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Coordination Chemistry Reviews 226 (2002) 93–101

COORDINATION CHEMISTRY REVIEWS

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Synthetic, spectroscopic and theoretical study of novel supramolecular structures composed of lanthanide phthalocyanine double-decker complexes

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Received 10 April 1999; accepted 21 September 2001

Contents

Abstract

This paper reviews the authors' attempts to create novel supramolecular structures composed of bis(phthalocyaninato)lanthanides and the analysis of their geometric and electronic structures. We synthesized tetra- and mono-crown-substituted bis(phthalocyaninato)lutetium, which show different aggregate forms under various conditions. The aggregate structures fall into three categories: (1) a D_{4h} vertically stacked structure formed from the tetra-crown complex and cations such as K^+ or NH_4^+; (2) a sliding form composed of tetra-crown complexes in methanol/chloroform mixed solvent; and (3) a pivoted form constructed from mono-crown substituted complexes with cations such as K^+. The electronic structure of the supramolecular structures and magnetic interactions within are discussed.

Keywords: Supramolecular structure; Phthalocyanine; Lanthanide; Crown ether; Double-decker complexes; Biradical

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0010-8545/02/$ - see front matter
PII: S0010-8545(01)00439-8

1. Introduction

Bis(phthalocyaninato) lanthanide(III) complexes, $Ln(Pc)_2$, are known to exist as stable radicals [1] holding an unpaired electron on a π orbital delocalized over two Pc rings [2]. In the solid phase, the complexes exhibit a unique intrinsic conductivity owing to the unpaired electron [3–5]. Static behavior of the π hole as a magnetic spin has been reported in single crystals of $Y(Pc)_2$, in which either ferromagnetic or antiferromagnetic interactions are observed depending on the crystal morphology [6]. Because of these interesting properties, the bis(phthalocyaninato) lanthanide complexes are expected to be functional building blocks for supramolecular (SM) structures functioning as molecular conducting wires or molecule-based magnets.

It is of great importance to study small systems composed of a limited number of components before examining larger or infinitely extended systems. As a starting point to create new types of SM structures, we have synthesized mono-15-crown-5-substituted $Lu(Pc)_2$ complexes, $Lu(CR_1Pc)(Pc)$ [7], and tetra-15-crown-5-substituted $Lu(Pc)_2$ complex, $Lu(CR_4Pc)(Pc)$ [8] (Fig. 1). These compounds were designed to form a SM structure comprising only two component Pc dimers. In these compounds, two $Lu(Pc)_2$ sites are bound by the 2:1 complex formation of 15-crown-5 and potassium cation [7,8]. Each structure contains two $Lu(Pc)_2$ sites and has two unpaired electrons on the sites separately, composing a biradical. These systems are the first examples of SM structures composed of the bis(phthalocyaninato) lanthanide complexes. The method utilizing crowns to bridge two Pc sites was first reported by Kobayashi and Lever in the monomeric Pc metal complexes ($M(CR_4Pc)$, $M = H_2$, Zn, Co, Ni and Cu) [9].

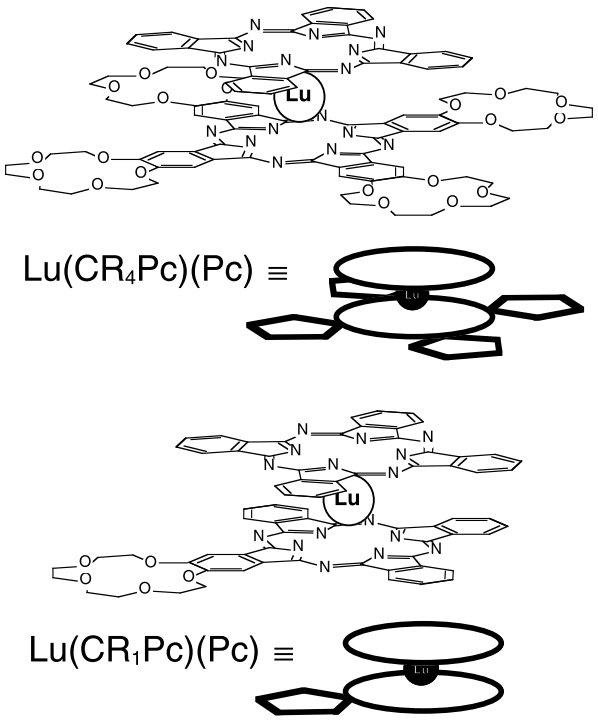


Fig. 1. Molecular structure of $Lu(CR_4Pc)(Pc)$ and $Lu(CR_1Pc)(Pc)$.

This paper reviews the synthesis [7,8], spectroscopic measurements [10,11] and theoretical investigations [10,11] on the SM structures of $Lu(CR_1Pc)(Pc)$ and $Lu(CR_4Pc)(Pc)$. We will show that there are three types of structures categorized by the number of bridging sites, which determine the freedom of motion of the systems. All three types of structures are in a biradical state, and show characteristic EPR spectra with different magnetic parameters. Using the magnetic parameters obtained from theoretical calculations and those from simulations of the observed EPR spectra, the structures of the SM aggregates will be discussed. The exchange interactions between the radical sites in the three superstructures will also be investigated.

2. Synthesis

2.1. $Lu(CR_4Pc)(Pc)$ [8]

The metal-free benzo-15-crown-5 substituted phthalocyanine [9] (H_2CR_4Pc, 0.2 g) and an equimolar amount of phthalocyaninato-lutetium acetate [12] ($Lu(Pc)(CH_3COO)(H_2O)_2$, 0.123 g) were put into dried 1-chloronaphthalene (10 ml). The mixture was refluxed for 8 h, cooled to room temperature, and added to 50 ml of hexane. The precipitate was extracted with chloroform, and chromatographed on an alumina column (Merck Aluminum oxide 90, particle size 0.063–0.200 mm) with chloroform as eluent. The initial green band was identified as $Lu(Pc)_2$ by UV absorption spectrum. Following the second blue band, $Lu(CR_4Pc)(Pc)$ was obtained as a green band. The green fraction was successively chromatographed twice. Concentration and addition of hexane gave a microcrystalline powder of $Lu(CR_4Pc)(Pc)$. The compound was identified by elemental analysis and mass spectrum (FAB method on JEOL JMS-HX110/HX110 utilizing MS1 only).

Anal. Calcd. (%) for $C_{96}H_{88}O_{20}N_{16}LuCHCl_3$: C, 56.01; H, 4.31; N, 10.77. Found: C, 55.79; H, 4.72; N, 10.13. MS: *m/e* 1960.4 (mol. Wt. 1960.4 for $C_{96}H_{88}O_{20}N_{16}Lu$).

2.2. $Lu(CR_1Pc)(Pc)$ [7]

Dicyanobenzo-15-crown-5 (1 g), dicyanobenzene (2.81 g), lutetium acetate (1.33 g) and 1,8-diazabicyclo[5.4.0]-7-undecene (3.82 g) were put in hexanol (100 ml), and refluxed for 6 h. The mixture was concentrated, added to hexane and filtered. The precipitate was extracted by dichloromethane and added to hexane

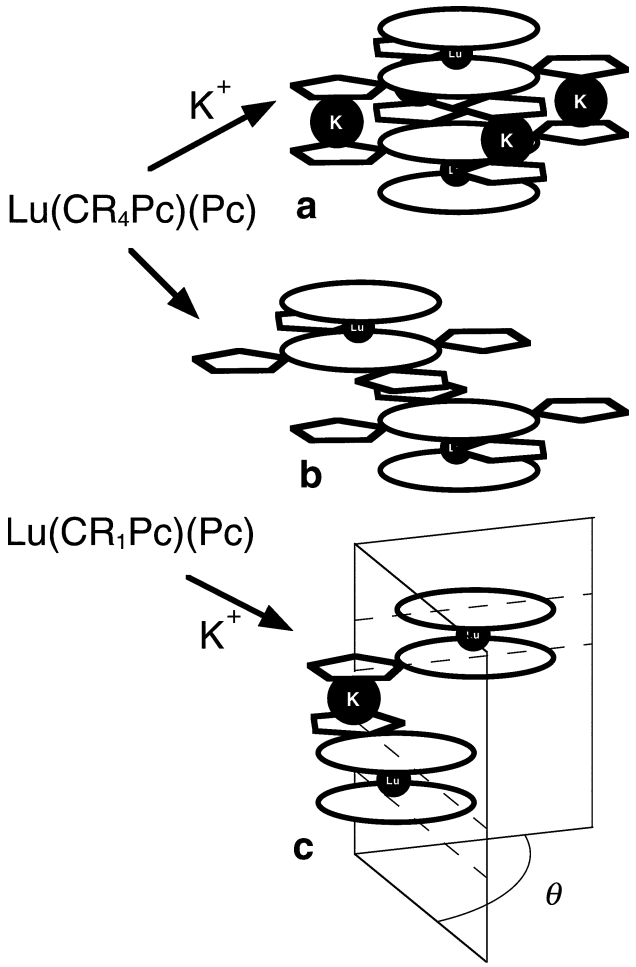


Fig. 2. Proposed SM structures composed of $Lu(CR_4Pc)(Pc)$ and $Lu(CR_1Pc)(Pc)$. (a) D_{4h} SM structure of $Lu(CR_4Pc)(Pc)$ in the presence of a potassium cation. (b) Solvent-induced SM structure of $Lu(CR_4Pc)(Pc)$. (c) SM structure of $Lu(CR_1Pc)(Pc)$ in the presence of a potassium cation.

to give a viscous mass, which contains non-, mono-, and poly-crown-substituted bis(phthalocyaninato)-lutetium and monomeric phthalocyaninato lutetium complexes. Succeeding reprecipitations by chloroform/hexane yielded 3.3 g of powdered crude product, which was then subjected to column chromatography to isolate $Lu(CR_1Pc)(Pc)$. First a chloroform solution of the crude product (typically 700 mg in 35 ml of the solvent) was developed with chloroform on an alumina column (Merck Aluminium oxide 90). The first band, which contained radical forms of non-, mono-, and multi-crown-substituted bis(phthalocyaninato)lutetium, was collected, concentrated and added to hexane to give a precipitate (about 120 mg from 700 mg of the crude product). Following a filtration, the precipitate was dissolved (typically 30 mg in 25 ml of the solvent) in chloroform/hexane (95/5, v/v) and put on a silica gel column (Merck Silica gel 60, particle size 0.040–0.063 mm). Using chloroform/hexane = 95/5, $Lu(Pc)_2$ was first eluted. The second band, which contained only $Lu(CR_1Pc)(Pc)$, was eluted with a sufficient separation from the first and third bands. From this procedure, about 8 mg of $Lu(CR_1Pc)(Pc)$ was isolated. The overall yield of $Lu(CR_1Pc)(Pc)$ was 3%. The compound was identified by elemental analysis and mass spectrum (FAB method on JEOL JMS AX-505HA). It was confirmed by the mass spectrum that the sample did not contain non- and poly-15-crown-5-substituted species.

Anal. Calcd. (%) for $C_{72}H_{46}N_{16}O_5Lu{\cdot}CHCl_3$: C, 58.08; H, 3.14; N, 14.85. Found (%): C, 58.05; H, 3.33; N, 14.79. MS: m/e 1389.3 (mol. wt. 1389.3 for $C_{72}H_{46}N_{16}O_5Lu$).

3. Spectral changes upon supramolecular (SM) structure formation

3.1. Electronic spectral changes [8]

The absorption and MCD spectra of $Lu(CR_4Pc)(Pc)$ are shown in Fig. 3 (solid line). The substitution by crown ether does not have a significant effect on the energies, intensities and shape of the bands in the region from near-infrared band to Q band. The Q band also shows a MCD A-term characteristic of a metallophthalocyanine. The bands at 7×10^3, 11×10^3 and 15×10^3 cm^{-1} are assigned to $|G^*\rangle$ (intervalence band), $|D-\rangle$ (corresponding to Q band of cation-radical Pc^-) and $|S-\rangle$ (corresponding to the Q band of Pc^{2-}) states, respectively, as in the case of $Lu(Pc)_2$ [13,14]. In the presence of a K^+ ion, the absorption band energies shift owing to the formation of the cation-induced SM structure (Fig. 2(a), Fig. 3, broken line). A blue shift is observed in all the major bands except $|G^*\rangle$ band. This observation can be explained by the exciton coupling theory; interaction between two transition dipoles perpendicular to the vector joining the dipoles leads to a blue shift. The blue shift is also observed with the 21×10^3 cm^{-1} band, which commonly appears in Pc cation radicals, indicating that the band is an in-plane transition. Recently, the 500 nm band seen in π-cation-radical Pcs, often referred to as the 'marker' or 'fingerprint' band, was concluded to be a degenerate in-plane transition [15], after a long argument upon its assignment. A red shift is expected in $|G^*\rangle$ band since the band has an out-of-plane transition moment. However, the shift was undetectably small.

The blue shift of the Q band of $Lu(CR_4Pc)(Pc)$ (0.18×10^3 cm^{-1}) is smaller than that of $Zn(CR_4Pc)$ (0.98×10^3 cm^{-1}) [9]. The smaller shift is due to the longer distance between the two transition dipoles. Assuming that the dipoles lie at the centers of respective component Pc dimers or monomers, the ratio of

the cube of the reciprocal dipole–dipole distances R is related to:

$$R([\mathrm{Lu(CR_4Pc)(Pc)}]_2)^{-3}/R([\mathrm{Zn(CR_4Pc)}]_2)^{-3} = (7.1\ \text{Å})^{-3}/(4.1\ \text{Å})^{-3} = 0.19$$

where the neighboring Pc–CR_4Pc distance and that of CR_4Pc–CR_4Pc are assumed to be 3.0 [14] and 4.1 Å [16], respectively. This agrees with the ratio of the observed blue shifts (0.18×10^3 $\mathrm{cm}^{-1}/0.98 \times 10^3$ $\mathrm{cm}^{-1} = 0.18$).

The $|G^*\rangle$ band of the Pc dimer radical does not disappear with SM formation. Thus, the π-holes are preserved in respective components.

Addition of methanol to chloroform solution of Lu(CR_4Pc)(Pc) does not cause pronounced changes in absorption and MCD spectra at room temperature. This makes a clear contrast with M(CR_4Pc); addition of methanol to the chloroform solution of the crown ether substituted Pc monomer gives rise to changes in spectrum which parallel the change with addition of K^+ [9].

3.2. EPR spectral changes

3.2.1. Cation-induced SM formation in Lu(CR_4Pc)(Pc) [8,11]

The π-radical Lu(CR_4Pc)(Pc) shows an EPR spectrum at $g = 2.002$ in frozen solution in chloroform at 77 K as shown in Fig. 4(a). The g-value and the spectral shape are similar to those of unsubstituted complex Lu$(Pc)_2$. Addition of CH_3COONa does not give any new signal (Fig. 4(b)). With addition of CH_3COOK, a new signal appears (Fig. 4(c-1)) on both sides of the mono-radical signal. The separation between the main peaks is 4.65 mT. The new signal has a typical EPR signal shape for an electronic triplet state in a random orientation. The triplet signal is evidence of formation of a SM structure in a biradical state.

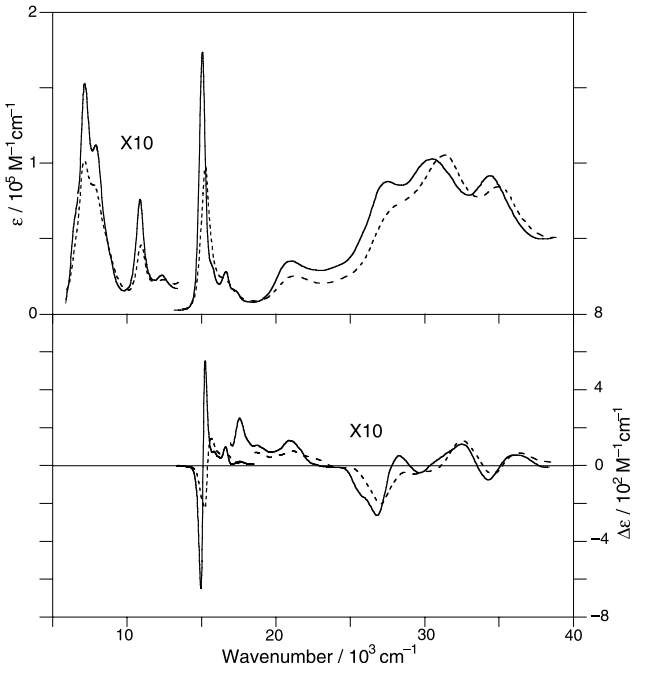


Fig. 3. Absorption (upper) and MCD (lower) spectra of Lu(CR_4Pc)(Pc) (solid lines) and a SM structure, [Lu(CR_4Pc)(Pc)]$_2K_4$, formed in the presence of CH_3COOK (broken lines) at room temperature [8]. Solvent is a mixture of chloroform and methanol (95/5, v/v). The concentration of CH_3COOK is 1.2×10^{-2} mol l^{-1}.

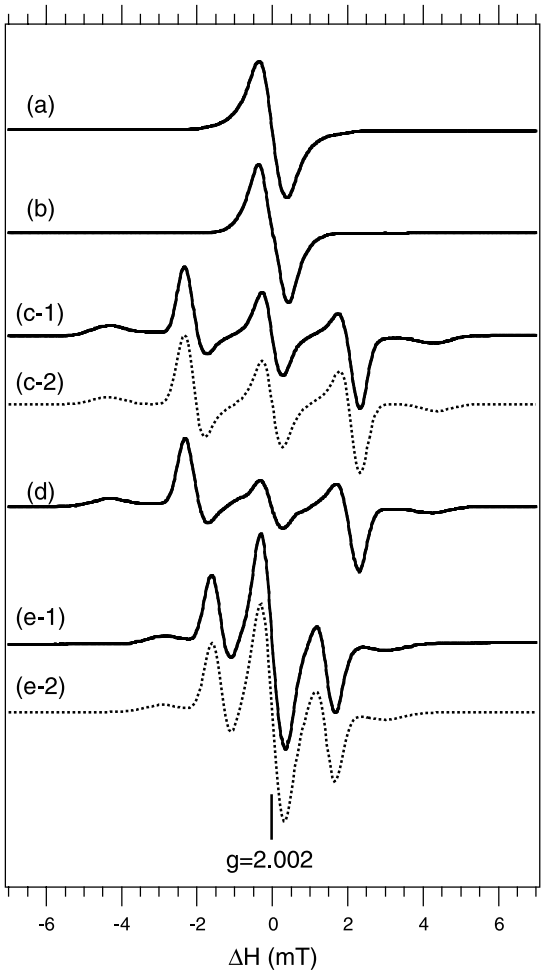


Fig. 4. X-band EPR spectra of Lu(CR_4Pc)(Pc) in the presence of (a) no cation, (b) CH_3COONa, (c-1) CH_3COOK, (d) CH_3COONH_4, (e-1) no cation in frozen solution at 77 K in (a) $CHCl_3$ and (b, c-1, d and e-1) $CHCl_3$:MeOH = 50:50. The concentration of the added salt is 1.2×10^{-1} M in (b), (c-1) and (d), and that of Lu(CR_4Pc)(Pc) is 1×10^{-4} M in all cases. The simulation for the spectrum (c-1) is shown in (c-2). The triplet EPR part was obtained with the zero-field splitting $D = 0.00407$ cm^{-1}, using a gaussian line shape of anisotropic line-width $w_{zz} = 0.48$ mT and $w_{xx} = w_{yy} = 0.28$ mT. The monoradical EPR part was obtained with isotropic hfs constants from Lu $a_{\mathrm{Lu}} = 0.05$ mT, $a_{\mathrm{N(1)}} = 0.04$ mT and $a_{\mathrm{N(2)}} = 0.04$ mT using lorentzian line shape with hwhm = 0.31 mT. The simulations for (e-1) are shown in (e-2). The triplet EPR part was obtained with zero-field splitting $D = 0.00277$ cm^{-1}, using a gaussian line shape of anisotropic line-width $w_{zz} = 0.56$ mT and $w_{xx} = w_{yy} = 0.28$ mT. The monoradical EPR part was obtained with the same parameters as in (c-2) except for the hfs constant for Lu ($a_{\mathrm{Lu}} = 0.07$ mT).

When CH_3COONH_4 is used, a similar signal to the K^+-induced EPR is observed as shown in Fig. 4(d). The separation between the main peaks is 4.63 mT, which is almost the same as the K^+ case. This indicates that the NH_4^+-induced structure has basically the same geometry as that of K^+-induced one.

3.2.2. Solvent-induced SM formation in Lu(CR_4Pc)(Pc) [11]

When no salt was added to the chloroform/methanol solution, a different signal from the triplet state was observed (Fig. 4(e-1)). The separation between the main peaks was 3.25 mT, which was smaller than that of the cation-induced triplet signals. This indicates that the mean distance between the two unpaired electrons in the present case is larger than that in the cation-induced case. Regardless of the ratio of the chloroform and methanol, addition of CH_3COOK annihilated the methanol-induced signal and gave rise to the K^+-induced signal.

The unsubstituted $Lu(Pc)_2$ did not show any new signal induced by the addition of methanol. This indicates that the presence of the crown parts is essential for the solvent-induced dimerization.

The 15-crown-5 forms a 1:1 complex with Na^+, which has a smaller radius than K^+. As expected, addition of CH_3COONa did not cause biradical formation (Fig. 4(b)). A more important point, however, is the fact that the addition of Na^+ annihilates the methanol-induced signal. This indicates that the crown moieties are occupied by Na^+, and even with a high ratio of methanol, methanol-induced biradical formation is inhibited due to the electrostatic repulsion between the positively charged $[Lu(CR_4Pc)(Pc)Na_n]^{n+}$ ions. Additionally, this experiment suggests that the CH_3COO^- ion does not contribute to the SM formation.

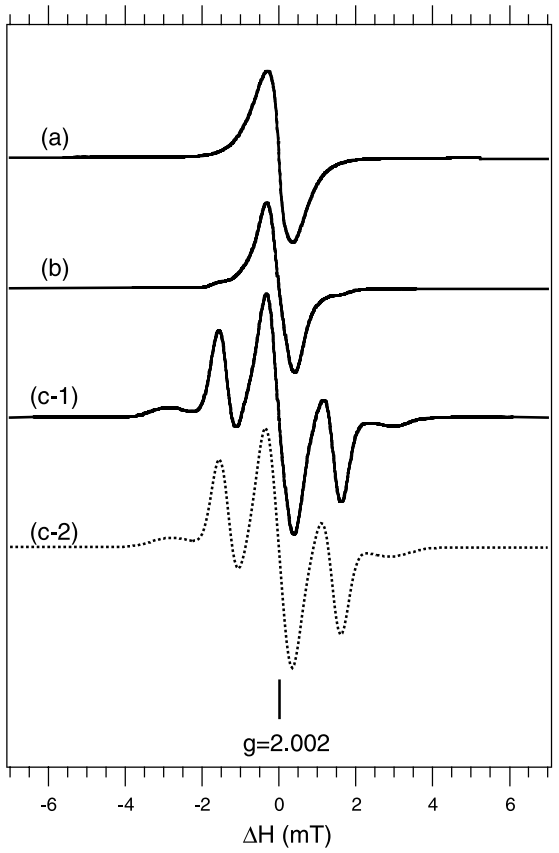


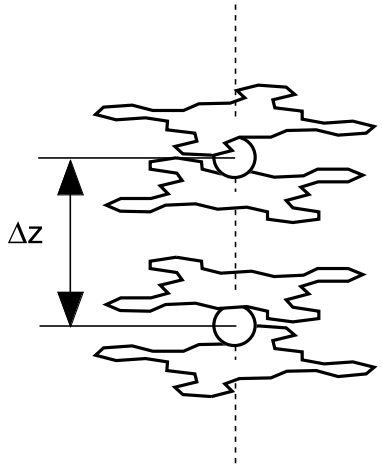
Fig. 5. X-band EPR spectra of Lu(CR_1Pc)(Pc) (a) in $CHCl_3$, (b) in $CHCl_3$:MeOH = 1:1, (c-1) with CH_3COOK (1.2×10^{-1} M) in $CHCl_3$:MeOH = 1:1. The concentration of Lu(CR_1Pc)(Pc) is 1×10^{-4} M. Each spectrum was taken at 77 K in a frozen solution. The simulations for (c-1) are shown in (c-2). The triplet EPR part is obtained with zero-field splitting $D = 0.00268$ cm^{-1}, using a gaussian line shape anisotropic line-width $w_{zz} = 0.56$ mT and $w_{xx} = w_{yy} = 0.28$ mT. The monoradical EPR part was obtained with isotropic hf constants from Lu $a_{Lu} = 0.08$ mT, $a_{N(1)} = 0.05$ mT and $a_{N(2)} = 0.04$ mT using lorentzian line shape with a hwhm = 0.31 mT.

3.2.3. Cation-induced SM formation in Lu(CR_1Pc)(Pc) [7,11]

Fig. 5 shows EPR measurements for the mono-crown Pc dimer. The signal in chloroform solution shown in Fig. 5(a) is similar to signals from $Lu(Pc)_2$ and Lu(CR_4Pc)(Pc). The measurement in a mixed solvent with chloroform and methanol at the ratio of 50/50 shows an additional signal on both sides of the original signal (Fig. 5(b)). However, the intensity of the new signal is much smaller than in the case of the tetra-crown Pc dimer. This indicates that the solvent-induced dimerization is less efficiently achieved when the number of crown parts is decreased. Addition of CH_3COOK gives a new signal (Fig. 5(c-1)). The separation between the main peaks is 3.12 mT. This value is smaller than that of the K^+-induced signal in Lu(CR_4Pc)(Pc) and similar to that of the solvent-induced signal in Lu(CR_4Pc)(Pc).

3.2.4. Simulations of the EPR spectra [11]

Fig. 4(c-2) is a simulation of the observed spectrum (c-1). The spectrum displayed is the sum of the signal of biradical (at $\Delta H = \pm 2.3$ and ± 4.3 mT) and that of monoradical (at $\Delta H = 0$ mT). The biradical component is obtained assuming a triplet state, with a zfs constant $|D| = 0.00407$ cm^{-1} and $g = 2.002$. The line shape employed is a gaussian shape to which all the hyperfine structures (hfs) from Lu and N nuclei are assumed to be incorporated. The hwhm was treated as a tensor with principal values of $w_{zz} = 0.48$ mT and $w_{xx} = w_{yy} = 0.28$ mT. This indicates that there is a large anisotropy in the line width. Since all the hf interactions are put into a gaussian line shape, its hwhm is directly reflected from the value of the hf constant. The anisotropy of the hwhm should be attributed to that of the hf constant of Lu or N nuclei.



Scheme 1.

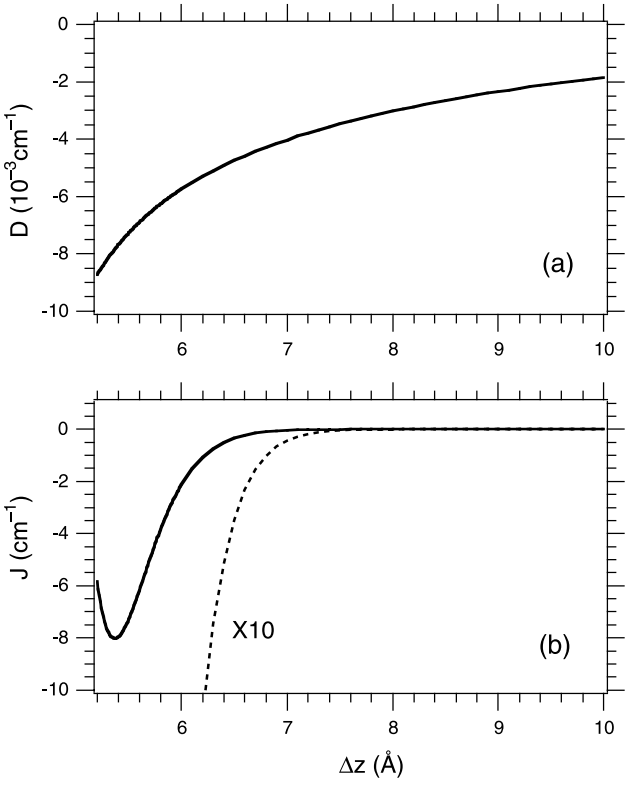


Fig. 6. Plots of (a) zero-field splitting constant D and (b) exchange interaction J as a function of the distance Δz defined in Scheme 1.

The simulation for the solvent-induced biradical signal of $Lu(CR_4Pc)(Pc)$ is shown in Fig. 4(e-2). The observed signal was reproduced with the zfs constants $|D| = 0.00277$ cm^{-1}, $E = 0$ cm^{-1} and anisotropic hwhm values, $w_{zz} = 0.56$ mT and $w_{xx} = w_{yy} = 0.28$ mT. The smaller zfs constant $|D|$ indicates that the mean distance between the two radical sites is longer than the cation-induced case.

The calculation for the cation-induced biradical signal of the mono-crown Pc dimer is shown in Fig. 5(c-2). The simulated spectrum was obtained with zfs constants $|D| = 0.00268$ cm^{-1} and $E = 0$ cm^{-1}, and a tensor line width with principal values $w_{zz} = 0.56$ mT and $w_{xx} = w_{yy} = 0.28$ mT. This case also shows anisotropy in the line width.

The third SM structure has a pivot-like bridge site, around which the two $Lu(Pc)_2$ sites can rotate. However, such rotation appears to be restricted because the zfs constant D (and E) is uniquely determined.

4. Theoretical calculation on the SM structure

The first theoretical study on the D_{4h} SM structure composed of two $Lu(CR_4Pc)(Pc)$ molecules was reported in Ref. [10]. In the D_{4h} SM structure, the variable that determines the zfs constants and exchange interaction is the distance between the two radical sites along the common C_4 axis. In contrast, the solvent-induced aggregation does not have any bridge that fixes relative geometry rigidly, and can have different symmetry. Because of the smaller zfs constant $|D|$, the solvent-induced structure is expected to have a larger distance than the cation-induced one. For the same reason, the SM structure of $Lu(CR_1Pc)(Pc)$ also has a larger mean-distance owing to the rotation around the pivot-like bridge. A comparative study on the geometry, zfs constants and exchange interactions in the three SM structures was carried out in Ref. [11].

4.1. Cation-induced D_{4h} SM structure [10,11]

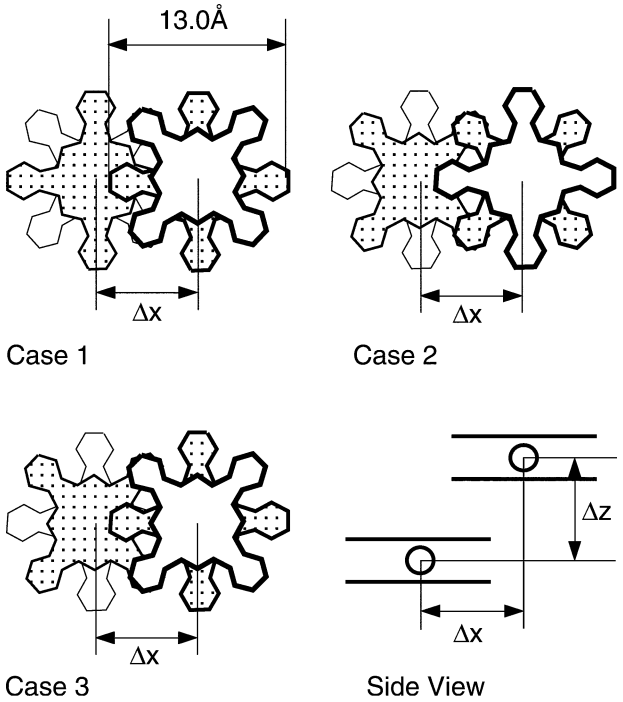
The zfs constant D for the D_{4h} biradical system was calculated using a geometry shown in Scheme 1. The result is shown in Fig. 6(a). Each unpaired electron is separately put on one of the two $Lu(Pc)_2$ sites, which are placed parallel with a center-to-center distance Δz. The D value is predicted to take negative values in the region $\Delta z > 6$ Å. Since the configuration is assumed to have an axial symmetry, another zfs constant E is zero. From the plot and the experimentally obtained zfs constant ($|D| = 0.00407$ cm^{-1}), the center-to-center distance is estimated at about 7.0 Å. This value is about 0.5 Å larger than the distance [17] in crystals of unsubstituted lanthanide bis(phthalocyaninato) complexes: 6.5 Å in $Lu(Pc)_2{\cdot}CH_2Cl_2$ [18,19], 6.47 Å in $Y(Pc)_2{\cdot}CH_2Cl_2$ [6], and 6.58 Å in $Nd(Pc)_2$ [20]. On the other hand, an X-ray diffraction experiment on columnar discotic mesophase of $Lu(Pc(CH_2OC_{18}H_{37})_8)_2$ has shown that the distance between the Lu atoms in a column is 7.3 Å [21]. The calculated value 7.0 Å in the present case appears reasonable since it is larger than that of unsubstituted complexes and shorter than that of a complex substituted with bulky alkyl chains with no bridges.

The exchange interaction $J = (1/2)\{^1E - ^3E\}$, where ^1E and ^3E are singlet and triplet energies, respectively, takes a negative value in the region larger than 6 Å as seen in Fig. 6(b). Its absolute value decreases as Δz increases along the C_4 axis. The variation of J with respect to Δz is much more sensitive than that of D. In the present model, J is estimated at $-0.35\ cm^{-1}$ when $\Delta z = 6.5$ Å, and $-0.04\ cm^{-1}$ when $\Delta z = 7.0$ Å. In the configuration where two Pc dimer radicals are aligned along the C_4 axis, the overall electronic state of the system is predicted to be a singlet.

4.2. Solvent-induced SM structure [11]

For the solvent-induced SM structure of Lu(CR_4Pc)(Pc), there are two possibilities for the arrangement of the two sites. If we assume the SM structure has the same C_4 axis as the above D_{4h} structure, Δz is estimated at 8.4 Å from Fig. 6(a). This is 1.4 Å longer than that of cation-induced structure, indicating that this is not a reasonable assumption.

Scheme 2 shows another possibility. In this geometry, Pc rings form a stack sliding to a direction parallel to the Pc planes. Δx is the amount of the displacement to a direction in the Pc planes. Three different models in Scheme 2 have been investigated. From the observed $|D|/|D_{\Delta x=0}|$ value ($0.00288\ cm^{-1}/0.00407\ cm^{-1} = 0.71$), Δx was estimated at 5.4 Å in Case 1, 5.7 Å in Case 2 and 5.8 Å in Case 3, with setting Δz at 7.0 Å. In the vicinity $\Delta x = 5$ Å, the J value was positive in the three cases. This suggests that the solvent-induced SM structure is in the triplet state.



Scheme 2.

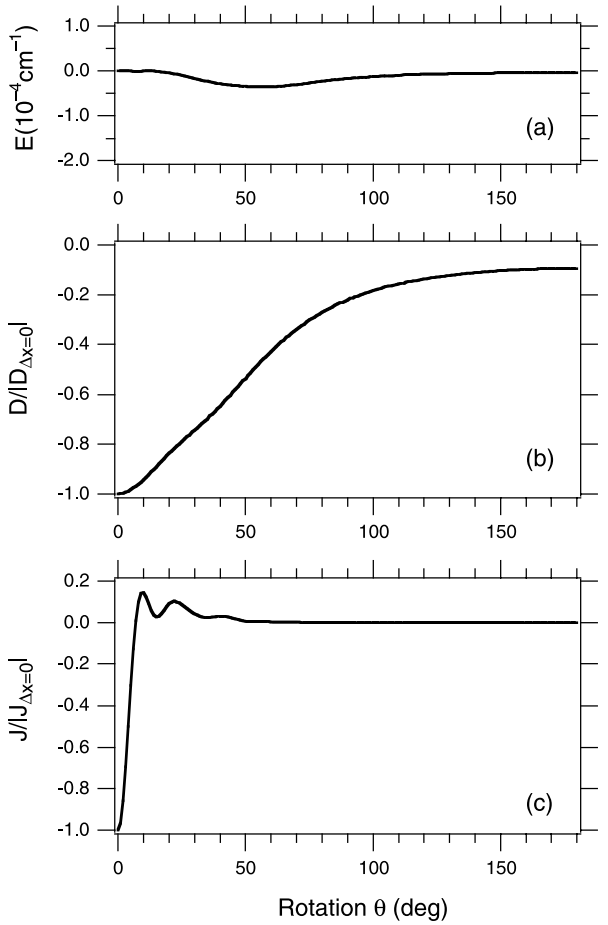


Fig. 7. Plots of (a) zero-field splitting constant E, (b) D and (c) exchange interaction J as a function of rotation angle θ defined in Scheme 3.

Interestingly, the calculated values are close to the corresponding values reported in the $Lu(Pc)_2{\cdot}CH_2Cl_2$ crystal (4.7 Å) and $Y(Pc)_2{\cdot}CH_2Cl_2$ crystal (4.6 Å). This suggests that the amount of slide along the Pc plane is determined solely by the nature of $Lu(Pc)_2$, although the crown parts play a role in bringing the complexes close together. Once two $Lu(Pc)_2$ are in a face-to-face position, sliding about 5 Å may stabilize the entire system.

4.3. Cation-induced SM structure composed of Lu(CR_1Pc)(Pc) [11]

Fig. 7 shows a calculation of E, D and J with varied θ, which is defined in Scheme 3. The axis of rotation, which passes through both centers of the crown parts, is placed at 9.5 Å away from the center of the Pc part of each CR_1Pc ring. In all regions of θ, E takes a negative value, reaching maximum absolute value at $\theta = 60°$. The absolute value of D decreases with θ, and

reaches 8% of $|D_{(\theta=0)}|$ at $\theta = 180°$. From the $|D|/|D_{\theta=0}|$ ratio of two cation-induced systems (0.00268/0.00407 = 0.66), θ is estimated at about 38°. The corresponding amount of slide in the xy plane is 5.8 Å (Δx in Scheme 3): two $Lu(Pc)_2$ sites have an overlap which is the same degree as that in the solvent-induced superstructure of $Lu(CR_4Pc)(Pc)$. This indicates that the freedom of rotation around the pivot is actually restricted by the same potential which sets up the solvent-induced structure of $Lu(CR_4Pc)(Pc)$.

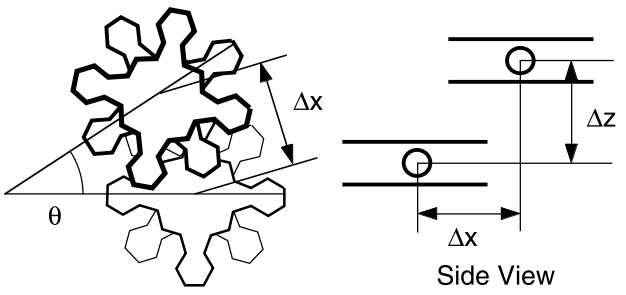
The variation of the exchange interaction J with θ is shown in Fig. 7(c). Similar behavior to that of the solvent-induced superstructure of $Lu(CR_4Pc)(Pc)$ is observed. As the angle θ increases from zero, J rapidly reaches zero and then takes a positive value. In the region $|\theta| > 7°$, J is positive and the SM structure is in a triplet state. From the estimated value of θ, the ground state of the system is predicted to be triplet.

5. Conclusion

We synthesized two types of asymmetrically substituted $Lu(Pc)_2$ complexes in order to investigate a SM structure composed of the Pc dimer radicals.

The tetra-crown Pc dimer, $Lu(CR_4Pc)(Pc)$, produces two types of SM structure depending on the conditions. One is the cation-induced D_{4h} structure, in which two $Lu(Pc)_2$ sites are arranged along a common C_4 symmetry axis. The electronic spectral change upon addition of potassium ion in the solution was explained by exciton coupling theory. The SM structure showed the EPR spectrum of a triplet state. The signal was simulated with zfs constant $|D| = 0.00407\ cm^{-1}$ (in the K^+-induced case). From theoretical calculation of the zfs constant, the center-to-center distance in the SM structure was estimated at 7.0 Å.

Another SM structure is a solvent-induced structure, which has a smaller zfs constant $|D| = 0.00288\ cm^{-1}$. The smaller zfs constant indicates that the structure has a longer center-to-center distance than the cation-induced SM structure. From the theoretical calculation, we concluded that the two $Lu(Pc)_2$ sites were arranged with a horizontal displacement of about 5 Å.



Scheme 3.

The mono-crown Pc dimer $Lu(CR_1Pc)(Pc)$ gave a K^+-induced SM structure with freedom of rotation around the potassium cation. The SM structure also showed a triplet EPR spectrum with a smaller zfs constant than that of tetra-crown Pc dimer. From calculation of the zfs constant, the rotation angle θ was estimated at about 30–40°. This indicates that the angle $\theta = 180°$, which corresponds to the minimum steric hindrance, is not energetically favorable. It is suggested that partial overlap between two $Lu(Pc)_2$ sites lowers the total energy of the aggregation.

By calculation of the exchange interaction J, when an aggregate possesses a common C_4 axis, the ground state is singlet. By latitudinal separation of the two $Lu(Pc)_2$ sites, the ground state becomes a triplet. The singlet and triplet states are switched also in the K^+-induced aggregation of $Lu(CR_1Pc)(Pc)$ by rotation around the pivot.

Acknowledgements

This work was partially supported by a Grant-in-Aid for Science Research No.10740303 from the Ministry of Education, Science Sports and Culture in Japan.

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