A novel efficient approach to heteronuclear triple-decker complexes of rare earth elements with phthalocyanines*

*A. Yu. Tsivadze,[a,b] A. G. Martynov,[a,b] M. A. Polovkova,[a,b] and Yu. G. Gorbunova[a,b]**

[a]*A. N. Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, 31 Leninsky prosp., 119071 Moscow, Russian Federation. Fax: +7 (499) 952 0462. E-mail: tsiv@phyche.ac.ru*

[b]*N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, 31 Leninsky prosp., 119991 Moscow, Russian Federation. Fax: +7 (499) 952 2566. E-mail: yulia@igic.ras.ru*

A novel approach to heteroleptic heteronuclear rare earth metal(III) trisphthalocyaninates was proposed with the complexes $[(15C5)_4Pc]M^*[(15C5)_4Pc]M(Pc)$ as examples (15C5 is 15-crown-5, Pc^{2-} is the phthalocyaninate dianion, and $M^* \neq M$ = Yb and Y). Unsubstituted lanthanum bisphthalocyaninate, $La(Pc)_2$, was used for the first time as a Pc^{2-} donor in the synthesis of such complexes. This substantially increased the yields of the target heteronuclear complexes over the previous literature data.

Key words: trisphthalocyaninates, crown ethers, heteronuclear complexes, rare earth metals, NMR spectroscopy, lanthanide-induced shift.

The preparation and study of molecular magnets is an actively developed area of modern transition-metal coordination chemistry. Since the discovery of a heterovalent 12-nuclear manganese complex in 1993,[1] the first representative of such compounds, various molecular magnets have been obtained and examined. Examples include *d*-metal complexes, in which the magnetic anisotropy is due to couplings between the transition metal ions containing unpaired electrons.[2]

In 2003, sandwich lanthanide phthalocyaninates were reported as potential molecular magnets.[3—5] Those complexes show magnetic anisotropy due to the field of the macrocyclic ligands bound to the lanthanide ions and feature a substantially wider temperature range of molecular magnetism compared to polynuclear *d*-metal complexes.

Fine adjustment of the physicochemical (including magnetic) characteristics of sandwich lanthanide complexes can be implemented by directed variation of macrocyclic ligands and complexing metals.[6—8] Triple-decker complexes can also be heteronuclear: their structures can contain either one diamagnetic and one paramagnetic lanthanide ion or two different paramagnetic ions. In addition, the synthesis of heteronuclear complexes will allow control of magnetic dipole *f—f* interactions between paramagnetic lanthanide ions.[9]

The known routes to heteronuclear trisphthalocyaninates involve the addition of lanthanide monophthalocyaninate prepared beforehand or generated *in situ* to a double-decker complex containing a different lanthanide ion.

For instance, a reaction of unsubstituted yttrium bisphthalocyaninate, $Y(Pc)_2$, with octabutoxyphthalocyanine, $H_2[(C_4H_9O)_8Pc]$, in the presence of lanthanide acetylacetonates, $Ln(acac)_3$, in boiling 1,2,4-trichlorobenzene (TCB, b.p. 216 °C) for 3 h gives the heteronuclear complexes $[(BuO)_8Pc]Ln(Pc)Y(Pc)$ (Ln = Tb—Yb).[10] Their isomeric complexes $[(BuO)_8Pc]Y(Pc)Ln(Pc)$ can be obtained in a similar way.[9] The yields of these complexes in the above reactions do not exceed 50%.

Addition of monophthalocyaninates prepared beforehand to double-decker complexes gives the homoleptic heteronuclear crown-phthalocyaninates $LnY[(15C5)_4Pc]_3$ (Ln = Tb and Lu),[11] the heteroleptic complexes $(R_8Pc)Eu[Bu^n{}_8Pc]Lu[Bu^n{}_8Pc]$ and $(R_8Pc)Eu[Bu^t{}_4Pc]Lu[Bu^t{}_4Pc]$ (R=H, Cl, and Bu^n),[12] as well as the complexes $(Pc)Ln[(C_8H_{17}O)_8Pc]Lu(Pc)$ (Ln = Gd—Yb).[13] As a rule, their yields do not exceed 40—50% (in some cases, ≤15%) and the isolation of the target products is complicated by thermal decomposition of the starting reagents and the reaction products followed by random recombination of the lanthanide ions and the phthalocyanine ligands.

Since currently available routes to heteronuclear trisphthalocyaninates do not provide their high yields, a search for efficient approaches to targeted syntheses of heteronuclear triple-decker phthalocyaninates remains a challenge.

Earlier, we have demonstrated[14,15] that a reaction of unsubstituted lanthanum bisphthalocyaninate $La(Pc)_2$ (**1**)

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with $M(acac)_3$ (M = Nd, Sm, Eu, Tb—Yb, and Y) in boiling 1-chloronaphthalene (b.p. 260 °C) results in rapid quantitative *in situ* generation of the monophthalocyaninate (Pc)Ln(acac), which in the presence of tetra-15-crown-5-phthalocyanine $H_2[(15C5)_4Pc]$ and $Ln(acac)_3$ yields the heteroleptic complexes $(Pc)Ln[(15C5)_4Pc]$-Ln(Pc) (15—25%) and $[(15C5)_4Pc]Ln[(15C5)_4Pc]Ln(Pc)$ (40—50%).

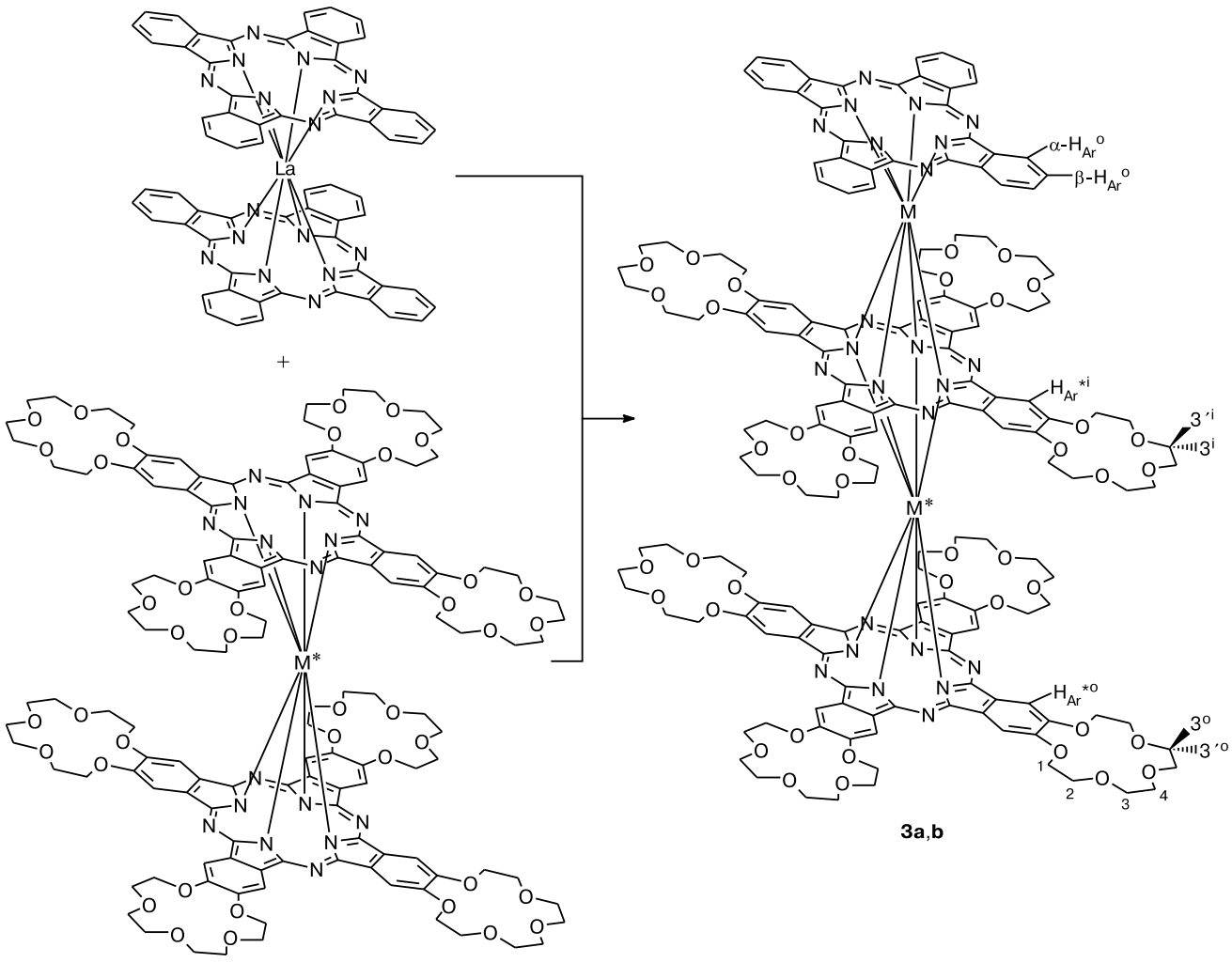
In the present work, we studied the possibility of using this approach for more efficient syntheses of heteroleptic heteronuclear triple-decker phthalocyaninates of various rare earth metals. Unsubstituted and crown-substituted phthalocyanines were employed as ligands and diamagnetic yttrium and paramagnetic ytterbium, as complexing metals.

Results and Discussion

To obtain heteronuclear crown-trisphthalocyaninate containing yttrium and ytterbium ions, we carried out a reaction between unsubstituted lanthanum bisphthalocyaninate $La(Pc)_2$ (**1**), previously prepared yttrium bis-(tetra-15-crown-5-phthalocyaninate) $Y[(15C5)_4Pc]_2$ (**2a**), and ytterbium acetylacetonate $Yb(acac)_3$ (Scheme 1).

The course of the reactions was monitored by electronic absorption spectroscopy. It turned out that the starting reagents were consumed completely after 10-min boiling of the reaction mixture: the UV-Vis spectra did not contain their absorption bands. Column chromatography on neutral Al_2O_3 (gradient elution with $CHCl_3$—0—2 vol.% MeOH) afforded a dark blue complex. Since

Scheme 1



3a,**b**

3a: M* = Y, M = Yb
3b: M* = Yb, M = Y

Reaction conditions: $M(acac)_3 \cdot nH_2O$, 1-chloronaphthalene.

the calculated and experimental *m/z* values, as well as the isotope distributions, were identical, the complex obtained was identified as heteronuclear crown-trisphthalocyaninate containing yttrium and ytterbium ions of the formula $[(15C5)_4Pc]Y[(15C5)_4Pc]Yb(Pc)$ (**3a**). The yield of complex **3a** was 75%. According to a similar procedure, we obtained the isomeric complex $[(15C5)_4Pc]Y[(15C5)_4Pc]$-Yb(Pc) (**3b**) in 61% yield from complexes **1**, $Yb[(15C5)_4Pc]_2$ (**2b**), and $Y(acac)_3$.

It should be noted that the yields of complexes **3a**,**b** are substantially higher than those of heteronuclear trisphthalocyaninates described earlier. This effect is due to the use of complex **1** as a donor of the phthalocyaninate dianion, which reduces the reaction time from many hours to several minutes and thus precludes the formation of by-products through thermal decomposition—recombination processes.

According to MALDI TOF mass spectra, the heteronuclear trisphthalocyaninates $[(15C5)_4Pc]M[(15C5)_4Pc]$-M*(Pc) are major reaction products from $M[(15C5)_4Pc]_2$, $La(Pc)_2$, and $M^*(acac)_3$. The presence of two different rare earth metal ions in complexes **3a**,**b** was confirmed by the identical calculated and experimental molecular masses and the identical characteristic isotope distributions of the molecular ions. However, MALDI TOF mass spectrometry fails to distinguish between the isomeric complexes. For this purpose, we used NMR spectroscopy.

In the ^1H NMR spectra of the complexes of paramagnetic lanthanides, the signals are shifted from their positions in the spectra of the diamagnetic analogs. These shifts are characterized by a so-called lanthanide-induced shift. Its sign and magnitude depend on both the lanthanide nature and the relative positions of the Ln^{3+} ion and the protons under consideration.[16—19] For this reason, ^1H NMR spectroscopy can be used to distinguish between the isomers $[(15C5)_4Pc]Ln[(15C5)_4Pc]Y(Pc)$ and $[(15C5)_4Pc]Y[(15C5)_4Pc]Ln(Pc)$. Since the lanthanide-induced shift is inversely proportional to the distance between the Ln^{3+} ion and the proton to be identified, the largest lanthanide-induced shifts for heteronuclear complexes should be assigned to the protons of the ligands directly bound to the paramagnetic ion.

The ^1H NMR spectra of the complexes $[(15C5)_4Pc]$-$M^*[(15C5)_4Pc]M(Pc)$ show signals for the aromatic α- and β-protons of the outer unsubstituted phthalocyanine macrocycle (α-, β-$H_{Ar}{}^o$), signals for the aromatic protons of the outer and inner crown-containing ligands ($H_{Ar}{}^{*i,o}$), and eight pairs of signals for the *exo*- and *endo*-protons of the methylene groups of the crown ether fragments (see Scheme 1). All the signals observed have the same relative integral intensities.

With isomeric complexes **3a** and **3b** as examples, we demonstrated that ^1H NMR spectroscopy allows reliable structural identification of heteronuclear complexes (Fig. 1). Comprehensive signal assignment was performed using 2D NMR spectroscopy ($^1H—^1H$ COSY).

The electronic absorption spectra of complexes **3a**,**b** have a shape typical of trisphthalocyaninates; the positions of the Q and B bands (Soret band) in the spectra of the isomeric complexes are independent of relative positions of the yttrium and ytterbium ions (Fig. 2). Note that the positions of the Q bands in the electronic absorption spectra of heteronuclear complexes **3a** and **3b** are intermediate between the Q bands of their isostructural homonuclear analogs.

To sum up, with complexes **3a,b** as examples, we proposed a novel route to heteronuclear trisphthalocyaninates using unsubstituted lanthanum bisphthalocyaninate as an efficient donor of the phthalocyaninate dianion. This approach provides the high rates of the complexation reac-

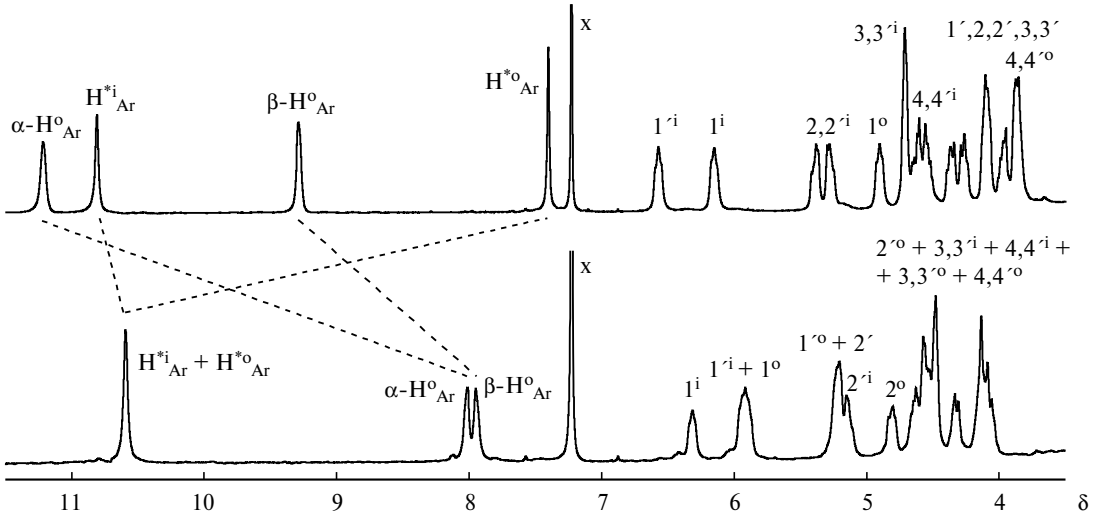


Fig. 1. ^1H NMR spectra of isomeric heteronuclear complexes **3a** and **3b** in $CDCl_3$ (x refers to the signal for the protons of residual $CHCl_3$).

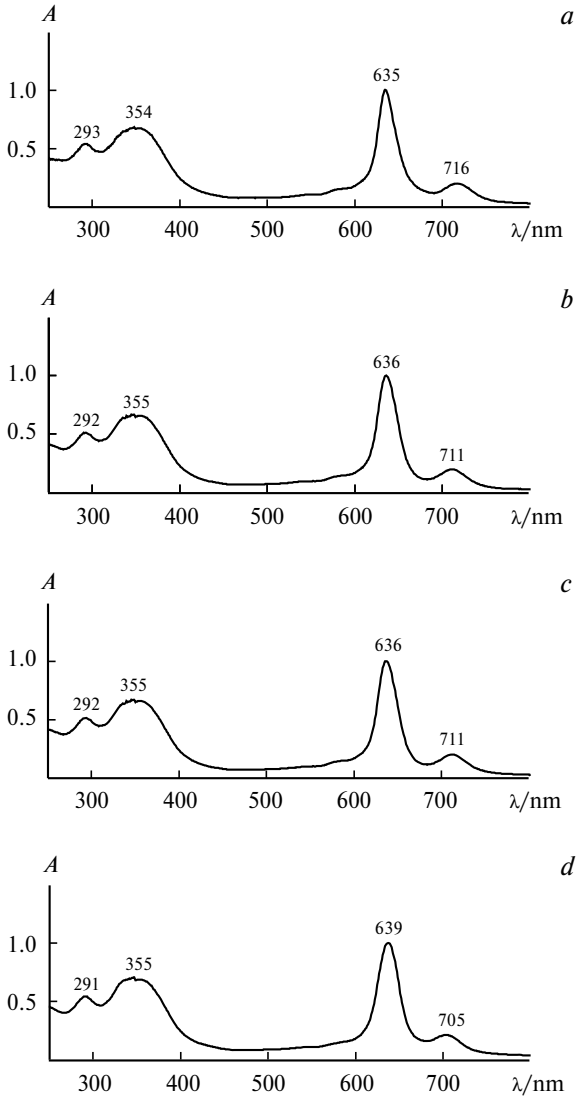


Fig. 2. Electronic absorption spectra of the heteroleptic triple decker complexes $[(15C5)_4Pc]M^*[(15C5)_4Pc]M(Pc)$ in $CHCl_3$: M* = M = Y (*a*); **3a**: M* = Y, M = Yb (*b*); **3b**: M* = Yb, M = Y (*c*); M* = M = Yb (*d*).

tions, which substantially increases the yields of the target complexes by preventing thermal decomposition of the sandwich complexes. The complexes obtained were characterized by physicochemical methods (MALDI TOF mass spectrometry, ^{1}H NMR spectroscopy, and electronic absorption spectroscopy). We demonstrated that the relative positions of the diamagnetic and paramagnetic ions in isomeric heteronuclear complexes **3a** and **3b** influence the lanthanide-induced shifts in their ^{1}H NMR spectra.

Experimental

The complexes $La(Pc)_2$ (**1**),[15] $M[(15C5)_4Pc]_2$ (M = Y (**2a**)[20] and Yb (**2b**)[21]), and $M(acac)_3 \cdot nH_2O$ (M = Y and Yb (see Ref. 22)) were prepared as described earlier. Chloroform (reagent grade) was predried over $CaCl_2$ and distilled over CaH_2. Methanol (Merck) was dried over 4A molecular sieves. 1-Chloronaphthalene (Acros Organics) was used as purchased. Column chromatography was carried out on neutral Al_2O_3 (Merck).

Electronic absorption (UV-Vis) spectra were recorded on a Cary-100 spectrophotometer (Varian) in 1—10-mm-thick quartz rectangular cells. MALDI-TOF mass spectra were measured on an Ultraflex mass spectrometer (Bruker Daltonics). ^{1}H NMR spectra were recorded on a Bruker Avance-II spectrometer (300.13 MHz) with internal deuterium lock at room temperature. Chemical shifts δ are referenced to the signals for the residual protons in $CDCl_3$ (δ 7.25) used as a solvent.

[Phthalocyaninato]ytterbiumbis[4,5,4′,5′,4″,5″,4‴,5‴-tetrakis(1,4,7,10,13-pentaoxatridecamethylene)phthalocyaninato]yttrium (3a). A mixture of complexes **1** (4.5 mg, 3.87 μmol), **2a** (10.2 mg, 3.87 μmol), and $Yb(acac)_3 \cdot nH_2O$ (5.7 mg, 11.61 mmol) was dissolved in 1-chloronaphthalene (3.6 mL) and refluxed under argon for 10 min. Then the reaction mixture was cooled to room temperature and chromatographed on neutral Al_2O_3 (gradient elution with $CHCl_3$—MeOH (0—2%)). The yield of the target complex **3a** was 75%. UV-Vis ($CHCl_3$), λ_{max}/nm (A_{rel}): 711 (0.21), 636(1), 355 (0.67), 292 (0.54). MALDI TOF MS: found *m/z* 3321.1; $C_{160}H_{160}N_{24}O_{40}YbY$; calculated M = 3321.1. ^{1}H NMR ($CDCl_3$), δ: 11.21 (s, 1 H, α-H_{Ar}^o); 10.81 (s, 1 H, H_{Ar}^{*i}); 9.29 (s, 1 H, β-H_{Ar}^o); 7.40 (s, 1 H, H_{Ar}^{*o}); 6.57 (br.m, 1 H, 1′-CH_2^i); 6.15 (br.m, 1 H, 1-CH_2^i); 5.37 (m, 1 H, 2′-CH_2^i); 5.28 (m, 1 H, 2-CH_2^i); 4.90 (m, 1 H, 1-CH_2^o); 4.71 (both s, 1 H each, 3,3′-CH_2^i); 4.60—4.56 (both m, 1 H each, 4,4′-CH_2^i); 4.36—3.87 (br.m, 7 H, 1′,2,2′, 3,3′,4,4′-CH_2^o).

[Phthalocyaninato]yttriumbis[4,5,4′,5′,4″,5″,4‴,5‴-tetrakis(1,4,7,10,13-pentaoxatridecamethylene)phthalocyaninato]ytterbium (3b). A mixture of complexes **1** (3.0 mg, 2.57 μmol), **2b** (7.0 mg, 2.57 μmol), and $Y(acac)_3 \cdot nH_2O$ (3.1 mg, 7.71 mmol) was dissolved in 1-chloronaphthalene (2.5 mL) and refluxed under argon for 10 min. Then the reaction mixture was cooled to room temperature and chromatographed on neutral Al_2O_3 (gradient elution with $CHCl_3$—MeOH (0—2%)). The yield of the target complex **3b** was 61%. UV-Vis ($CHCl_3$), λ_{max}/nm (A_{rel}): 711 (0.20), 636 (1), 355 (0.71), 291 (0.56). MALDI TOF MS: found *m/z* 3321.9; $C_{160}H_{160}N_{24}O_{40}YbY$; calculated M = 3321.1. ^{1}H NMR ($CDCl_3$), δ: 10.59 (s, 2 H, $H_{Ar}^{*i} + H_{Ar}^{*o}$); 8.01 (s, 1 H, α-$H_{Ar}^o$); 7.94 (s, 1 H, β-$H_{Ar}^o$); 6.31 (br.m, 1 H, 1-$CH_2^i$); 5.91 (br.m, 2 H, 1′-$CH_2^i$ + 1-CH_2^o); 5.20 (br.m, 2 H, 1′-CH_2^o + + 2-CH_2^i); 5.15 (br.m, 1 H, 2′-CH_2^i); 4.80 (br.m, 1 H, 2-CH_2^o); 4.63—4.05 (m, 9 H, 2′,3,3′,4,4′-CH_2^o + 3,3,4,4′-CH_2^i).

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