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Synthesis and chemical behaviour of triple-decker lanthanum tetra-15-crown-5-phthalocyaninate

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The triple-decker lanthanum crownphthalocyaninate $La_2[(15C5)_4Pc]_3$, where $[(15C5)_4Pc]^{2-}$ is the [4,5,4′,5′,4″,5″,4‴,5‴-tetrakis-(1,4,7,10,13-pentaoxatridecamethylene)phthalocyaninate anion], was found to undergo hydrolytic decomposition in solution, as studied by UV–VIS spectroscopy.

The particular feature of rare earth elements (REE) is their ability to form sandwich double- and triple-decker complexes with tetrapyrrolic macrocyclic ligands (porphyrins and phthalocyanines).[1] Lanthanum tris[octa(butoxy)phthalocyaninate] $La_2[(BuO)_8Pc]_3$ was the only isolated and spectrally characterised lanthanum triple-decker phthalocyaninate.[2] This complex was prepared *via* the reaction between lanthanum acetate and $H_2[(BuO)_8Pc]$ in refluxing octan-1-ol. We performed the above reaction for $H_2[(15C5)_4Pc]$, but the formation of metal complexes was not observed.[3] Thus, we tried to perform the reaction between lanthanum acetylacetonate and $H_2[(15C5)_4Pc]$[4,5] to obtain triple-decker lanthanum crownphthalocyaninate and to study its spectral properties and stability.

The reaction between $H_2[(15C5)_4Pc]$ and $La(acac)_3{\cdot}H_2O$ in refluxing 1,2,4-trichlorobenzene was monitored by UV–VIS spectroscopy.[†] In 1 h, the bands of the starting ligand $H_2[(15C5)_4Pc]$ (λ_{max} 701 and 662 nm) vanished, and the complex band at 646 nm was observed.

Positive-ion MALDI TOF mass spectra were obtained in 3,5-dimethoxy-4-hydroxycynnamic acid (sinapic acid, SA) as a matrix. The high resolution MALDI TOF mass spectrum of the reaction mixture (Figure 1) exhibited the molecular ion peak of $HLa_2[(15C5)_4Pc]_3^+$ around *m/z* 4098.20 (calculated 4098.78), confirming the chemical composition of the target compound. The observed and simulated isotopic distributions for $HLa_2[(15C5)_4Pc]_3^+$ are in good agreement. Together with this peak, the peaks of $HLa[(15C5)_4Pc]_2^+$, $[(15C5)_4Pc]La(SA)_2^+$ and $H_3[(15C5)_4Pc]^+$ were also observed. There were no bands of $H_2[(15C5)_4Pc]$ in the UV–VIS spectra; thus, we supposed that $La_2[(15C5)_4Pc]_3$ underwent fragmentation under MALDI conditions. Note that no fragmentation peaks were observed in the MALDI TOF mass spectra of triple-decker crown-phthalocyaninates of other lanthanides.

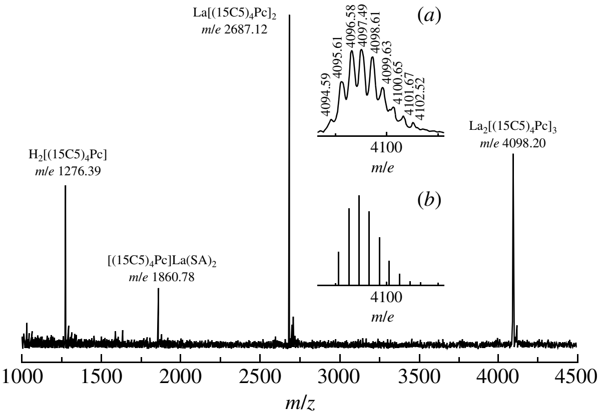

Figure 1 MALDI TOF mass spectrum of the reaction mixture and isotopic distribution for $HLa_2[(15C5)_4Pc]_3^+$: (*a*) observed and (*b*) simulated.

In order to isolate $La_2[(15C5)_4Pc]_3$, we performed the chromatographic separation of the reaction products on neutral alumina with gradient chloroform–methanol elution. However, according to MALDI TOF mass spectra, all the isolated fractions contained only lanthanum diphthalocyaninate $La[(15C5)_4Pc]_2$

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[†] The electronic (UV–VIS) spectra were recorded on a Cary-100 spectrophotometer (Varian) in $CHCl_3$ in quartz cells (1–10 mm). The positive-ion MALDI TOF mass spectra were recorded on an Ultraflex mass spectrometer (Bruker Daltonics) with the use of the reflection mode with a target voltage of 20 mV. 3,5-Dimetoxy-4-hydroxycynnamic acid was used as a matrix. The samples were prepared by dissolving the complex 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. The ^{1}H 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 an internal standard. The IR spectra were measured on a Nexus FT-IR spectrometer (Nicolet).

Tetra-15-crown-5-phthalocyanine was synthesised as described elsewhere[9] and purified by column chromatography on neutral alumina (elution with $CHCl_3$ + 5 vol% MeOH). UV–VIS [$CHCl_3$, λ_{max}/nm (lg ε)]: 701 (5.10), 661 (4.01), 644 (4.66), 601 (4.38), 420 (4.48), 348 (4.88). ^{1}H NMR ($CDCl_3$) δ: 8.91 (s, 8H, H_{Ar}), 4.77 (m, 16H, 1-CH_2), 4.22 (m, 16H, 2-CH_2), 3.93 (m, 32H, 3,4-CH_2). MALDI TOF MS, *m/e*: found 1276.39 [MH]$^+$, calc. for $C_{64}H_{75}N_8O_{20}$ 1276.34.

Lanthanum acetylacetonate monohydrate was synthesised as reported elsewhere.[10]

Tris[tetra-15-crown-5-phthalocyaninate] dilanthanum. A mixture of $H_2[(15C5)_4Pc]$ (10.2 mg, 8 μmol) and $La(acac)_3{\cdot}H_2O$ (11.3 mg, 24 μmol) in 2 ml of trichlorobenzene was refluxed under a slow stream of argon for 1 h. The resulting green-blue solution was cooled. The bands of tetra-15-crown-5-phthalocyanine were not observed in the UV–VIS spectrum of the reaction mixture, evidencing the complete conversion of $H_2[(15C5)_4Pc]$. The reaction mixture was precipitated from hexane and chromatographed on Bio-Beads SX-1 (elution with chloroform). UV–VIS [$CHCl_3$, λ_{max}/nm (*A*, relative units)]: 646 (1.00), 361 (0.48). MALDI TOF MS, *m/e*: $La_2[(15C5)_4Pc]_3$: found 4098.20 [MH]$^+$, calc. for $C_{192}H_{217}O_{60}N_{24}La_2$ 4098.78; $La[(15C5)_4Pc]_2$: found 2687.12 [MH]$^+$, calc. for $C_{128}H_{145}N_{16}O_{40}La$, 2687.12; $[(15C5)_4Pc]La(SA)_2$: found 1860.78 [MH]$^+$, calc. for $C_{86}H_{96}N_8O_{30}La$ 1860.65; $H_2[(15C5)_4Pc]$: found 1276.39 [MH]$^+$, calc. for $C_{64}H_{75}N_8O_{20}$ 1276.34.

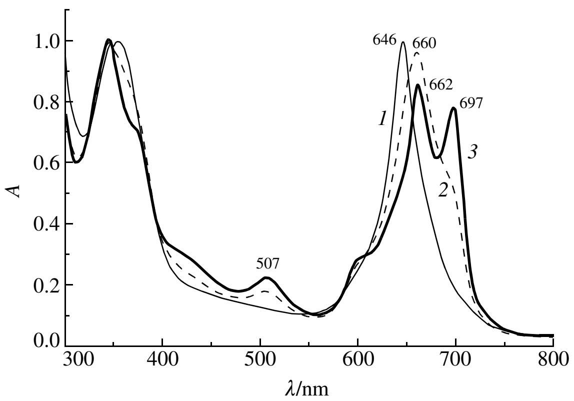

Figure 2 Evolution of the UV–VIS spectra of $La_2[(15C5)_4Pc]_3$ in $CHCl_3$ with time: (*1*) immediately after gel-permeation chromatography, (*2*) after 2 h and (*3*) after a day.

and tetra-15-crown-5-phthalocyanine $H_2[(15C5)_4Pc]$. Thus, we supposed that $La_2[(15C5)_4Pc]_3$ decomposed during chromatography on alumina.

We managed to separate the reaction products by gel-permeation chromatography on Bio-Beads SX-1 (Bio-Rad) with chloroform elution. We isolated fractions, which contained a complex with the Q-band at 646 nm. This band corresponded to the presence of $La_2[(15C5)_4Pc]_3$ in the solution. However, according to UV–VIS spectroscopy, this compound gradually decomposed with the formation of a mixture of complexes. Such a mixture exhibited two Q-bands at 662 and 697 nm and band at 507 nm. This spectrum corresponded to the mixture of $La[(15C5)_4Pc]_2$ and $H_2[(15C5)_4Pc]$, which were isolated by chromatography on neutral alumina.

The evolution of $La_2[(15C5)_4Pc]_3$ UV–VIS spectrum during a day (Figure 2) allowed us to propose the mechanism of complex decomposition.

During a few hours, the bathochromic shift and broadening of the Q-band from 646 to 660 nm occur. It can be the evidence of the hydrolytic decomposition of $La_2[(15C5)_4Pc]_3$ with the formation of the protonated double-decker complex $HLa[(15C5)_4Pc]_2$ and lanthanum monophthalocyaninate $[(15C5)_4Pc]La(OH)$.

A similar mechanism was proposed previously for the decomposition of indium tris(phthalocyaninate) $In_2(Pc)_3$, when it was heated in 4-methylpyridine (4-MePy), which contained 1 vol% water.[6] In the course of reaction, monocrystals of unsubstituted phthalocyanine $H_2(Pc)$, protonated indium diphthalocyaninate $HIn(Pc)_2$ and also the unusual binuclear complex $(Pc)In(\mu\text{-}OH)_2In(Pc)$ with the 4-MePy molecule bonded to one of the bridging OH groups *via* a hydrogen bond, were obtained. When dry 4-MePy was applied, no decomposition of the starting complex was observed.

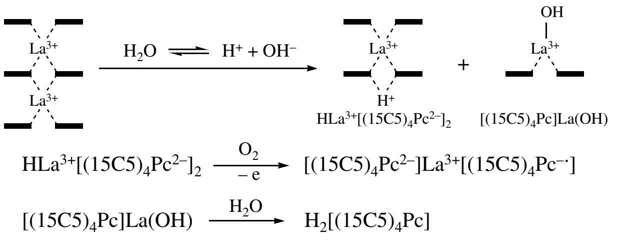

Figure 3 The proposed mechanism of $La_2[(15C5)_4Pc]_3$ decomposition.

According to UV–VIS spectroscopy, the subsequent chemical transformations of decomposition products of $La_2[(15C5)_4Pc]_3$ were the oxidation of protonated diphthalocyaninate $HLa[(15C5)_4Pc]_2$ in air with the formation of the neutral radical diphthalocyaninate $La[(15C5)_4Pc]_2^{0\cdot}$ and decomposition of monophthalocyaninate with the formation of tetra-15-crown-5-phthalocyanine. The UV–VIS bands of these compounds were observed in one day after isolation of $La_2[(15C5)_4Pc]_3$. Figure 3 shows the proposed mechanism of decomposition.

The stability of the compound in a solid phase is also low. After the precipitation of the compound from the reaction mixture with hexane, the sample of the solid complex was kept in a refrigerator at –15 °C; however, it also underwent decomposition during a few days. The alike low stability of lanthanum phthalocyaninates was previously reported for the double-decker lanthanum *tert*-butylnaphthalocyaninate, which decomposes even under an N_2 atmosphere in a solid state.[7]

To support the proposed mechanism of triple-decker complex decomposition, we performed the reaction between $H_2[(15C5)_4Pc]$, $La(acac)_3{\cdot}H_2O$ and unsubstituted lanthanum diphthalocyaninate $La(Pc)_2$. According to MALDI TOF mass spectrometry, the formation of the heteroleptic triple-decker complex $[(15C5)_4Pc]$-$La(Pc)La(Pc)$ was observed.[8] Its decomposition led to the heteroleptic lanthanum diphthalocyaninate $[(15C5)_4Pc]La(Pc)$.

Thus, tris[tetra-15-crown-5-phthalocyaninate] of lanthanum, which has the biggest ionic radius among all REEs, is unstable and undergoes hydrolytic decomposition in solution with the formation of a double-decker complex and phthalocyanine; the trace amounts of water are supposed to take part in this process.

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