounds in the 1800-200 cm^{-1} range (Fig. 3). Both the IR and the Raman spectra were considered for full description of the vibrational behavior of the investigated species. Below we discuss characteristic vibrational modes of the ligand that change upon the complexation with Ln(III) ions.

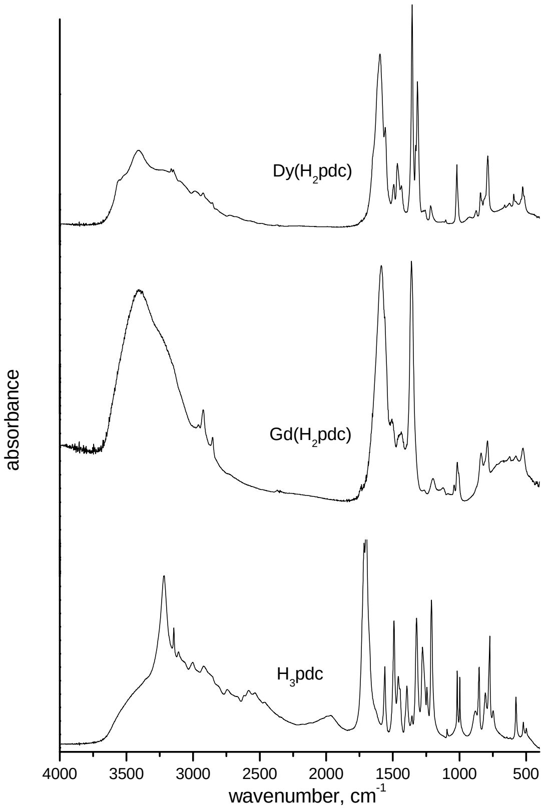

Fig. 2. IR spectra of H_3pdc and its Gd(III) and Dy(III) complexes.

O-H stretching modes, ν(OH)

According to the calculations, the IR band at 3220 cm^{-1} for the ligand is assigned to the O-H stretching mode [22]. Due to the intramolecular O…H-O bonds this mode is shifted in the ligand to lower wavenumbers in comparison with the free ν(OH) vibrations. In the ν(OH)/H_2O region the spectra of Gd(III) and Dy(III) complexes show one medium band at about 3230 cm^{-1}, attributed to the presence of coordinated water. This band overlaps with the ν(NH_2) band.

The assignment of the O-H and N-H stretching bands appearing in the same region is rather difficult. These bands appear overlapped in the same spectral region, and the involvement of these groups in hydrogen bonds affects their wavenumbers and produces a relevant band broadening in the IR and Raman spectra.

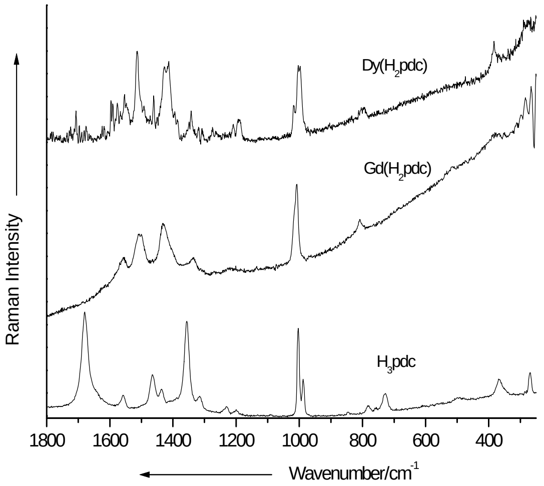

Fig. 3. Raman spectra of solid state of H_3pdc and its Gd(III) and Dy(III) complexes. Excitation: 514.5 nm, 50 mW.

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

The most informative for the metal-ligand binding mode in the Ln(III) complexes studied is the behavior of ν(C=O) mode. According to our DFT calculations [22], the bands in the 1720-1630 cm^{-1} region were assigned to the asymmetric and symmetric stretching vibration of the carboxylic and carbonylic groups. Some of the components of these stretching modes are active in the IR spectra and other ones are active in the Raman spectra of the compounds. The strong IR bands at 1717, 1700 and 1633 cm^{-1} and the Raman bands at 1679 and 1641 cm^{-1} were assigned to ν(C=O) modes of the carboxylic and carbonylic groups in the ligand, respectively (Tables 1 and 2). We have to mention that the ligand's vibrational spectra appear not enough suitable base for direct prediction of its coordination mode to the Ln(III). The finding obtained could be explained with the intramolecular H-bond effect on vibrational modes of the ligand, reported by us earlier [22]. In general the strong peaks in the spectra of the complexes are around 1600-1400 cm^{-1}, which is characteristic of the expected adsorption for asymmetric and symmetric vibrations for uni and bidentate carboxylate groups. It has already been observed by several authors that the difference Δν between the asymmetric and symmetric COO^- stretching frequencies is greater in complexes than in simple salts. In accordance with our theoretical calculations, a bidentate binding of the COO^- group in the complexes was suggested and such binding was also reported in the literature [8]. That is why we suggest the structure of the complexes as presented on Fig. 4.

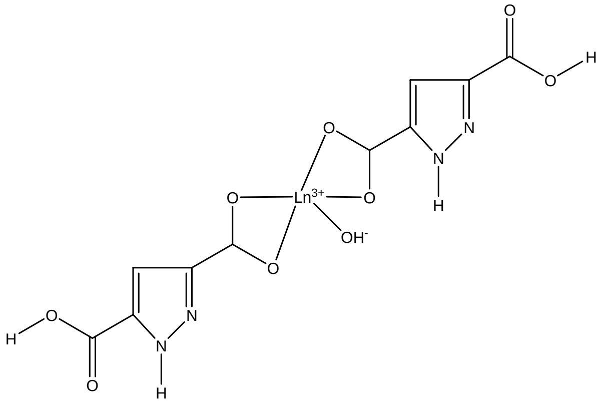

Fig. 4. The proposed structure of the lanthanide(III) complexes with 3,5-pyrazoledicarboxylic acid

According to our calculations [22] the bands observed at 1322 (IR) and 1316 (Raman) cm^{-1} for the ligand were assigned to the ν(C-O) modes with low intensity in the Raman spectra. The bands around 1200 cm^{-1} almost weak in IR and very weak in Raman, were attributed to the asymmetrical C-O stretching mode and they were slightly changed in the complexes.

N-H and C-H stretching modes

The stretching vibrations around 3500 cm^{-1} in all spectra are attributed to secondary aromatic amine. In the 3600-2700 cm^{-1} region we can observe the N-H stretching mode as a shoulder at 3353 cm^{-1} for the H_3pdc, and as a strong and medium strong band for the Gd complex (3406 cm^{-1}) and Dy complex (3404 cm^{-1}). The out of plane NH bending mode in the IR spectra are present for the H_3pdc (522 cm^{-1}), Gd complex (525 cm^{-1}) and Dy complex (524 cm^{-1}), while in the Raman spectra are absent. The absence of large systematic shifts of these bands in the spectra of the complexes implies that there is no interaction between the amino nitrogen and the lanthanide(III) ions.

Tag along bands at around 3100 cm^{-1} can be attributed to the C-H stretching mode. The wavenumber region 2700-2500 cm^{-1} in IR and Raman spectra, repectively, is typical of strongly hydrogen bonded intermolecular complexes due to a strong anharmonic coupling (Fermi resonance) of the NH stretching vibrations with overtones and combinations of lower frequency modes of the bonded molecules [22].

Ring stretching modes, ν(CC)

The coordination of Ln(III) to the carboxylic oxygens affected also to some extent the IR and Raman bands due to the pyrazole-ring modes. In the IR spectra of H_3pdc, and its Gd and Dy complexes (Fig. 2) the medium and very strong bands at 1560, 1588 and 1597 cm^{-1} were assigned to the symmetrical stretching mode of the pyrazole ring, while in the Raman spectra this vibration is represented by the weak peak at 1558 cm^{-1} for the ligand, and the strong bands at 1598 and 1553 cm^{-1} for the Gd and Dy complexes, respectively. Other bands connected with the pyrazol ring stretching modes in the IR spectra are the bands at 1460, 1395, 1357 cm^{-1} (for the H_3pdc), 1439, 1363 cm^{-1} (for the Gd complex) and 1438, 1359 cm^{-1} (for the Dy complex). All these bands are shifted to lower wavenumbers both in the IR and Raman spectra (Tables 1 and 2). The in plane bending modes of the pyrazole ring can be observed at around 1500 cm^{-1} in the IR and Raman spectra for all componds (Figs. 2, 3; Tables 1 and 2). The bands at around 880 and 600 cm^{-1} in the IR and Raman spectra can be assigned to the out of plane pyrazole ring banding mode. The bands that are typical for the pyrazole-ring vibrations were not shifted significantly in the spectra of Gd(III) and Dy(III) complexes, which indicated that the Ln(III) cations did not produce substantial polarization on the pyrazole ring.

CH bending modes, δ(CCH) and ring in-plane and out-of-plane deformations

The CH in-plane bending modes, $\delta(CH)_{ip}$, were observed at their usual positions in the 1250 – 1020 cm^{-1} region. The most of these bands are stronger in the Raman than in the IR spectra. Medium IR bands are observed in the 880-750 cm^{-1} region and they were assigned to out-of-plane deformation vibrations of the hydrogen atoms in the ring, $\delta(CH)_{op}$. The bands due to the CH bending modes and to the ring deformations are slightly changed in the vibrational spectra of the complexes. The assignment of all observed IR and Raman bands in this spectral range is difficult, because of the presence of highly coupled modes and combination bands that may overlap with those due to fundamentals, and they interact with one another, leading to distortions of the observed bands.

Ln-O stretching and O-Ln-O bending modes

The spectra in the region below 600 cm^{-1} are particularly interesting, since they provide information about the metal-ligand vibrations. The Raman spectra are particularly useful in studying the metal-oxygen stretching vibrations, since these vibrations give rise to medium intensity bands in Raman, but are weak in the infrared spectra.

The analysis of the calculated frequencies showed that the weak bands observed in this region in the vibrational spectra of Ln(III) complexes are due to the Ln-O stretching modes. The new bands at about 510-520 cm^{-1}, which appear only in the IR and Raman spectra of the Gd(III) and Dy(III) complexes, can be due to the metal-oxygen vibrations. In the low wavenumber region in the Raman spectrum of H_3pdc (Fig. 3) we can observe a medium band at 366 cm^{-1}, which is shifted in the Raman spectra of the Gd(III) and Dy(III) complexes and becomes weaker. This one can be due to the metal-oxygen vibration modes.

The metal affects the carboxylate anion as well as the ring structure. The ionic potential of the metal is the most important parameter responsible for the influence of the metal on the rest of the molecule. The carboxylic acids interacts with the metals as symmetric, bidentate carboxylate anions and both oxygen atoms of the carboxylate are symmetrically bonded to the metal. In this sens, we can observe in the Raman spectra of the Gd(III) and Dy(III) complexes, the bands at 224 and 212 cm^{-1}, which can be due to the O-M-O vibration modes.

Because of the predominant electrostatic character of the Ln–O bonding the bands corresponding to the ν(Ln-O) modes have low intensities, they are coupled with other modes and hence, their assignment is very difficult. Our previous theoretical calculations [14] predict that the bands due to $\nu(Ln\text{-}O)_{water}$ and $\nu(Ln\text{-}O)_{OH}$ modes should also appear at about 200 cm^{-1}. At the same positions are the observed corresponding vibrational modes in the Raman spectra of Ln(III) complexes.

4. Conclusions

The vibrational properties of 3,5-pyrazoledicarboxylic acid and its Ln(III) complexes have been investigated by FT-Raman and FT-IR spectroscopies and supported by previously published by us theoretical calculations [22]. The difference between observed and calculated wavenumber values of the most of the fundamental modes is very small. The vibrational analyses assisted in deeper understanding and explaining the experimental Raman and IR spectra of Ln(III) complexes with 3,5-pyrazoledicarboxylic acid. Vibrational evidence for bidentate coordination of carboxylic oxygens to the Gd(III) and Dy(III) ions was found. On the basis of the above detailed vibrational study we were able to suggest the most probable structural formula of the investigated complexes (Fig. 4).

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