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Synthesis and structure of homo- and heteronuclear rare earth element complexes with tetra-15-crown-5-phthalocyanine

Irina V. Nefedova, Yulia G. Gorbunova,* Sergey G. Sakharov and Aslan Yu. Tsivadze

N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation.
Fax: + 7 495 955 4874; e-mail: yulia@igic.ras.ru

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The complexes $M_2(R_4Pc)_3$ (M = Y^{III}, Tb^{III}) and $MM'(R_4Pc)_3$ (M = Y^{III}, Tb^{III}, M′ = Lu^{III}), and R_4Pc^{2-} = [4,5,4′,5′,4″,5″,4‴,5‴-tetrakis(1,4,7,10,13-pentaoxatridecamethylene)phthalocyaninate anion], were synthesised and characterised by UV-VIS and ^1H NMR spectroscopy and MALDI TOF mass spectrometry.

The particular feature of the coordination chemistry of rare earth elements with macrocyclic tetrapyrrolic ligands is the ability to form complexes with different metal–ligand ratios of 1:1, 1:2 and 2:3, namely, mono- and sandwich double- and triple-decker complexes.[1,2]

In contrast to well-studied sandwich double-decker rare earth phthalocyaninates, there was little data concerning triple decker complexes.[1] The structure of such complexes was firstly established by X-ray analysis in 1999, when [tris(tetra-15-crown-5-phthalocyaninate)]dilutetium was studied.[3]

Crownphthalocyaninates attract much attention because they can act as building blocks for supramolecular systems with various architectures. Some of their electrophysical characteristics exceed the analogous compounds with other substituents. There are few direct synthetic methods[4–7] for rare earth triple-decker phthalocyaninate synthesis. Usually, these complexes are by-products in the synthesis of double-decker compounds.[8–11]

N. Ishikawa[5,6] reported on the synthesis and investigation of heteronuclear heteroleptic rare earth trisphthalocyaninates. These compounds are of much interest because they exhibit the *f–f* interaction between lanthanide ions along with the π–π interaction between macrocyclic ligands, leading to the properties of molecular magnetics, inherent in these compounds.

Ishikawa[5,6] proposed the direct interaction between rare earth double-decker phthalocyaninate, phthalocyanine ligand and rare earth acetylacetonate in a high-boiling solvent. Another method[4] suggests the application of lithium phthalocyaninate instead of free-base phthalocyanine. Lui *et al.*[4] applied this method to obtain rare earth homonuclear heteroleptic triple decker complexes. However, there is no data concerning rare earth homoleptic heteronuclear complexes.

The aim of this work was to develop the direct synthesis of homo- and heteronuclear homoleptic rare earth trisphthalocyaninates by the example of tetra-15-crown-5-phthalocyanine complexes. We focused our attention on yttrium, lutetium and terbium complexes. Such a choice can be explained by the fact that yttrium and lutetium ions are diamagnetic, thus, their complexes can be studied by NMR spectroscopy. On the other hand, the Tb^{3+} ion is paramagnetic, acting as a shift reagent in NMR spectroscopy. Note that terbium phthalocyaninates exhibit the strongest induced shift among all lanthanides.[5,7,12,13]

In order to obtain homonuclear homoleptic yttrium and terbium tris(tetra-15-crown-5-phthalocyaninates), we developed the method of direct interaction between tetra-15-crown-5-phthalocyanine and metal acetylacetonate (molar ratio of 1:3) in boiling trichlorobenzene (TCB) for 1.5 h (Figure 1).† Afterwards, the complex was eluted from Al_2O_3 with chloroform–methanol (98:2 by volume). The yields of $Tb_2(R_4Pc)_3$ and $Y_2(R_4Pc)_3$ are equal to 68 and 72%, respectively.

In order to obtain heteronuclear complexes, we applied two approaches.

The first one was similar to the Ishikawa method.[5,6] Double-decker complex $M(R_4Pc)_2$ (M = Tb, Lu), tetra-15-crown-5-phthalocyanine and yttrium acetylacetonate mixture (molar ratio of 1:2:10) was refluxed in TCB. Then, the reaction mixture was filtered and hexane was added. The blue precipitate was filtered off, dissolved in chloroform and applied to a chromatographic column with Al_2O_3. The complexes were separated *via* gradient elution with chloroform–methanol. It was demonstrated that this approach leads to the formation of three complexes: two homonuclear and one heteronuclear. When $TbY(R_4Pc)_3$ was synthesised, the total yield of triple-decker complexes was equal to 58%, including $TbY(R_4Pc)_3$ (21%), $Y_2(R_4Pc)_3$ (31.6%) and $Tb_2(R_4Pc)_3$ (5.4%). In case of $LuY(R_4Pc)_3$ synthesis, the total yield of triple-decker complexes was 62%, including $LuY(R_4Pc)_3$ (31%), $Y_2(R_4Pc)_3$ (20.6%) and $Lu_2(R_4Pc)_3$ (10.4%).

Ishikawa *et al.*[5,6] reported that this approach leads to heteroleptic rare earth triple-decker complexes in 80% yield. However, the presence of a free ligand along with yttrium acetylacetonate leads to an yttrium triple-decker complex. Moreover, we found the possibility of $M(R_4Pc)_2$ (M = Tb, Lu) destruction leading to $M_2(R_4Pc)_3$.

Thus, we developed another approach to direct rare earth heteronuclear synthesis by the example of Lu and Y complexes because it was demonstrated that they are formed in higher yield.

This method suggests the refluxing of a mixture of $Lu(R_4Pc)_2$ and preliminary obtained $[Y(R_4Pc)]\cdot(AcAc)\cdot DBU$ (DBU is 1,8-diazabicyclo[5.4.0]undec-7-ene) (molar ratio of 1:1) in TCB for 1 h (Figure 1). The reaction pathway was monitored by UV-VIS spectra. Figure 2 demonstrates the UV-VIS spectra of starting complexes and resulting compounds. The reaction mixture was treated as described earlier, and three triple-decker complexes

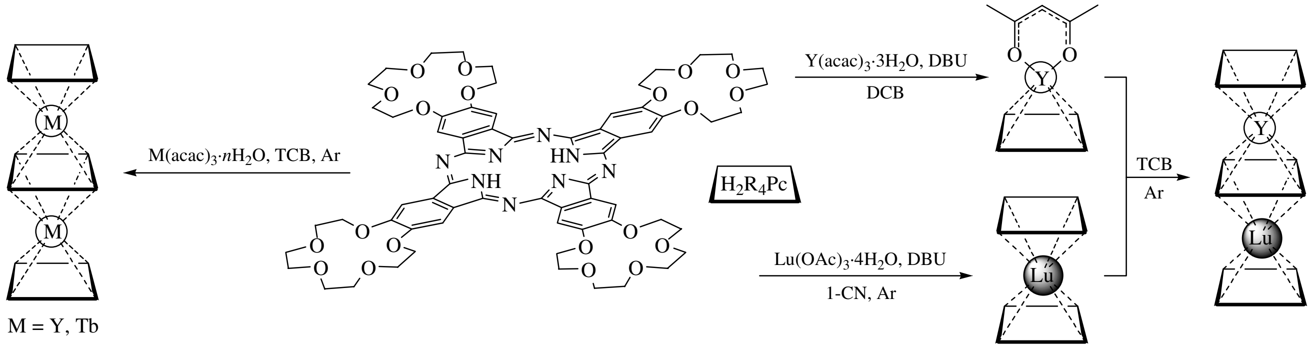


Figure 1 Synthesis of homo- and heteronuclear yttrium, terbium and lutetium triple-decker complexes with tetra-15-crown-5-phthalocyanine.

were isolated. The total yield was equal to 71%, the yields of $LuY(R_4Pc)_3$, $Y_2(R_4Pc)_3$ and $Lu_2(R_4Pc)_3$ were 41.8, 15 and 14.2%, respectively. In this reaction, the oxidation state of metals was not changed. We suppose that acetylacetonate ion may act as a reducing agent and then undergo olygomerisation and ring formation by analogy with reported data.[14] This idea can be supported by the fact that a reaction with corresponding acetates does not occur.

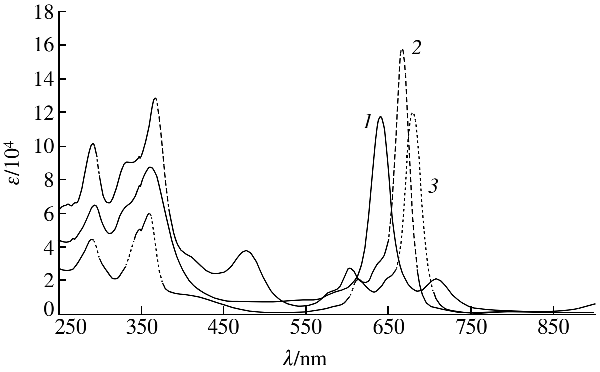


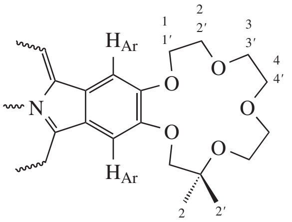
Figure 2 UV-VIS spectra in chloroform (*1*) $LuY(R_4Pc)_3$, (*2*) $Lu(R_4Pc)_2$ and (*3*) $(AcAc)Y(R_4Pc){\cdot}DBU$.

Thus, we established that both approaches lead to the mixture of three products: $M_2(R_4Pc)_3$, $Y_2(R_4Pc)_3$ and $MY(R_4Pc)_3$ (M = Tb, Lu), which can be separated by chromatography with gradient elution with chloroform–methanol. Note that our method leads to a higher yield of a heteronuclear triple-decker complex in comparison with Ishikawa's approach.

The isolated chromatographically individual complexes are dark-blue crystalline powders, which are well soluble in polar organic solvents. The isolated complexes composition was determined by UV-VIS spectroscopy. We also used time-of-flight matrix assisted laser desorption ionization (MALDI TOF) mass spectrometry. Satisfactory coincidence of experimental and calculated *m*/*z* values and characteristic isotopic distributions of molecular ions indicate the complex composition and purity.

We also investigated the ^1H NMR spectra of triple-decker complexes (Table 1). The analysis of signals in NMR spectra was performed by analogy with reported data.[5,7,12,13,15] The NMR spectrum of an yttrium homonuclear triple-decker complex with tetra-15-crown-5-phthalocyanine is similar to the previously reported spectrum of a lutetium complex.[15] Two broad singlets with the chemical shifts δ –149.3 and –51.0 ppm are observed in

Table 1 ^1H NMR data for triple-decker complexes in $CDCl_3$.



Complex		H_{Ar}	Crown-ether protons $(H^{1,1'-4,4'})^a$
$Tb_2(R_4Pc)_3$	(Inner)	–149.30	–65.56 $(H^{1,1'})$, –33.92 $(H^{2,2'})$, –15.72 $(H^{3,3'})$, –4.80 $(H^{4,4'})$
	(Outer)	–51.00	–30.92 $(H^{1'})$, –20.83 (H^{1}), –17.88 $(H^{2'})$, –12.55 (H^{2}), –9.24 $(H^{3'})$, –8.58 (H^{3}), –6.19 $(H^{4'})$, –2.58 (H^{4})
$TbY(R_4Pc)_3$	(Inner)	–68.60	–37.49 $(H^{1'}_{outer})$, –28.83 $(H^{1'}_{inner})$,
	(Outer-Tb)	–73.12	–24.57 (H^{1}_{inner}), –17.94, –16.64, –13.70, –12.87, –9.83, –9.25, –7.95, –7.73, –6.52, –6.35, –4.58 (2H), –3.08
	(Outer-Y)	24.22	9.41 $(H^{1'})$, 3.29, 3.13, 1.79, 1.76, 1.43, 1.32, 1.26
$Y_2(R_4Pc)_3$	(Inner)	8.24	5.00 $(H^{1,1'})$, 4.63 $(H^{2,2'})$, 4.08 $(H^{3,3'})$, 4.03 $(H^{4,4'})$
	(Outer)	7.84	4.47 (H^{1}), 4.27 $(H^{1'})$, 4.00 (H^{2}), 3.93 $(H^{2'})$, 3.92–3.76 $(H^{3,3',4,4'})$
$LuY(R_4Pc)_3$	(Inner)	8.37	5.10 $(H^{1,1'})$, 4.71 $(H^{2,2'})$, 4.23 $(H^{3,3'})$, 4.16 $(H^{4,4'})$
	(Outer)	7.94	4.56 (H^{1}), 4.35 $(H^{1'})$, 4.06 (H^{2}), 4.00 $(H^{2'})$, 3.95–3.78 $(H^{3,3',4,4'})$
$Lu_2(R_4Pc)_3{}^b$	(Inner)	8.41	5.16 $(H^{1,1'})$, 4.76 $(H^{2,2'})$, 4.22 $(H^{3,3'})$, 4.16 $(H^{4,4'})$
	(Outer)	7.96	4.61(H^{1}), 4.40 $(H^{1'})$, 4.08 (H^{2}), 4.01$(H^{2'})$, 3.95–3.85 $(H^{3,3',4,4'})$

[a] Primed symbols denote the crown-ether protons, pointing into the phthalocyanine ring. [b] Published data.[15]

[†] Electronic absorption spectra were measured on a Cary-100 (Varian) spectrophotometer in quartz rectangular cells of 1–10 mm thickness. The positive-ion MALDI TOF mass spectra were recorded on a Reflex-III mass spectrometer (Bruker Daltonics) with the use of the reflection mode with a target voltage of 20 mV. 4-Hydroxycinnamic acid was used as a matrix. The samples were prepared by dissolving the complexes in chloroform ($c = 10^{-4}$–10^{-6} M) and mixing the resulting solution in a 1:1 ratio with a solution of the matrix (20 mg cm^{-3}) in 30% aqueous acetonitrile. ^1H NMR spectra were recorded on a Bruker AC-200 spectrometer using $CDCl_3$ as a solvent. Chemical shifts were measured at 303 K using the signals of residual protons in $CDCl_3$ (δ 7.25 ppm) as the internal standard.

Tetra-15-crown-5-phthalocyanine. The compound was synthesised according to the published method[16] with subsequent chromatographic purification on Al_2O_3 (eluent: chloroform–methanol, 95:5 by volume).

Lutetium and terbium bis(tetra-15-crown-5-phthalocyaninates) were synthesised according to a previously reported procedure.[7,10]

Yttrium tetra-15-crown-5-phthalocyaninate acetylacetonate was synthesised as described below. A solution of H_2R_4Pc (20 mg, 15.7 μmol) in 2 ml of 1,2-dichlorobenzene was put into a flask equipped with a reflux condenser; then, $Y(AcAc)_3{\cdot}3H_2O$ (19.2 mg, 47.1 μmol) and DBU (94 μl, 628 μmol) were added [molar ratio $H_2R_4Pc{:}Y(AcAc)_3{\cdot}3H_2O{:}DBU$, 1:3:40]. The reaction mixture was refluxed at 180 °C for 1 h. After cooling, the reaction mixture was filtered, hexane was added and microcrystalline powder was precipitated. As a result, yttrium tetra-15-crown-5-phthalocyaninate acetylacetonate $[Y(R_4Pc)]{\cdot}(AcAc){\cdot}DBU$ was obtained in a quantitative yield. UV-VIS [$CHCl_3$, λ_{max}/nm (*A*, relative units)]: 679 (1.00), 613 (0.17), 360 (0.50), 290 (0.37).

Yttrium tris(tetra-15-crown-5-phthalocyaninate). A solution of H_2R_4Pc (20 mg, 15.7 μmol) in 2 ml of 1,2,4-trichlorobenzene was put into a flask equipped with a reflux condenser; then, $Y(AcAc)_3{\cdot}3H_2O$ (19.2 mg, 47.1 μmol) was added [molar ratio $H_2R_4Pc{:}Y(AcAc)_3{\cdot}3H_2O$, 1:3]. The reaction mixture was refluxed at TCB (bp 210 °C) for 1.5 h. After cooling, the reaction mixture was filtered, hexane was added and microcrystalline powder was precipitated. It was purified by chromatography on Al_2O_3, $Y_2(R_4Pc)_3$ was eluted with $CHCl_3$–MeOH (98:2 by volume) in 72% yield. UV-VIS [$CHCl_3$, λ_{max}/nm (*A*, relative units)]: 698 (0.21), 642 (1.00), 361 (0.79), 293 (0.64). MALDI TOF, *m*/*z*: found 3997.1; calc. for $Y_2(R_4Pc)_3$ 3997.76.

Terbium tris(tetra-15-crown-5-phthalocyaninate). The synthesis and purification were performed as described for $Y_2(R_4Pc)_3$. Yield, 68%. UV-VIS [$CHCl_3$, λ_{max}/nm (*A*, relative units)]: 697 (0.30), 644 (1.00), 359 (0.81), 292 (0.71). MALDI TOF, *m*/*z*: found 4134.4; calc. for $Tb_2(R_4Pc)_3$ 4135.31.

Lutetium–yttrium tris(tetra-15-crown-5-phthalocyaninate). Method 1. A solution of $Lu(R_4Pc)_2$ (10 mg, 3.7 μmol) in 2 ml of 1,2,4-trichlorobenzene was put into a flask equipped with a reflux condenser; then, H_2R_4Pc (9.4 mg, 7.4 μmol) and $Y(AcAc)_3{\cdot}3H_2O$ (16.3 mg, 37 μmol) were added [molar ratio $Lu(R_4Pc)_2{:}H_2R_4Pc{:}Y(AcAc)_3{\cdot}3H_2O$, 1:2:10]. The reaction mixture was refluxed at TCB for 1.5 h. After cooling, the reaction mixture was filtered, hexane was added and microcrystalline powder was precipitated. It was purified by chromatography on Al_2O_3, $LuY(R_4Pc)_3$ was eluted with $CHCl_3$–MeOH (97.5:2.5 by volume) in 31% yield.

Method 2. A solution of $Lu(R_4Pc)_2$ (10 mg, 3.7 μmol) in 2 ml of 1,2,4-trichlorobenzene was put into a flask equipped with a reflux condenser; then, $[Y(R_4Pc)]{\cdot}(AcAc){\cdot}DBU$ (6 mg, 3.7 μmol) was added [molar ratio $Lu(R_4Pc)_2{:}Y(R_4Pc){\cdot}(AcAc){\cdot}DBU$, 1:1]. The reaction mixture was refluxed at TCB for 1.5 h. The reaction mixture was treated as described in Method 1. $LuY(R_4Pc)_3$ was isolated as a major product in 41.8% yield. UV-VIS [$CHCl_3$, λ_{max}/nm (*A*, relative units)]: 708 (0.18), 640 (1.00), 361 (0.75), 291 (0.55). MALDI TOF, *m*/*z*: found 4082.5; calc. for $LuY(R_4Pc)_3$ 4083.3.

Terbium–yttrium tris(tetra-15-crown-5-phthalocyaninate). $TbY(R_4Pc)_3$ synthesis was performed as described in Method 1 for $LuY(R_4Pc)_3$, the yield is 21%. UV-VIS [$CHCl_3$, λ_{max}/nm (*A*, relative units)]: 702 (0.21), 643 (1.00), 360 (0.75), 293 (0.61). MALDI TOF, *m*/*z*: found 4067.1, calc. for $TbY(R_4Pc)_3$] 4064.8.

^1H NMR (200 MHz, $CDCl_3$) data for the synthesised compounds are reported in Table 1.

the ^{1}H NMR spectrum of a terbium triple-decker complex, which correspond to aromatic protons of one inner macrocyclic ring and two outer rings. The integral intensity ratio is equal to 1:2. The resonance signal of aromatic protons of inner deck is upfield shifted by 157 ppm in comparison with an analogous yttrium complex. Heteronuclear $\mathrm{LuY(R_4Pc)_3}$ complexes exhibit proton resonance signals, which hold an intermediate position between corresponding homonuclear compounds. Note that, in the ^{1}H NMR spectrum of heteronuclear $\mathrm{TbY(R_4Pc)_3}$ complex, the signal of aromatic protons of the outer deck, close to yttrium, is shifted downfield in comparison with a homonuclear yttrium complex. The inner deck aromatic protons exhibit δ –68.6 ppm, the outer deck protons, close to terbium, are at δ –73.12 ppm. Hence, we demonstrated that NMR spectra are characteristic enough to establish the composition of heteronuclear complex, especially in case of simultaneous diamagnetic and paramagnetic ions presence.

Thus, we developed highly selective pathways towards homo- and heteronuclear homoleptic rare earth triple-decker crownphthalocyaninate synthesis by the examples of yttrium(III), terbium(III) and lutetium(III) ions.

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