

Infrared spectra of phthalocyanine and naphthalocyanine in sandwich-type (na)phthalocyaninato and porphyrinato rare earth complexes

Part 12. The infrared characteristics of phthalocyanine in heteroleptic bis(phthalocyaninato) rare earth complexes[☆]

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Abstract

The infra-red (IR) spectroscopic data for a series of 13 heteroleptic bis(phthalocyaninato) rare earth complexes $M(\text{Pc})[\text{Pc}(\text{OC}_8\text{H}_{17})_8]$ [$M = \text{Y, Pr, \dots, Lu}$ except Pm ; $\text{H}_2\text{Pc} = \text{phthalocyanine}$; $\text{H}_2\text{Pc}(\text{OC}_8\text{H}_{17})_8 = 2,3,9,10,16,17,24,25$ -octakis(octyloxy)phthalocyanine] have been collected with resolution of 2 cm^{-1} . The IR spectra for $M(\text{Pc})[\text{Pc}(\text{OC}_8\text{H}_{17})_8]$ are more complicated than those of homoleptic bis(phthalocyaninato) rare earth counterparts $M(\text{Pc})_2$ and $M[\text{Pc}(\text{OC}_8\text{H}_{17})_8]_2$ due to the decreased molecular symmetry of these double-decker compounds, C_{4v} . For this series of heteroleptic bis(phthalocyaninato) rare earth compounds, the $\text{Pc}^{\bullet-}$ marker band at $1315\text{--}1322\text{ cm}^{-1}$, attributed to the pyrrole stretching, is found to be dependent on the central rare earth size, shifting slightly to the higher energy along with the decrease of rare earth radius. The coupling of isoindole deformation and aza stretching at $1057\text{--}1063\text{ cm}^{-1}$ and the coupling of pyrrole and aza stretching at $1497\text{--}1504\text{ cm}^{-1}$ are also metal-sensitive. The frequency of the vibration at $880\text{--}884\text{ cm}^{-1}$ is also dependent on the rare earth ionic size. The assignments of the vibration bands for these compounds have been made by comparison with the IR spectra of unsubstituted and in particular the 2,3,9,10,16,17,23,24-octakis(octyloxy)-substituted bis(phthalocyaninato) rare earth analogues $M(\text{Pc})_2$ and $M[\text{Pc}(\text{OC}_8\text{H}_{17})_8]_2$.

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1. Introduction

Sandwich type phthalocyaninato rare earth double-decker complexes have been extensively studied due to their potential applications for molecular electronic, optronic, and iono-electronic devices [1,2]. Vibrational spectroscopies have proved to be versatile methods among various techniques for characterizing thin films of phthalocyanines in solid state devices. Quite recently, the infra-red (IR) and Raman

spectroscopic characteristics of (na)phthalocyanine in various kinds of sandwich bis- and tris[(na)phthalocyaninato] and mixed (porphyrinato)[(na)phthalocyaninato] rare earth complexes have been systematically investigated by this research group [3,4], inspired with the precedent studies of Aroca and co workers [5,6], Homborg and co workers [7], and Tran-Thi et al. [8]. Concerning the IR vibrational spectroscopic characteristics of phthalocyanine ligand in bis(phthalocyaninato) rare earth complexes, three series of homoleptic compounds of the whole series of rare earth metals, namely $M(\text{Pc})_2$, $M[\text{Pc}(\text{OC}_8\text{H}_{17})_8]_2$, and $M[\text{Pc}(t\text{Bu})_4]_2$ [$M = \text{Y, La, \dots, Lu}$ except for Pm ; $\text{H}_2\text{Pc}(t\text{Bu})_4 = 2(3),9(10),16(17),24(25)$ -tetra(*tert*-butyl)phthalocyanine] have been systematically

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studied in order to have a profound and complete understanding of the effects of rare earth metals and substituents on their IR properties [3c]. However, there has been no systematic research on the IR spectroscopy of the heteroleptic bis(phthalocyaninato) rare earth analogues due to the absence of such double-deckers of the whole series of rare earth metals, which is related with the preparation, purification, and isolation difficulty of such species of complexes. In the course of our work to develop new species of sandwich compounds, we have recently developed a new and convenient synthetic route to heteroleptic bis(phthalocyaninato) rare earth complexes [9], with which the heteroleptic bis(phthalocyaninato) complexes of the series of rare earth metals can be easily prepared and isolated. In the present paper, we give a systematic and detailed description of the IR absorption properties for the phthalocyanine ligand in heteroleptic bis(phthalocyaninato) rare earth compounds $M(\text{Pc})[\text{Pc}(\text{OC}_8\text{H}_{17})_8]$ ($M = \text{Y}, \text{Pr}, \dots, \text{Lu}$ except for Pm). The influence of the decreased molecular symmetry of these complexes on the IR characteristics of phthalocyanine has also been studied in comparison with those of $M(\text{Pc})_2$ and $M[\text{Pc}(\text{OC}_8\text{H}_{17})_8]_2$.

2. Experimental

The heteroleptic bis(phthalocyaninato) rare earth complexes were prepared according to published procedures [9]. Their sandwich nature has been well established through a series of spectroscopic methods including high-resolution mass, UV–vis, near-IR and NMR techniques. IR spectra were recorded in KBr pellets with 2 cm^{-1} resolution using a BIORAD FTS-165 spectrometer.

3. Results and discussion

According to the single crystal X-ray diffraction structural analyses of unsubstituted or substituted bis(phthalocyaninato) rare earth complexes [10,11], the static symmetry is D_4 or D_{4d} depending on the twist (skew) angle between the two macrocyclic rings. Structurally characterized heteroleptic bis(phthalocyaninato) rare earth compounds remain very rare so far, and to our knowledge limited to $M(\text{Pc})[\text{Pc}(\alpha\text{-OC}_5\text{H}_{11})_4]$ ($M = \text{Sm}, \text{Eu}, \text{Er}$) containing non-peripherally 1,8,15,22-tetrakis(3-pentyloxy)phthalocyanine reported very recently by this group [12]. There seems no crystallographic report on the molecular structure of heteroleptic bis(phthalocyaninato) rare earth compounds containing peripherally octa(alkoxy)-substituted phthalocyanine ligand as our efforts in growing single crystals of $M(\text{Pc})[\text{Pc}(\text{OC}_8\text{H}_{17})_8]$ with good quality for X-ray diffraction analysis have also failed. However, according to our recent work on the molecular structure of 2,3,9,10,16,17,24,25-tetrakis(15-crown-5)phthalocyanine-containing heteroleptic bis(phthalocyaninato) europium compound $\text{Eu}(\text{Pc})[\text{Pc}(\text{15C5})_4]$ [$\text{H}_2\text{Pc}(\text{15C5})_4 = 2,3,9,10,16,17,24,25$ -tetrakis(15-

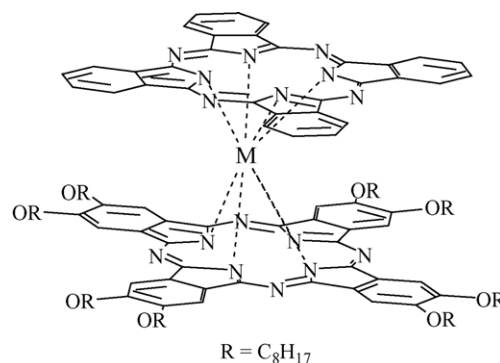


Fig. 1. Schematic molecular structure of heteroleptic bis(phthalocyaninato) rare earth complexes $M(\text{Pc})[\text{Pc}(\text{OC}_8\text{H}_{17})_8]$.

crown-5)phthalocyanine] [13], the skew angle between the two phthalocyanine macrocyclic ligands is very close to 45° . The equilibrium geometry of $\text{Eu}(\text{Pc})[\text{Pc}(\text{15C5})_4]$ is therefore C_{4v} . This should be also true for the present alkoxy-substituted analogues $M(\text{Pc})[\text{Pc}(\text{OC}_8\text{H}_{17})_8]$ (Fig. 1) considering the similar effect of 15-crown-5 ether and octyloxy groups attached at the peripheral positions of phthalocyanine ring on the rigid Pc core structure. The relatively lower molecular symmetry, C_{4v} for $M(\text{Pc})[\text{Pc}(\text{OC}_8\text{H}_{17})_8]$ than D_4 or D_{4d} , has been verified by the complicated IR spectra of the present series of heteroleptic bis(phthalocyaninato) rare earth complexes in comparison with those of homoleptic counterparts $M(\text{Pc})_2$ and $M[\text{Pc}(\text{OC}_8\text{H}_{17})_8]_2$ [3a,c], which is exemplified by the IR spectra of the dysprosium complexes $\text{Dy}(\text{Pc})_2$, $\text{Dy}(\text{Pc})[\text{Pc}(\text{OC}_8\text{H}_{17})_8]$, and $\text{Dy}[\text{Pc}(\text{OC}_8\text{H}_{17})_8]_2$ compared in Fig. 2. For the rigid core moiety of $M(\text{Pc})$ and $M\text{Pc}(\text{OC}_8\text{H}_{17})_8$ with C_{4v} symmetry containing 57 atoms (without considering the substituents), there are 65 IR active modes that dominate the IR spectra among the 165 total normal vibrational modes according to the theoretical expectation. The presence of eight octyloxy groups on the periphery of one phthalocyanine ring in heteroleptic double-decker molecules further multiplies the number of IR active modes in $M(\text{Pc})[\text{Pc}(\text{OC}_8\text{H}_{17})_8]$.

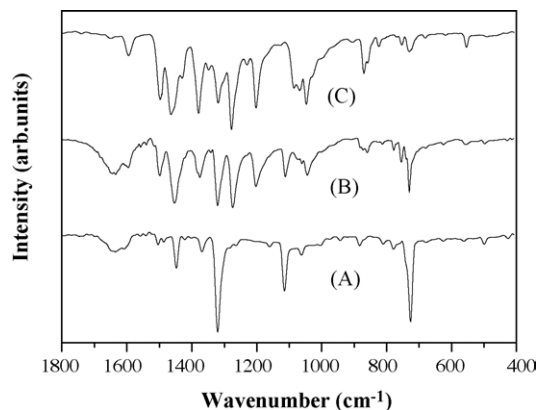


Fig. 2. Comparison of the IR spectra of (A) $\text{Dy}(\text{Pc})_2$, (B) $\text{Dy}(\text{Pc})[\text{Pc}(\text{OC}_8\text{H}_{17})_8]$, and (C) $\text{Dy}[\text{Pc}(\text{OC}_8\text{H}_{17})_8]_2$ in the region of $400\text{--}1800 \text{ cm}^{-1}$ with 2 cm^{-1} resolution.

Table 1

Characteristic IR bands (cm^{-1}) of phthalocyanine for $\text{M}(\text{Pc})[\text{Pc}(\text{OC}_8\text{H}_{17})_8]$ ($\text{M} = \text{Y}, \text{Pr}, \dots, \text{Lu}$ except Pm) with 2 cm^{-1} resolution

Pr	Nd	Sm	Eu	Gd	Tb	Dy	Y	Ho	Er	Tm	Yb	Lu	Assignment
412w	413w	410w	416w		420w	414w	419w	416w	418w	412w	417w		
432w	432w	430w	432w	434w	431w	429w	429w	429w	440w	431w	431w	429w	
489w	496w	497w	497	498w	498w	499w	499w	499w	500w	499w	500w	501w	
556w		555w	554w	559w	556w	556w	557w	555w	556w	557w	556w	556w	
625w	624w	626w	626w	618w	626w	626w	624w	625w	625w	625w	626w	626w	Pc breathing
678w	677w	678w	678w	676w	679w	679w	680w	680w	680w	681w	680w	681w	Pc breathing
729s	729s	729s	729s	729s	730s	730s	731s	730s	731s	732s	731s	732s	C–H wag
753m	752m	754m	751m	755m	752m	755m	755m	756m	756m	757m	756m	757m	Pc ring
776w	776w	776w	776w	777w	778w	778w	778w	777w	778w	780w	779w	779w	
810w	811w	812w	812w	814w	813w	813w	813w	813w	814w	813w	814w	814w	
859m	860m	859m	859m	859m	860m	859m	859m	858m	859m	858m	859m	859m	
871w		872w		872w	873w	873w	873w	872w	873w	874w	873w	873w	
		880w	880w	881w	883w	882w	882w	882w	883w	883w	884w	884w	Coupling of isoindole deformation and aza stretching
1001w	1002w	1001w	1002w	1000w	1001w	1002w	1002w	999w	1000w	1002w	1001w	1000w	Pyrrole-N in-plane bending
1047m	1045m	1044m	1044m	1042m	1046m	1045m	1045m	1045m	1045m	1044m	1044m	1044m	C–O–C stretching (sym)
1057m	1058m	1058m	1059m		1061m	1061m	1061m	1062m	1062m	1063m	1062m	1063m	Coupling of isoindole deformation and aza stretching
1076w	1069w		1069w		1073w	1073w	1074w	1073w	1074w	1072w	1072w	1072w	C–H bend
1113m	1112m	1111m	1111m	1113m	1113m	1112m	1112m	1112m	1112m	1113m	1113m	1113m	Isoindole breathing
1204m	1202m	1202m	1202m	1203m	1203m	1203m	1203m	1203m	1203m	1204m	1203m	1203m	C–H bend
1276s	1274s	1273s	1272s	1275s	1274s	1274s	1274s	1274s	1274s	1274s	1274s	1275s	C–O–C stretching (asym)
1315m	1316s	1318s	1319s	1319s	1320s	1320s	1321s	1320s	1321s	1322s	1322s	1322s	pyrrole stretching
1342w	1341w	1341w	1341w	1341w	1340w	1342w	1341w	1342w	1342w	1342w	1342w	1342w	pyrrole stretching
	1374 ^a	1372s	1374 ^a	1373s	1375 ^a	1375s	1375 ^a	1374s	1376 ^a	1377s	1376s	1377s	C–H bending (–CH ₃ , sym)
1385s	1385s		1385s		1384s		1384s		1383s				C–H bending (–CH ₃ , sym)
1419w	1418w		1418w		1421w		1420w			1406w	1406w	1407w	Isoindole stretching
1447s	1447s	1448s	1455s	1449s	1455s	1454s	1455s	1455s	1455s	1455s	1455s	1455s	C–H bending (–CH ₃ , asym)
1497m	1496m	1497m	1497m	1497m	1498m	1498m	1498m	1499m	1499m	1500m	1501m	1504m	Coupling of pyrrole and aza stretching
			1516w		1514w	1515w	1516w	1516w	1518w		1517w	1518w	Aza stretching
1540w	1540w	1540w	1540w	1539w	1539w	1540w	1539w	1540w	1540w	1539w	1540w	1540w	Benzene stretching
1557w	1557w	1558w	1558w	1557w	1558w	1558w	1557w	1558w	1558w	1558w	1557w	1558w	Benzene stretching
1595m	1596m	1593m	1598m	1595m	1596m	1595m	1597m	1596m	1596m	1596m	1597m	1597m	Benzene stretching
1635m	1634m	1635m	1635m	1635m	1635m	1635m	1635m	1635m	1635m	1635m	1635m	1635m	Benzene stretching
1645m	1644m	1645m	1645m	1645m	1645m	1645m	1645m	1645m	1645m	1645m	1645m	1645m	Benzene stretching
1738w	1731w	1731w	1738w	1729w	1732w	1734w	1734w	1729w	1736w	1736w	1730w	1737w	Benzene stretching
2854s	2854s	2854s	2850s	2855s	2853s	2853s	2857s	2852s	2853s	2853s	2854s	2853s	C–H stretching (–CH ₂ –, sym)
2869 ^a	2878 ^a	2868 ^a	2869 ^a	2866 ^a	2869 ^a	2865 ^a	2869 ^a	2868 ^a	2869 ^a	2870 ^a	2868 ^a	2867 ^a	C–H stretching (–CH ₃ , sym)
2923s	2924s	2925s	2926s	2922s	2923s	2923s	2924s	2924s	2925s	2924s	2926s	2924s	C–H stretching (–CH ₂ –, asym)
2951 ^a	2950 ^a	2951 ^a	2962 ^a	2950 ^a	2950 ^a	2952 ^a	2958 ^a	2958 ^a	2951	2952 ^a	2950 ^a	2952 ^a	C–H stretching (–CH ₃ , asym)

^a Shoulder peak.

It is worth noting that the IR spectra of heteroleptic bis(phthalocyaninato) analogues of the Eu and Y metals, $\text{M}(\text{Pc})[\text{Pc}(\text{OC}_5\text{H}_{11})_8]$, and $\text{M}(\text{Pc})[\text{Pc}(\text{C}_7\text{H}_{11})_8]$ [$\text{M} = \text{Eu}, \text{Y}; \text{H}_2\text{Pc}(\text{OC}_5\text{H}_{11})_8 = 2,3,9,10,16,17,24,25$ -octakis(pentyloxy)phthalocyanine, $\text{H}_2\text{Pc}(\text{C}_7\text{H}_{11})_8 = 2,3,9,10,16,17,24,25$ -octakis(heptyl)phthalocyanine] have been recorded in our first trial to investigate the vibrational properties of phthalocyanine in sandwich tetrapyrrole rare earth complexes [3a]. The newly recorded IR spectra of $\text{M}(\text{Pc})[\text{Pc}(\text{OC}_8\text{H}_{17})_8]$ are in good accordance with the previous measurements, in particular for $\text{M}(\text{Pc})[\text{Pc}(\text{OC}_5\text{H}_{11})_8]$.

Fig. 3 compares the IR spectra in the region of fundamental frequencies of $400\text{--}1800 \text{ cm}^{-1}$ of three compounds $\text{M}(\text{Pc})[\text{Pc}(\text{OC}_8\text{H}_{17})_8]$ ($\text{M} = \text{Nd}, \text{Dy}, \text{and Yb}$) with resolution of 2 cm^{-1} , typical for the light, middle, and

heavy rare earths, respectively. In Table 1, characteristic IR vibrational frequencies of the phthalocyanine ligand in heteroleptic bis(phthalocyaninato) compounds of the series of rare earths are summarized and their interpretation in terms are tried by analogy with the IR and Raman characteristics of $\text{M}(\text{Pc})_2$ and especially $\text{M}[\text{Pc}(\text{OC}_8\text{H}_{17})_8]_2$ [4] and the vibrational properties of phthalocyanine [14] with assistance from the recent theoretical research into the vibrational spectra of monomeric phthalocyanine derivatives [15]. However, it is hard to achieve one-to-one matching of observed vibrational frequencies to the internal vibrations in the IR vibrational spectra of heteroleptic bis(phthalocyaninato) rare earth compounds due to the existence of strong couplings of some vibrational coordinates of the large conjugated phthalocyanine rings. In the

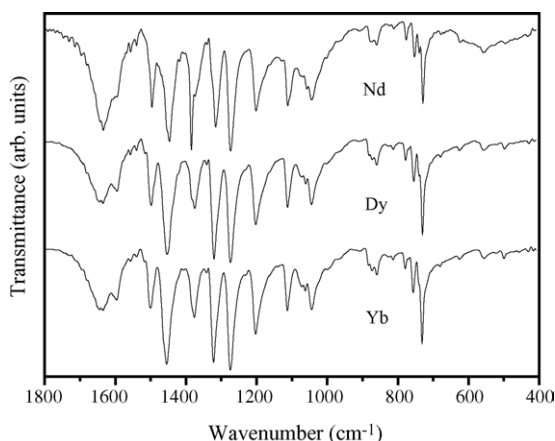


Fig. 3. IR spectra of $M(\text{Pc})[\text{Pc}(\text{OC}_8\text{H}_{17})_8]$ ($M = \text{Nd}, \text{Dy}$ and Yb) in the region of $400\text{--}1800\text{ cm}^{-1}$ with 2 cm^{-1} resolution.

present case, the aim to distinguish the observed frequencies to the unsubstituted and substituted phthalocyanine rings, respectively, cannot be reached either.

Based on the previously systematic studies over the IR spectroscopic properties of homoleptic bis(phthalocyaninato) counterparts of the whole series of rare earth metals [3c], the IR spectra of the present series of heteroleptic compounds $M(\text{Pc})[\text{Pc}(\text{OC}_8\text{H}_{17})_8]$ differ considerably from the simple patterns of the IR spectra of $M(\text{Pc})_2$, but resemble those of $M[\text{Pc}(\text{OC}_8\text{H}_{17})_8]_2$ except for the increasing complexity and vibration bands in the spectra because of the reduced molecular symmetry. A comparison between the IR spectra of $M(\text{Pc})_2$, $M(\text{Pc})[\text{Pc}(\text{OC}_8\text{H}_{17})_8]$, and $M[\text{Pc}(\text{OC}_8\text{H}_{17})_8]_2$ together with typical bands of alkoxy groups renders it possible to identify the IR vibrational fundamentals due to the phthalocyanine moieties and the influence of the IR vibrational on heteroleptic bis(phthalocyaninato) rare earth complexes.

In the region of fundamental frequencies of $400\text{--}1800\text{ cm}^{-1}$ of the IR spectra of $M(\text{Pc})[\text{Pc}(\text{OC}_8\text{H}_{17})_8]$, pyrrole stretching at $1315\text{--}1322\text{ cm}^{-1}$ maintains their intensity as in $M(\text{Pc})_2$ but is more intense than in $M[\text{Pc}(\text{OC}_8\text{H}_{17})_8]_2$, appearing as the most intense bands, which also acts as the phthalocyanine monoanion radical marker band. The C–H wagging of $M(\text{Pc})[\text{Pc}(\text{OC}_8\text{H}_{17})_8]$ at ca. 725 cm^{-1} loses some intensity than the one in $M(\text{Pc})_2$, but stronger than that in $M[\text{Pc}(\text{OC}_8\text{H}_{17})_8]_2$. The substitution of some H by OC_8H_{17} groups in the peripheral β positions of one phthalocyanine ring in $M(\text{Pc})[\text{Pc}(\text{OC}_8\text{H}_{17})_8]$ is considered to be responsible for decreasing the relative intensity of the out-of-plane C–H vibrations. It can be observed that in the IR spectra of $M(\text{Pc})[\text{Pc}(\text{OC}_8\text{H}_{17})_8]$, the symmetric C–O–C stretching bands at 1045 cm^{-1} , the C–H band at 1203 cm^{-1} , the symmetric C–H banding at 1375 cm^{-1} , and the coupling of pyrrole and aza stretching at 1500 cm^{-1} , are all loses some intensity than those in the IR spectra of $M[\text{Pc}(\text{OC}_8\text{H}_{17})_8]_2$. On the other hand, in the IR spectra of $M(\text{Pc})[\text{Pc}(\text{OC}_8\text{H}_{17})_8]$, the antisymmetric C–O–C stretching bands at 1275 cm^{-1} and the antisymmetric C–H banding at

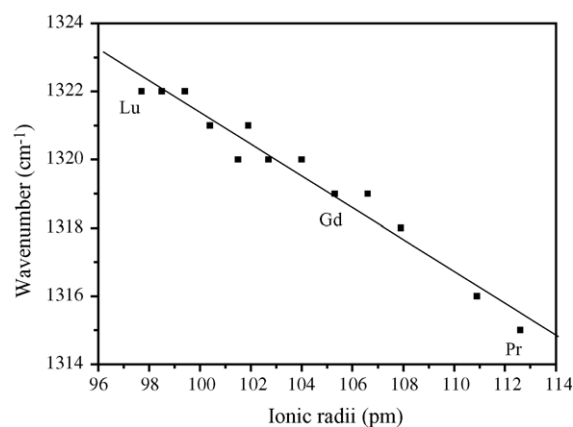


Fig. 4. Plot of wavenumber of the pyrrole stretching of $M(\text{Pc})[\text{Pc}(\text{OC}_8\text{H}_{17})_8]$ ($M = \text{Y}, \text{Pr}, \dots, \text{Lu}$ except Pm) at ca. $1315\text{--}1322\text{ cm}^{-1}$ as a function of the ionic radius of M^{III} .

1455 cm^{-1} maintain their intensity as in $M[\text{Pc}(\text{OC}_8\text{H}_{17})_8]_2$. These results suggest that in the region of fundamental frequencies of IR spectra of the heteroleptic bis(phthalocyaninato) complexes $M(\text{Pc})[\text{Pc}(\text{OC}_8\text{H}_{17})_8]$, $400\text{--}1800\text{ cm}^{-1}$, the antisymmetric vibrational bands of the octyloxy substituents are in the same intensity as in the homoleptic bis(phthalocyaninato) complexes $M[\text{Pc}(\text{OC}_8\text{H}_{17})_8]_2$, whereas the symmetric vibrational ones, on the contrary, lose some intensity in association with the decrease of the octyloxy substituent numbers. The remaining peaks in the IR spectra of the whole series of heteroleptic double-decker complexes have been partially assigned by analogy with those of $M(\text{Pc})_2$ and $M[\text{Pc}(\text{OC}_8\text{H}_{17})_8]_2$ (Table 1).

As in $M[\text{Pc}(\text{OC}_8\text{H}_{17})_8]_2$, with respect to the Pc ring stretching bands in $M(\text{Pc})[\text{Pc}(\text{OC}_8\text{H}_{17})_8]$, the four absorptions at ca. 2854 cm^{-1} (symmetric), 2869 cm^{-1} (antisymmetric), 2923 cm^{-1} (symmetric), and 2951 cm^{-1} (antisymmetric) attributed to the C–H stretching vibrations of the $-\text{CH}_2-$ and $-\text{CH}_3$ groups of the eight octyloxy side chains maintains their intensity despite of the decrease in the side chain number compared with that in $M[\text{Pc}(\text{OC}_8\text{H}_{17})_8]_2$. In comparison with the IR spectra of $M(\text{Pc})[\text{Pc}(\alpha\text{-OC}_5\text{H}_{11})_4]$ [4f] and $M[\text{Pc}(\alpha\text{-OC}_5\text{H}_{11})_4]_2$ [16], it can be easily understood that the intensity of these absorption bands not only depend on the alkoxy side chain number but also on the length of the alkoxy side chains.

In the IR spectra of $M(\text{Pc})[\text{Pc}(\text{OC}_8\text{H}_{17})_8]$, the vibrations at $1057\text{--}1063\text{ cm}^{-1}$ due to the coupling of isoindole deformation and aza stretching, at $1315\text{--}1322\text{ cm}^{-1}$ attributed to pyrrole stretchings, and at $1497\text{--}1504\text{ cm}^{-1}$ assigned to the coupling of pyrrole and aza stretching are sensitive to the ionic size of central rare earth ion (Table 1). Along with decrease of rare earth radius, the energies of the above-mentioned vibration modes linearly shift to the blue (Fig. 4). This finding is in line with those found for other bis[(na)phthalocyaninato] rare earth counterparts and reveals the increasing $\pi\text{--}\pi$ interaction in the double-decker molecules along with lanthanide contraction [3].

4. Conclusions

The infrared spectra for a series of heteroleptic bis(phthalocyaninato) rare earth complexes $M(\text{Pc})[\text{Pc}(\text{OC}_8\text{H}_{17})_8]$ have been recorded and systematically studied. In comparison with those of homoleptic analogues $M(\text{Pc})_2$ and $M[\text{Pc}(\text{OC}_8\text{H}_{17})_8]_2$, the IR spectra of $M(\text{Pc})[\text{Pc}(\text{OC}_8\text{H}_{17})_8]$ take more complicated features, revealing the decreased molecular symmetry of these double-decker compounds.

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