*Mendeleev Commun.*, 2001, 11(6), 214–215

# Synthesis of crown ether–substituted yttrium(III) bisphthalocyanine

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10.1070/MC2001v011n06ABEH001507

A double-decker complex of yttrium(III) with tetra-15-crown-5-phthalocyanine has been synthesised and characterised by spectroscopic methods.

The chemistry of rare earth phthalocyanines is of interest for the development of new functional materials because the sandwich double-decker monoradical complexes of rare earth elements exhibit unique optical and physical properties.[1–3] The syntheses and functional properties of lanthanide phthalocyanines were described in the literature; however, only a few works were devoted to yttrium phthalocyanines.[4–6] Yttrium complexes with unsubstituted phthalocyanine (Pc) with the composition $[Y^{3+}]:[Pc^{2-}] = 1:1$, 1:2 and 2:3 were synthesised[4,5] by a template method in an *o*-phthalonitrile melt with the addition of yttrium acetate. $Y(Pc)_2^{\cdot}$ was also prepared by refluxing $Li_2(Pc)$ and $Y(acac)\cdot 3H_2O$ in 1,2,4-trichlorobenzene for 10 h in a nitrogen atmosphere.[6] $Y[Pc(C_7H_{15})_8]_2^{\cdot}$ and $Y[Pc(OC_5H_{11})_8]_2^{\cdot}$ were synthesised by the interaction of $Y(acac)\cdot 3H_2O$ with corresponding 4,5-disubstituted phthalonitriles in the presence of 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU) in amyl alcohol under reflux for 12 h under nitrogen.[6]

The double-decker lutetium phthalocyanine complexes described earlier,[7] in which crown-ether substituents are an integrated part of the macrocyclic phthalocyanine ring, can exhibit the cation-induced organisation of supramolecular assemblies, which are superior to similar compounds with other substituents in the electrophysical characteristics.[7]

Crown ether–substituted yttrium phthalocyanines were not described previously.

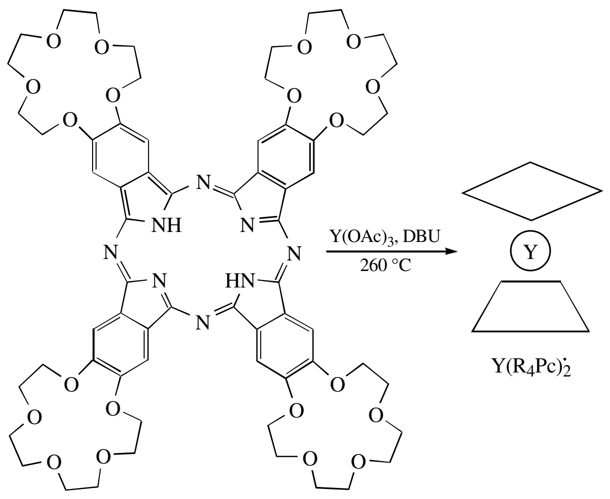
The synthesis of lanthanide crown phthalocyanines by the direct interaction of $H_2R_4Pc$ [$R_4Pc^{2-}$ = 4,5,4′,5′,4″,5″,4‴,5‴-tetrakis-(1,4,7,10,13-pentaoxatridecamethylene)phthalocyaninate ion] with a metal salt in the presence of a strong base was used for obtaining $Y^{3+}$ complexes with tetra-15-crown-5-phthalocyanine.[8,9] This synthetic method allowed us to prepare complexes of a given structure; the reaction was performed in a boiling solvent to obtain mono- (in 1,2-dichlorobenzene) or multi-decker compounds (in 1-chloronaphthalene).

The synthesis was performed starting from $H_2R_4Pc$, which was synthesised according to a described procedure,[10] and $Y(OAc)_3\cdot 4H_2O$ in the presence of DBU as an organic base in 1-chloronaphthalene under reflux (260 °C) in an argon atmosphere.

Optimum conditions for the complete transformation of the initial ligand into metal complexes were chosen by varying the main parameters of the synthesis (the molar ratio between reactants and the ligand concentration). The conversion was monitored by electronic absorption spectroscopy. The complete transformation of $H_2(R_4Pc)$ into an $Y^{3+}$ complex took place after 2 h at an $Y(OAc)_3\cdot 4H_2O:H_2R_4Pc:DBU$ molar ratio of 1.5:1:13 and a ligand concentration of $2\times10^{-2}$ mol dm$^{-3}$. The double-decker $Y(R_4Pc)_2^{\cdot}$ complex was separated by liquid column chromatography on $Al_2O_3$ (eluent: $CHCl_3$–MeOH, 98:2 by volume) with 20% yield.

The structure of the separated complex was found from the parameters of the UV-VIS spectrum† in chloroform, which were characteristic of sandwich lanthanide crown-bisphthalocyanines.[8]

The dark green crystalline powder obtained is soluble in polar organic solvents. Table 1 summarises data on the UV-VIS spectrum of the prepared compound and published data on the spectra of double-decker complexes of Lu, Yb and Gd with tetra-15-crown-5-phthalocyanine. A comparative analysis of these data allowed us to conclude that the synthesised complex has a double-decker structure.



$Y(R_4Pc)_2^{\cdot}$

We studied the concentration dependence of the intensities of the main bands in the UV-VIS spectrum of $Y(R_4Pc)_2^{\cdot}$ in chloroform and found that the Bouguer–Lambert–Beer law is obeyed up to a concentration of $2.5\times10^{-4}$ mol dm$^{-3}$. A negative deviation from linearity was observed in more concentrated solutions as a consequence of aggregation processes.

The structure of the prepared complex was also supported by FAB mass spectrometry. The mass spectrum exhibited a signal with *m*/*z* 2635.9, which corresponds to the molecular ion $[Y(R_4Pc)_2]^+$ (the calculated value of *m*/*z* is 2635.5).

We measured the EPR‡ spectrum of the compound to confirm its radical nature. The presence of a singlet signal with $g = 2.0031$ in the EPR spectrum of a chloroform solution of the compound is caused by an unpaired electron in the molecule of $[(R_4Pc^{2-})Y^{3+}(R_4Pc^{\dot{-}})]^0$.

We also measured the electronic absorption spectrum in the near-IR region.§ The presence of absorption bands at 920, 1430 and 1560 nm, which are ascribed[12] to the donor–acceptor exchange interaction between the $Pc^{2-}$ dianion and the $Pc^{\dot{-}}$ radical monoanion, also confirms the radical nature of the complex.

**Table 1** UV-VIS spectra of the double-decker complexes of Y, Gd, Yb and Lu with tetra-15-crown-5-phthalocyanine in chloroform.

| $Y(R_4Pc)_2^{\cdot}$ $\lambda_{max}$/nm (lg $\varepsilon$) | $Gd(R_4Pc)_2^{\cdot}$ $\lambda_{max}$/nm (lg $\varepsilon$)[8] | $Yb(R_4Pc)_2^{\cdot}$ $\lambda_{max}$/nm (lg $\varepsilon$)[8] | $Lu(R_4Pc)_2^{\cdot}$ $\lambda_{max}$/nm (lg $\varepsilon$)[11] |
|---|---|---|---|
| 670 (5.01) | 675 (5.08) | 670 (5.18) | 665 (5.20) |
| 481 (4.48) | 488 (4.53) | 479 (4.60) | 476 (4.66) |
| 368 (5.01) | 368 (5.00) | 369 (5.12) | 367 (5.13) |
| 334 (4.92) | 337 (4.93) | | |
| 292 (4.93) | 292 (4.96) | 292 (5.06) | |

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† The UV-VIS spectra were measured on a Varian Cary-100 instrument.

‡ The EPR spectrum was measured by Dr. G. A. Zvereva on a Radiopan SE-X-2542 spectrometer at room temperature.

§ The near-IR spectrum was measured by Dr. A. S. Lileev on a Specord NIR-61 instrument (Carl Zeiss Jena).

The intense bands at 1278, 1202, 1126, 1103 and 935 $cm^{-1}$ present in the vibration IR spectrum¶ of the synthesised complex (as a Nujol mull), which are assigned to the stretching vibrations of crown ether fragments,[8,13] provide support for the presence of these substituents in phthalocyanine ligands.

Thus, we performed the directed synthesis of the yttrium complex $Y(R_4Pc)_2^{\cdot}$ with tetra-15-crown-5-phthalocyanine ligands of the composition 1:2. The structure of the complex was confirmed by UV-VIS, IR and EPR spectroscopy and FAB mass spectrometry.

This work was supported by the Russian Foundation for Basic Research (grant nos. 99-03-32644, 00-15-97377 and 01-03-06241).

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*Received: 25th July 2001; Com. 01/1833*

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¶ The IR spectrum was measured on a Nexus spectrometer (Nicolet).