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Diphthalocyaninatolanthanum as a New Phthalocyaninato-Dianion Donor for the Synthesis of Heteroleptic Triple-Decker Rare Earth Element Crown-Phthalocyaninato Complexes

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A novel synthetic approach towards heteroleptic triple-decker crown-phthalocyaninato complexes $[(15C5)_4Pc]M[(15C5)_4Pc]M(Pc)$ and $(Pc)M[(15C5)_4Pc]M(Pc)$ [where $(15C5)_4Pc^{2-}$ = 2,3,9,10,16,17,24,25-tetrakis(15-crown-5)-phthalocyaninato dianion; Pc^{2-} = phthalocyaninato dianion; M = Sm, Tb, Dy, Tm and Y] has been developed. It utilises the application of diphthalocyaninatolanthanum, $La(Pc)_2$, as a new source of the phthalocyaninato dianion instead of well known $Li_2(Pc)$. In contrast to the highly hygroscopic $Li_2(Pc)$, $La(Pc)_2$ is quite air-stable and its use allowed a significant decrease in reaction times. All the synthesised complexes were characterised by UV/Vis and ^1H NMR spectroscopy as well as MALDI TOF mass spectrometry. The X-ray structure of heteroleptic triple-decker crown-phthalocyaninato $(Pc)Sm[(15C5)_4Pc]Sm(Pc)$ was determined. These new heteroleptic phthalocyaninato complexes are interesting because of their potential as components in new supramolecular materials.

Introduction

The development of novel supramolecular devices requires both an understanding of the supramolecular interactions between individual molecules and also the possibility of tuning the structure of the supramolecular aggregates which determine the device performance.[1]

Tetrapyrrolic macrocycles (porphyrins, phthalocyanines, etc.) exhibit highly delocalised π electron systems and are thus prominent components of novel supramolecular materials with unique optical, electrochemical and magnetic properties. When tetrapyrrolic ligands are held in close proximity by metal ions in sandwich-type double- and triple-decker complexes, there exist strong intramolecular π-π interactions between macrocycles which results in the characteristic features of this class of compound. These interactions depend both on the nature of the ligand and the metal ion and can be tuned by the synthesis of heteroleptic and heteronuclear complexes.[2]

The intermolecular stacking π-π interactions are the main driving force of the formation of supramolecular assemblies by tetrapyrrolic compounds.[3a] The introduction of functional groups into the periphery of the macrocycles provides an opportunity for obtaining supramolecules of various architectures based on ionic interactions,[3b] hydrogen bonds[3c] etc. The introduction of crown-ether substituents enables the formation of supramolecular assemblies by the addition of alkali metal ions. In the case of the double-decker lutetium crown-phthalocyaninato $Lu[(15C5)_4Pc]_2{}^0$, the formation of a 1D oligomeric supramolecular aggregate $\{Lu[(15C5)_4Pc]_2\cdot 4K^+\}_n$, $M_w = 8.1\times10^5\,g\,mol^{-1}$, was identified by UV/Vis studies,[4a] light scattering measurements[4b] and atom force microscopy.[4c]

The heteroleptic double-decker 15-crown-5-phthalocyaninato complexes $[(15C5)_4Pc]M(Pc)$ were synthesised previously for studying the intermolecular interactions between double-decker complexes.[5] The raise-by-one-story method was applied in the cases of the Sm, Dy and Tm complexes, whereas for the La complex a new synthetic approach was developed. This was based on the synthesis of the intermediate heteroleptic triple-decker complex $[(15C5)_4Pc]La(Pc)La(Pc)$ by means of the interaction between $H_2[(15C5)_4Pc]$, $La(Pc)_2$ and $La(acac)_3\cdot nH_2O$. It was shown that $[(15C5)_4Pc]La(Pc)La(Pc)$ undergoes decomposition with the formation of the heteroleptic double-decker complex $[(15C5)_4Pc]La(Pc)$ due to the low stability of triple-decker lanthanum complexes.[6]

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The formation of the intermediate heteroleptic heteronuclear triple-decker complexes $[(15C5)_4Pc]M(Pc)La(Pc)$ was assumed to occur as a result of the reaction between $H_2[(15C5)_4Pc]$, $La(Pc)_2$ and acetylacetonato complexes of the other lanthanides. Unexpectedly, there were isolated two types of heteroleptic homonuclear triple-decker phthalocyaninato species. Thus, we herein report the novel synthetic approach towards heteroleptic triple-decker phthalocyaninato compounds which enabled us to obtain, at first, $(Pc)M[(15C5)_4Pc]M(Pc)$ and $[(15C5)_4Pc]M[(15C5)_4Pc]M(Pc)$.

It was previously demonstrated that amphiphilic heteroleptic triple-decker complexes $[(15C5)_4Pc]M[(15C5)_4Pc]M[(C_8H_{17}O)_8Pc]$ [M = Eu, Ho, Lu] form Langmuir–Blogett films which can been fabricated into field-effect transistor devices with almost the highest carrier mobilities achieved thus far for all LB film-based organic field-effect transistors.[7a] The mixed ligand triple-decker complex $[(15C5)_4Pc]Eu[(15C5)_4Pc]Eu(TPP)$ forms well-ordered monolayers on an Au(111) surface. The molecular orientation of the complex is reversed during the electrochemical redox reaction.[7b] Thus, we suppose, that the heteroleptic tris(phthalocyaninato) complexes reported herein could be important components of new supramolecular materials.

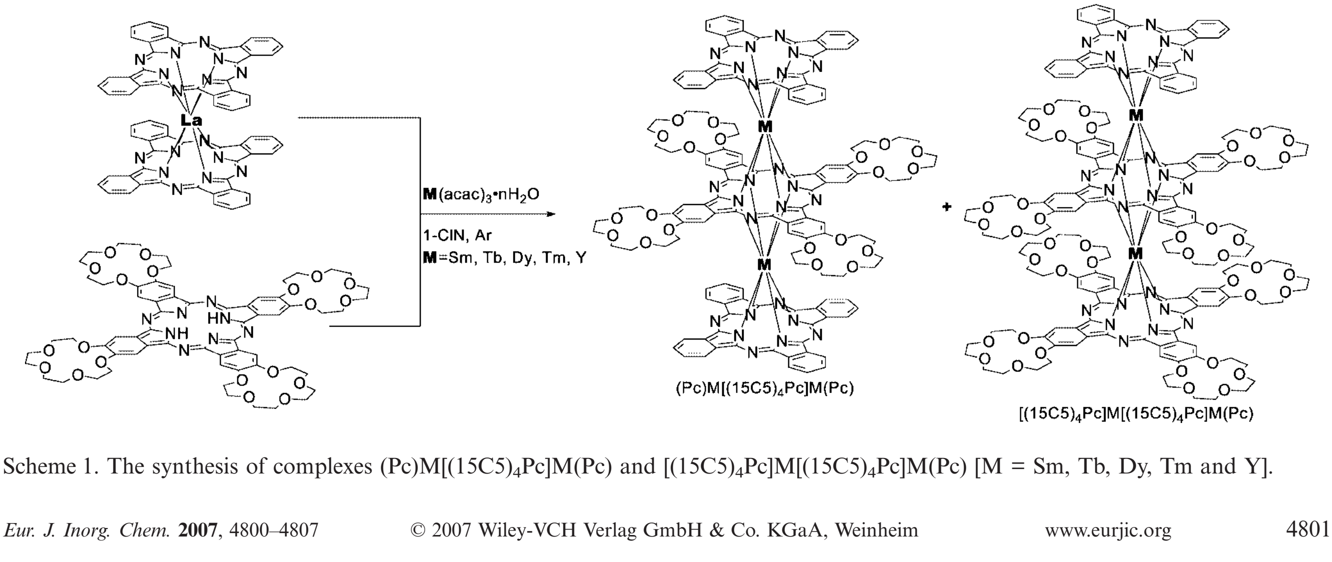
Results and Discussion

Synthesis of $(Pc)M[(15C5)_4Pc]M(Pc)$ and $[(15C5)_4Pc]M[(15C5)_4Pc]M(Pc)$

We performed the reactions between $H_2[(15C5)_4Pc]$, $La(Pc)_2$ and $M(acac)_3{\cdot}H_2O$ [M = Sm, Tb, Dy, Tm and Y] in 1-chloronaphthalene at reflux. It was expected that the intermediate heteroleptic heteronuclear complex $[(15C5)_4Pc]M(Pc)La(Pc)$ would eliminate the $La(Pc)^+$ fragment with the formation of the target heteroleptic double-decker complexes. Indeed, chromatographic separation of the reaction mixture afforded the corresponding $[(15C5)_4Pc]M(Pc)$ complex although the yield was low (<5%). Unexpectedly, the major products were heteroleptic homonuclear triple-decker complexes, viz. $(Pc)M[(15C5)_4Pc]M(Pc)$ and $[(15C5)_4Pc]M[(15C5)_4Pc]M(Pc)$ which contained no lanthanum ions (Scheme 1). The progress of the reaction was monitored by UV/Vis spectroscopy. The bands of the initial material $La(Pc)_2$ disappeared immediately after the reaction mixture started to reach reflux and the band of intermediate monophthalocyaninato species was observed. We suppose that the decomposition of $La(Pc)_2$ with the formation of the Pc^{2-} species may occur under the synthetic conditions used. Pc^{2-} reacts with metal acetylacetonato complexes and $H_2[(15C5)_4Pc]$ with the formation of heteroleptic triple-decker complexes. Free lanthanum ions remain in solution and do not participate in subsequent reactions as was demonstrated by MALDI TOF mass spectrometry. The reaction time decreased from 1 h in the case of M = Tm and Y to 30 min for Tb and Dy and to 10 min for Sm. The complexes $(Pc)M[(15C5)_4Pc]M(Pc)$ form with lower yield for M = Y and Tm (10–12%) in comparison with M = Sm, Tb and Dy (19–25%). The yields of the $[(15C5)_4Pc]M[(15C5)_4Pc]M(Pc)$ complexes do not significantly change with a decrease in the ionic radii (39–46%) (Table 1). Previously, the related heteroleptic triple-decker complexes $(Pc)M[(C_8H_{17}O)_8Pc]M(Pc)$ and $[(C_8H_{17}O)_8Pc]M[(C_8H_{17}O)_8Pc]M(Pc)$ were prepared using a wide range of metals.[8] Phthalocyaninatodilithium $Li_2(Pc)$ was used as a soluble donor of Pc^{2-} and the reactions were carried out over more than 12 h. The authors carried out the reaction between $M[(C_8H_{17}O)_8Pc]_2$ and $(Pc)M(acac)$ which was generated in situ from Li_2Pc and $M(acac)_3{\cdot}nH_2O$.

The partial decomposition of sandwich complexes under the synthetic conditions and the formation of scrambling products are common in the preparation of heteroleptic compounds. Previously[8] it was demonstrated that in the synthesis of $[(C_8H_{17}O)_8Pc]M[(C_8H_{17}O)_8Pc]M(Pc)$, the formation of the scrambling product $(Pc)M[(C_8H_{17}O)_8Pc]M(Pc)$ occurs due to decomposition of the starting double-decker complex $M[(C_8H_{17}O)_8Pc]_2$. The contraction of the rare-earth element (REE) ion along the investigated series of elements leads to an increase of the target compound yield and a decrease in the formation of side products.

Lanthanum has the biggest covalent radius in the series of REEs and so its complexes are less stable than those of middle and late REEs. Unsubstituted diphthalocyaninato-



Scheme 1. The synthesis of complexes $(Pc)M[(15C5)_4Pc]M(Pc)$ and $[(15C5)_4Pc]M[(15C5)_4Pc]M(Pc)$ [M = Sm, Tb, Dy, Tm and Y].

Table 1. Yields and MALDI TOF mass spectrometric data for heteroleptic triple-decker crown-substituted phthalocyaninato complexes.

	% Yield	MALDI TOF MS, m/z [a]	
		Observed	Calculated
$(Pc)M[(15C5)_4Pc]M(Pc)$[b]			
M			
Sm	23	2599.14	2599.11
Tb	19	2614.48	2614.64
Dy	25	2323.10	2623.38
Tm	10	2635.94	2636.26
Y	12	2474.57	2476.20
$[(15C5)_4Pc]M[(15C5)_4Pc]M(Pc)$[c]			
M			
Sm	39	3360.35	3359.90
Tb	38	3375.79	3374.97
Dy	45	3384.52	3384.17
Tm	46	3396.65	3397.04
Y	39	3236.51	3236.99

[a] Average m/z are given. [b] $[M]^+$ calculated for $C_{128}H_{104}M_2N_{24}O_{20}$. [c] $[M]^+$ calculated for $C_{160}H_{160}N_{24}O_{40}M_2$.

lanthanum should be even less stable towards the decomposition process than $M[(C_8H_{17}O)_8Pc]_2$ [M = Pr–Tm] and liberate Pc^{2-} under the synthetic conditions utilised. Comparative studies of the chemical behaviour of other $M(Pc)_2$ complexes in this reaction will be reported elsewhere.

The low stability of some early lanthanide sandwich phthalocyaninato complexes, which has been mentioned previously,[9] makes them prospective donors of phthalocyaninato-dianions for the synthesis of more stable complexes. However, this feature has never been utilised for the synthesis of sandwich complexes with other metals by means of the metal exchange reaction. This reaction is comparatively rarely applied in the chemistry of tetrapyrrolic compounds in contrast to reactions of direct metallation and template synthesis. The above mentioned phthalocyaninatolithium was also used for the synthesis of REE monophthalocyaninato complexes.[10] Magnesium complexes can be transmetallated in acidic media[11] and cadmium ions in porphyrin complexes can be exchanged by cobalt or zinc ions in polar solvents.[12] However, REE exchange was never reported previously. Thus, the reaction described herein is also interesting in relation to the development of the coordination chemistry of tetrapyrrolic compounds.

Thus, we have proposed the alternative Pc^{2-} donor – diphthalocyaninatolanthanum $La(Pc)_2$ – for the synthesis of heteroleptic triple-decker complexes. In contrast to highly hygroscopic $Li_2(Pc)$, $La(Pc)_2$ is quite air-stable and its application allowed us to significantly decrease the reaction times in comparison with the synthesis of the related heteroleptic trisphthalocyaninato complexes $(Pc)M[(C_8H_{17}O)_8Pc]M(Pc)$ and $[(C_8H_{17}O)_8Pc]M[(C_8H_{17}O)_8Pc]M(Pc)$.[8]

Spectroscopic Characterisation

All the synthesised heteroleptic complexes were isolated by column chromatography on neutral alumina using gradient elution with $CHCl_3$/MeOH mixtures and were subsequently characterised by various physical and chemical methods.

No elemental analyses were performed because the complexes undergo sublimation under the experimental conditions without complete decomposition and combustion.

Table 2. UV/Vis spectroscopic data for heteroleptic triple-decker crown-substituted phthalocyaninato complexes.

$(Pc)M[(15C5)_4Pc]M(Pc)$				
M	UV/Vis, $CHCl_3$, λ_{max} / nm			
Sm	682 (sh.)	643	334	293
Tb	695	641	333	292
Dy	700	640	333	293
Tm	709	635	333	292
Y	702	639	333	294
$[(15C5)_4Pc]M[(15C5)_4Pc]M(Pc)$				
Sm	690 (sh.)	644	353	292
Tb	696	642	355	292
Dy	702	640	354	291
Tm	713	636	355	292
Y	705	639	355	291

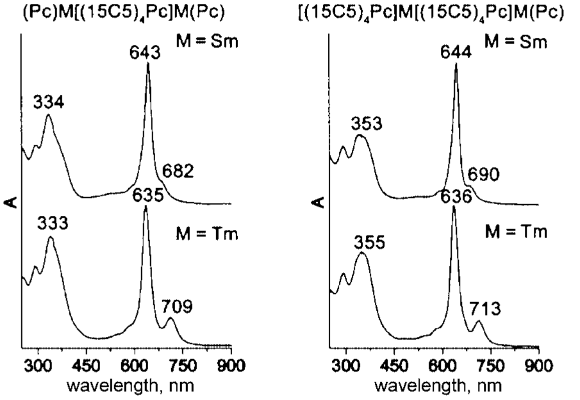


Figure 1. UV/Vis spectra of the heteroleptic triple-decker complexes $(Pc)M[(15C5)_4Pc]M(Pc)$ and $[(15C5)_4Pc]M[(15C5)_4Pc]M(Pc)$ [M = Sm, Tm] in $CHCl_3$.

Moreover, crown-ethers can contain solvent molecules which can affect the results of elemental analyses. However, these new complexes gave satisfactory MALDI-TOF mass spectra (Table 1) and the observed average *m*/*z* values and isotopic distribution patterns are in good agreement with simulated spectra. It should be pointed out that in the MALDI TOF mass spectra there were no peaks observed which could correspond to the lanthanum complexes.

The position and the shape of the Q-band in the UV/Vis spectra are mainly determined by the metal ion. It hypsochromically shifts and splits into two components upon a decrease in the metal ion's radius. It is noteworthy that the shape of the Soret band is lanthanide independent and is determined by the number and position of the crown-ether substituents (Table 2, Figure 1). The increase of the number of electron-donating crown-ether substituents leads to a bathochromic shift of the Soret band and to an increase in the relative intensity of the N-band at 292 nm.

^{1}H NMR spectra for all the heteroleptic triple-decker complexes were recorded in $CDCl_3$ and the data are collected in Table 3. Hydrazine-hydrate was added to the solutions to suppress their possible partial air oxidation so that well-resolved NMR spectra could be obtained

The positions the of signals are strongly affected by the lanthanide induced shift (LIS) effect[13] in the case of paramagnetic lanthanides. LIS depends both on the lanthanide

Table 3. ^{1}H NMR spectroscopic data for heteroleptic triple-decker crown-substituted phthalocyaninates.

(Pc)M[(15C5)$_4$Pc]M(Pc)		
M	H_{Ar} δ values (ppm)	–OCH_2– δ values (ppm)
Sm	8.02 (dd, ^3J = 5.4 Hz, ^4J = 2.8 Hz, 16 H, α-H_{Ar}^{o}) 7.56 (dd, ^3J = 5.4 Hz, ^4J = 2.8 Hz, 16 H, β-H_{Ar}^{o}) 6.59 (s, 8 H, H_{Ar}^{*i})	4.42 (m, 16 H, 1-CH_2^{i}), 4.29 (m, 16 H, 2-CH_2^{i}), 4.06 (m, 32 H, 3,4-CH_2^{i})
Tb	–154.76 (s, 8 H, H_{Ar}^{*i}) –67.60 (s, 16 H, α-H_{Ar}^{o}) –30.07 (s, 16 H, β-H_{Ar}^{o})	–67.60 (s, 16 H, 1-CH_2^{i}), –35.27 (s, 16 H, 2-CH_2^{i}), –21.68 (s, 16 H, 3-CH_2^{i}), –19.23 (s, 16 H, 4-CH_2^{i})
Dy	–74.00 (s, 8 H, H_{Ar}^{*i}) –21.51 (s, 16 H, α-H_{Ar}^{o}) –11.57 (s, 16 H, β-H_{Ar}^{o})	–31.59 (s, 16 H, 1-CH_2^{i}), –15.37 (s, 16 H, 2-CH_2^{i}), –8.70 (s, 16 H, 3-CH_2^{i}), –7.46 (s, 16 H, 4-CH_2^{i})
Tm	53.58 (s, 8 H, H_{Ar}^{*i}) 25.10 (s, 16 H, α-H_{Ar}^{o}) 17.76 (s, 16 H, β-H_{Ar}^{o})	23.40 (s, 16 H, 1-CH_2^{i}), 15.99 (s, 16 H, 2-CH_2^{i}), 11.64 (s, 16 H, 3-CH_2^{i}), 10.89 (s, 16 H, 4-CH_2^{i})
Y	8.58 (dd, ^3J = 5.4 Hz, ^4J = 2.4 Hz, 16 H, α-H_{Ar}^{o}) 8.25 (s, 8 H, H_{Ar}^{*i}) 7.92 (dd, ^3J = 5.4 Hz, ^4J = 2.4 Hz, 16 H, β-H_{Ar}^{o})	5.13 (m, 16 H, 1-CH_2^{i}), 4.67 (m, 16 H, 2-CH_2^{i}), 4.31 (m, 16 H, 3-CH_2^{i}), 4.26 (m, 16 H, 4-CH_2^{i})
[(15C5)$_4$Pc]M[(15C5)$_4$Pc]MPc		
Sm	8.03 (dd, ^3J = 5.5 Hz, ^4J = 3.0 Hz, 8 H, α-H_{Ar}^{o}) 7.67 (dd, ^3J = 5.5 Hz, ^4J = 3.0 Hz, 8 H, β-H_{Ar}^{o}) 7.37 (s, 8 H, H_{Ar}^{*o}) 6.66 (s, 8 H, H_{Ar}^{*i})	4.47–3.74 (overlapping multiplet, 128 H)
Tb	–157.94 (s, 8 H, H_{Ar}^{*i}) –56.34 (s, 16 H, H_{Ar}^{*o} and α-H_{Ar}^{o}) –34.72 (s, 8 H, β-H_{Ar}^{o})	–69.43 and –66.77 (2 s, 2 × 8 H, 1,1′-CH_2^{i}),[a] –36.99 and –36.25 (2 s, 2 × 8 H, 2,2′-CH_2^{i}), –33.84 (s, 8 H, 1-CH_2^{o}), –22.27 and –22.10 (2 s, 2 × 8 H, 3,3′-CH_2^{i}), –18.88 and –18.58 (2 s, 2 × 8 H, 4,4′-CH_2^{i}), –17.78 (s, 8 H, 1′-CH_2^{o}), –14.48 (s, 8 H, 2-CH_2^{o}), –10.84 (s, 16 H, 2′,3-CH_2^{o}), –10.30 (s, 8 H, 3′-CH_2^{o}), –7.37 (s, 8 H, 4-CH_2^{o}), –4.28 (s, 8 H, 4′-CH_2^{o})
Dy	–74.15 (s, 8 H, H_{Ar}^{*i}) –24.32 (s, 16 H, H_{Ar}^{*o} and α-H_{Ar}^{o}) –15.01 (s, 8 H, β-H_{Ar}^{o})	–32.66 and –31.23 (2 s, 2 × 8 H, 1,1′-CH_2^{i}), –16.34 and –15.94 (2 s, 2 × 8 H, 2,2′-CH_2^{i}), –13.41 (s, 8 H, 1-CH_2^{o}), –9.20 and –9.07 (2 s, 2 × 8 H, 3,3′-CH_2^{i}), –7.39 and –7.26 (2 s, 2 × 8 H, 4,4′-CH_2^{i}), –6.68 (s, 8 H, 1′-CH_2^{o}), –5.08 (s, 8 H, 2-CH_2^{o}), –2.95 (s, 16 H, 2′,3-CH_2^{o}), –1.47 (s, 8 H, 3′-CH_2^{o}), –1.05 (s, 8 H, 4-CH_2^{o}), 0.35 (s, 8 H, 4′-CH_2^{o})
Tm	55.07 (s, 8 H, H_{Ar}^{*i}) 27.12 (s, 8 H, H_{Ar}^{*o}) 25.46 (s, 8 H, α-H_{Ar}^{o}) 19.16 (s, 8 H, β-H_{Ar}^{o})	26.29 and 25.46 (2 s, 2 × 8 H, 1,1′-CH_2^{i}), 16.50 and 16.32 (2 s, 2 × 8 H, 2,2′-CH_2^{i}), 16.14 (s, 8 H, 1-CH_2^{o}), 11.80 (s, 16 H, 1′-CH_2^{o} and 2-CH_2^{o}), 10.73 and 10.62 (2 s, 2 × 8 H, 3,3′-CH_2^{i}), 10.38 (s, 8 H, 2′-CH_2^{o}), 9.89 (s, 8 H, 3-CH_2^{o}), 7.91 (2 s, 2 × 8 H, 4,4′-CH_2^{i}), 6.84 (s, 8 H, 3′-CH_2^{o}), 6.53 (s, 8 H, 4-CH_2^{o}), 5.65 (s, 8 H, 4′-CH_2^{o})
Y	8.58 (dd, ^3J = 5.2 Hz, ^4J = 2.8 Hz, 8 H, α-H_{Ar}^{o}) 8.27 (s, 8 H, H_{Ar}^{*i}) 8.02 (dd, ^3J = 5.2 Hz, ^4J = 2.8 Hz, 8 H, β-H_{Ar}^{o}) 7.95 (s, 8 H, H_{Ar}^{*o})	5.17 (m, 16 H, 1,1′-CH_2^{i}), 4.76 and 4.61 (2 s, 2 × 8 H, 2,2′-CH_2^{o}), 4.63 (m, 16 H, 2,2′-CH_2^{i}), 4.25–3.84 (m, 64 H, 3,4-CH_2^{i}, 2,2′,3,3′,4,4′-CH_2^{o})[a]

[a] Primes ′ indicate *exo*-protons.

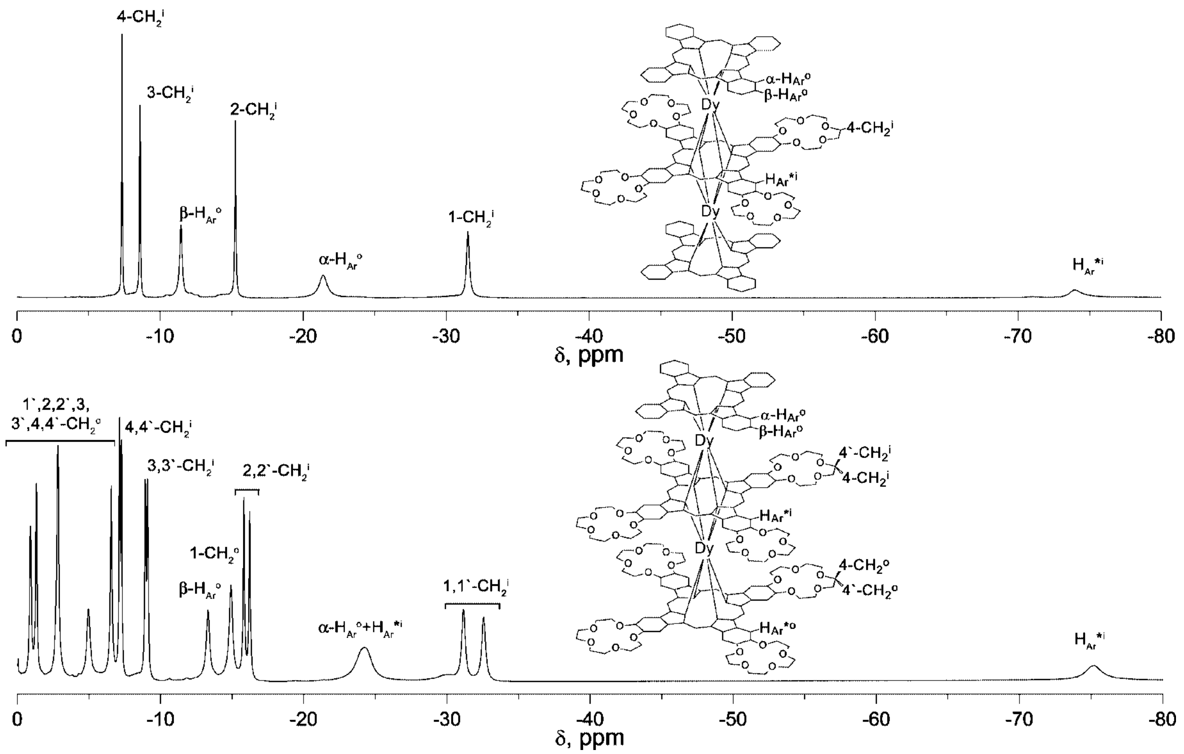


Figure 2. ^1H NMR spectra of (Pc)Dy[(15C5)$_4$Pc]Dy(Pc) and [(15C5)$_4$Pc]Dy[(15C5)$_4$Pc]Dy(Pc) in $CDCl_3$.

ion and on the orientation of the proton relative to the paramagnetic nuclei. For Dy and Tb complexes, a strong upfield shift can be observed resulting in negative values for the chemical shifts of all resonance signals. Sm causes a slight upfield shift whereas Tm leads to a strong downfield shift of the resonance signals. Because of the paramagnetic broadening, the spin-spin coupling constants cannot be observed in the case of the Tb, Dy and Tm complexes. In the spectra of the Sm and Y complexes the multiplets, which correspond to the resonance signals of the unsubstituted ligands, are well resolved. The attribution of signals can be made using the previously reported assignment of signals in the ^1H NMR spectra of (Pc)M[($C_8H_{17}O$)$_8$Pc]M(Pc) and [($C_8H_{17}O$)$_8$Pc]M[($C_8H_{17}O$)$_8$Pc]M(Pc).[13a]

In the NMR spectra of (Pc)M[(15C5)$_4$Pc]M(Pc), the resonance signals from the α- and β-aromatic protons of the outer unsubstituted rings (α- and β-$H_{Ar}{}^{o}$), the aromatic protons of the inner crown-substituted ligands ($H_{Ar}{}^{*i}$) and the methylene protons of crown-ether macrocycles can be observed. Two protons at each CH_2 group are equivalent resulting in four resonance signals (Figure 2).

Along with the resonance signals of α- and β-$H_{Ar}{}^{o}$ and $H_{Ar}{}^{*i}$ there can also be observed a signal for the aromatic protons of the outer crown-substituted ligand $H_{Ar}{}^{*o}$ in the NMR spectra of [(15C5)$_4$Pc]M[(15C5)$_4$Pc]M(Pc). Due to lower the symmetry of the molecules, two protons at each methylene-group of the crown-ethers are nonequivalent with respect to the neighbouring ligands (*exo* and *endo*). This significantly complicates the aliphatic region of ^1H NMR spectra of [(15C5)$_4$Pc]M[(15C5)$_4$Pc]M(Pc) in comparison with (Pc)M[(15C5)$_4$Pc]M(Pc) (Figure 2).

Structural Studies

The molecular structure of (Pc)Sm[(15C5)$_4$Pc]Sm(Pc) was determined by single-crystal X-ray analysis. Although the structures of some heteroleptic trisphthalocyaninato complexes have been determined previously,[14] no structural data on heteroleptic triple-decker crown-phthalocyaninato complexes have been reported so far. Moreover, to date,[15a] no binuclear samarium phthalocyaninato complexes have been structurally characterised with the exception of (η^2-dpm)$_4$Sm$_2$(μ-Pc) (dpm = 2,2,6,6-tetramethylheptane-3,5-dionato ion).[15b]

According to the X-ray analysis of (Pc)Sm[(15C5)$_4$Pc]Sm(Pc), each Sm atom is sandwiched between an outer Pc ring and the inner [(15C5)$_4$Pc] ring giving a symmetrical structure (see Figures 3 and 4). Two Sm atoms are located at a nonbonding Sm···Sm distance of 3.5111(4) Å. They are linked with four nitrogen atoms from the central bridging crown-substituted macrocycle [Sm–N(9) 2.613(3) Å, Sm–N(11) 2.599(3) Å] and each of them is linked with four isoindole nitrogen atoms of the outer Pc ligands [(Sm–N(1) 2.372(3) Å, Sm–N(3) 2.385(3) Å, Sm–N(5) 2.397(3) Å, Sm–N(7) 2.395(3) Å)]. Each metal adopts a distorted square antiprismatic geometry with an average twist angle of 43°. The inequality of the Sm–N distances and the significant decrease in the Sm–N_{outer} distance compared with the Sm–N_{inner} distance is in agreement with the previously reported data for the homoleptic lutetium phthalocyaninato $Lu_2[Pc(15C5)_4]_3$[16] and the heteroleptic triple-decker complexes (Pc)M[(OC_8H_{17})$_8$Pc]M′(Pc)[14a] and [(α-OC_5H_{11})$_4$-Pc]M(Pc)M(Pc)[14b] (Table 4).

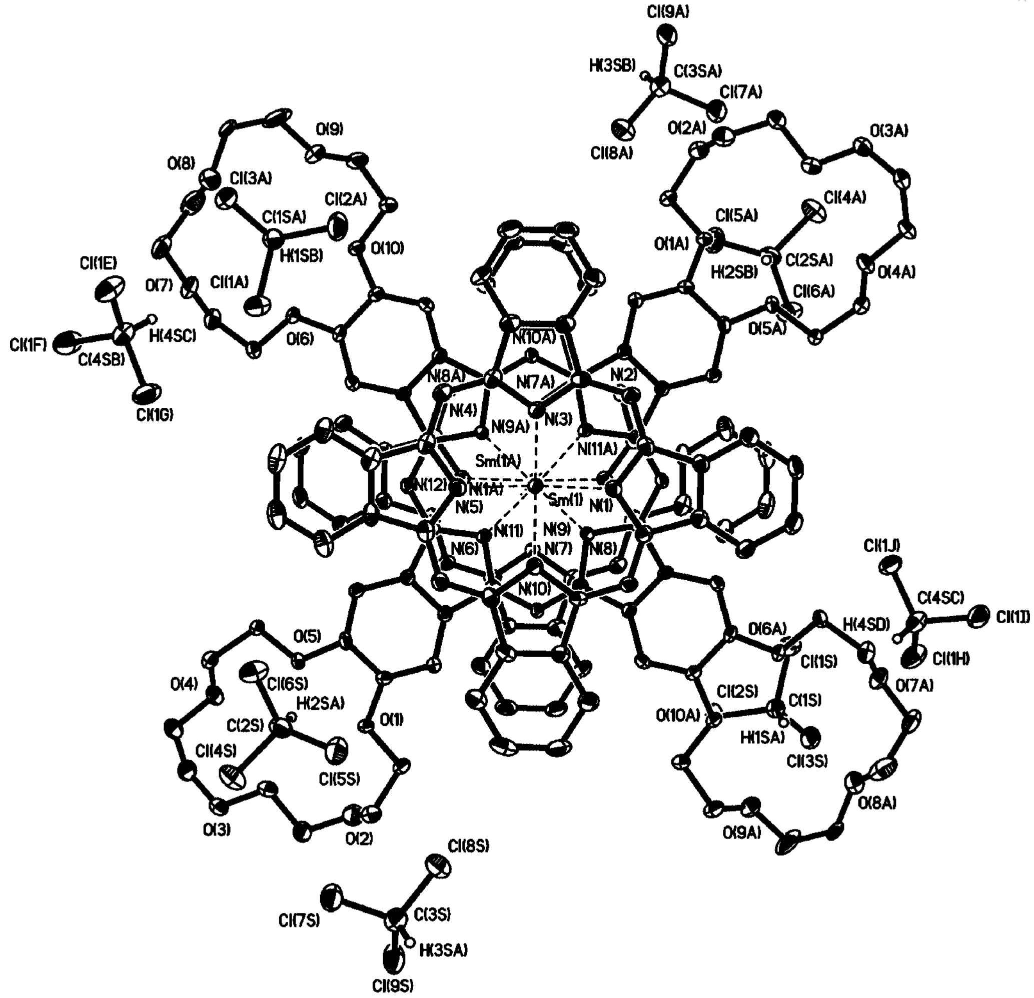


Figure 3. Molecular structure of the complex (Pc)Sm[(15C5)$_4$Pc]Sm(Pc)·8CHCl$_3$ with thermal ellipsoids drawn at the 50% probability level, top view.

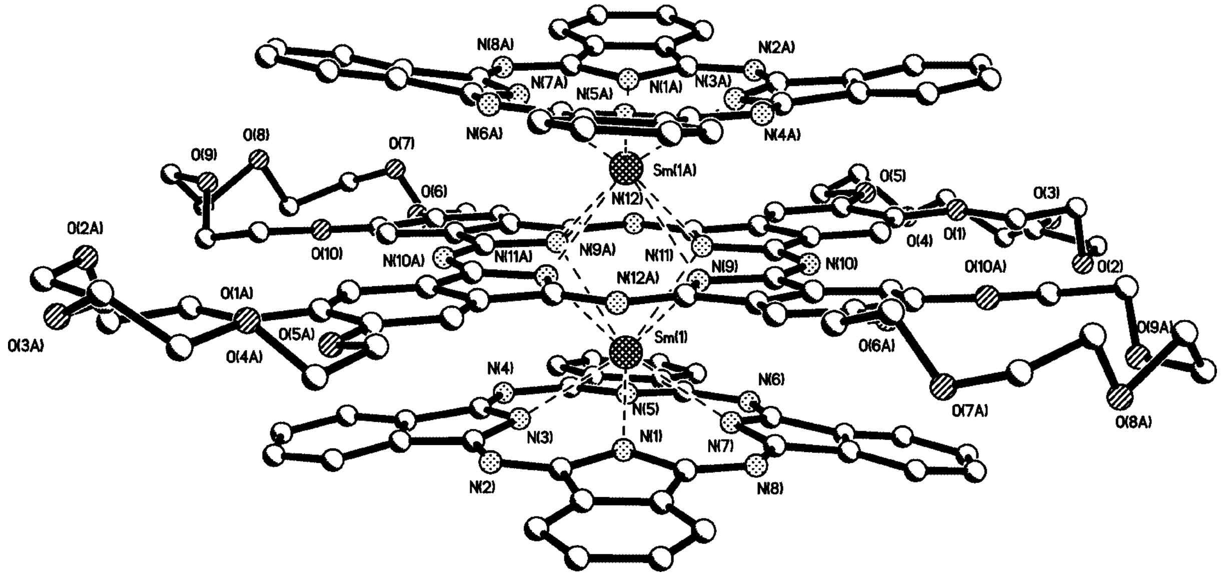


Figure 4. Molecular structure of the complex (Pc)Sm[(15C5)$_4$Pc]Sm(Pc), side view.

Table 4. Comparison of M–N$_{iso}$ for different lanthanide trisphthalocyaninates.

Complex	M–N$_{outer}$ / Å	M–N$_{inner}$ / Å	Ref.
(Pc)Sm[(15C5)$_4$Pc]Sm(Pc)	2.372(3)–2.397(3)	2.599(3)–2.613(3)	present work
Lu$_2$[(15C5)$_4$Pc]$_3$	2.297(7)–2.323(7)	2.538(8)–2.587(7)	[16]
(Pc)Er[(OC$_8$H$_{17}$)$_8$Pc]Er(Pc)	2.332	2.573	[14a]
(Pc)Lu[(OC$_8$H$_{17}$)$_8$Pc]Lu(Pc)	2.283	2.507	[14a]
(Pc)Er[(OC$_8$H$_{17}$)$_8$Pc]Lu(Pc)	2.30	2.55	[14a]
[(α-OC$_5$H$_{11}$)$_4$Pc]Gd(Pc)Gd(Pc)	2.364, 2.386	2.634, 2.654	[14b]
[(α-OC$_5$H$_{11}$)$_4$Pc]Lu(Pc)Lu(Pc)	2.297, 2.307	2.588	[14b]

The Sm···Sm distance of 3.5111(4) Å in (Pc)Sm[(15C5)$_4$Pc]Sm(Pc) is different from the metal–metal separation in the binuclear complex [(η^2-dpm)$_4$Sm$_2$(μ-Pc)] [Sm···Sm 3.627(3) Å].[15] This can be explained both by the nature of the axial ligands and the phthalocyanine bridge. The Sm–N$_{outer}$ distance (2.37–2.39 Å) is close to the Sm–N distance in the double-decker ionic phthalocyaninato complexes $[Sm(Pc^{2-})_2]^-(NBu_4)^+$ (Sm–N 2.452–2.471 Å)[17a] and $[Sm(Pc^{\cdot-})_2]^+Br^-$ (Sm–N 2.457 Å).[17b] It is also significantly shorter than in $[Sm(Pc^{\cdot-})_2]^+(ClO_4)^-$ (Sm–N 2.607 Å).[17b] It is noteworthy that eight solvated CHCl$_3$ molecules are present in the crystallographic cell. The hydrogen atoms of 6 molecules form very weak contacts with the oxygen atoms of the crown-ether substituents, notwithstanding affecting their conformation [H(1SA)···O(8),O(9) 2.66 Å, H(2SA)···O(1) 2.59 Å, H(2SA)···O(5) 2.22 Å, H(4SA)··· O(7) 2.14 Å]. The molecules adopt a brick wall type packing arrangement.

Conclusions

A simple methodology for preparing a series of heteroleptic crown-substituted REE(III) triple-decker phthalocyaninato complexes (Pc)M[(15C5)$_4$Pc]M(Pc) and [(15C5)$_4$Pc]M[(15C5)$_4$Pc]M(Pc) [M = Sm, Tb, Dy, Tm and Y] has been developed. This method involves the application of the diphthalocyaninatolanthanum La(Pc)$_2$ as a new Pc^{2-} donor species. The advantages of this method are that it results in the complexes being formed in high yield under mild conditions and a significant decrease in the reaction times. All the complexes were fully characterised by MALDI TOF mass spectrometry as well as UV/Vis and ^{1}H NMR spectroscopy. The molecular structure of (Pc)Sm[(15C5)$_4$Pc]Sm(Pc) was also determined and it represents the first structure reported for a heteroleptic triple-decker crown-phthalocyaninato complex.

Experimental Section

The compounds H$_2$[(15C5)$_4$Pc],[18a] La(Pc)$_2$[5] and M(acac)$_3$·H$_2$O[18b] were prepared according to published procedures. 1-Chloronaphthalene was used as received (1-ClN, Acros Organics). Chloroform was dried with anhydrous CaCl$_2$ followed by distillation over CaH$_2$. Methanol was dried with 4 Å molecular sieves. Column chromatography was carried out on neutral alumina (Merck, 0.063–0.200 mm, activity II–III according to Brockmann).

The electronic (UV/Vis) spectra were recorded on a Cary-100 spectrophotometer (Varian) in CHCl$_3$ in quartz cells (1–10 mm). MALDI-TOF mass spectra were recorded on an Ultraflex mass spectrometer (Bruker Daltonics) with nicotinic acid as a matrix. Sonication was performed in an ElmasonicS70H ultrasonic bath (Elma) at 37 kHz. ^{1}H NMR spectra were recorded on Bruker Avance-400 spectrometer (400 MHz) in CDCl$_3$ solution in the presence of 10 µL of a 1% solution of N$_2$H$_4$·H$_2$O in [D$_6$]DMSO. Chemical shifts, δ values, are reported in ppm relative to the internal standard (residual CHCl$_3$, δ = 7.25 ppm) at T = 298 K.

Preparation of Heteroleptic Triple-Decker Complexes: A mixture of La(Pc)$_2{}^0$ (15.0 mg, 12 µmol), H$_2$[(15C5)$_4$Pc] (16.4 mg, 12 µmol) and M(acac)$_3$·H$_2$O (36 µmol) (M = Sm, Tb, Dy, Tm, Y) was dissolved in 1-ClN (4 mL) with sonication and heated to reflux until no further changes in the UV/Vis spectrum of the reaction mixture were observed. The resultant blue solution was subsequently cooled. The reaction mixture treated with hexane to bring about precipitation and was then filtered. The precipitate was dissolved in CHCl$_3$ and chromatographed on neutral alumina. CHCl$_3$ was used to remove M(Pc)$_2{}^{0\cdot}$ and M$_2$(Pc)$_3$. The complexes (Pc)M[(15C5)$_4$Pc]M(Pc) were eluted with a mixture of CHCl$_3$ and 0.75 vol.-% MeOH. The complexes [(15C5)$_4$Pc)M[(15C5)$_4$Pc]M(Pc) were eluted with a mixture of CHCl$_3$ and 1.25 vol.-% MeOH. The physical and chemical data and yields for all the complexes are summarised in Tables 1, 2 and 3.

X-Ray Crystallographic Analysis of (Pc)M[(15C5)$_4$Pc]M(Pc): Single crystals of (Pc)M[(15C5)$_4$Pc]M(Pc)·8CHCl$_3$ were grown by slow diffusion of heptane into a chloroform solution of the complex. The crystals (C$_{136}$H$_{112}$Cl$_{24}$N$_{24}$O$_{20}$Sm$_2$, M = 3554.00, crystal size 0.07 × 0.08 × 0.40 mm) are triclinic, space group $P\bar{1}$, a = 13.2279(9), b = 15.5561(11), c = 19.0738(14) Å, α = 69.145(1), β = 74.402(1), γ = 89.489(2)°, V = 3516.2(4) Å^3, Z = 1, $\rho_{calcd.}$ = 1.678 g cm^{-3}, μ(Mo-K_α) = 13.60 cm^{-1}. The intensities of 39384 reflections (16902 independent reflections, R_{int} = 0.0616) were measured on a Bruker SMART APEX II diffractometer (graphite monochromated Mo-K_α radiation, λ = 0.71073 Å, ω-scan technique, $2\theta_{max}$ = 56°, T = 100 K). The APEX II software[19] was used for collecting frames of data, indexing reflections, determination of lattice constants, integration of intensities of reflections, scaling and absorption correction (T_{min}/T_{max} = 0.707/0.911) and SHELXTL[20] was used for space group and structure determination, refinements, graphics and structure reporting. The structure was solved by direct methods and refined by the full-matrix least-squares technique against F^2 with the anisotropic temperature factors for all non-hydrogen atoms. All hydrogen atoms were placed geometrically and included in the structure factor calculations in the riding motion approximation. The refinement converged to wR_2 = 0.1085 and a GOF = 0.994 for all independent reflections [R_1 = 0.0463 was calculated against F for 12032 observed reflections with $I > 2\sigma(I)$], 936 refined parameters.

CCDC-641195 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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