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The First Synthesis of Sandwich-type Titanium Bisphthalocyanines

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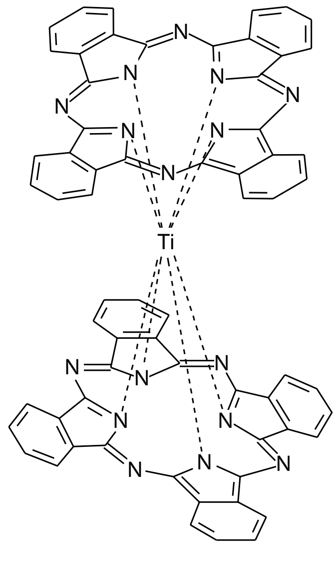
A method of synthesis of hitherto unknown unsubstituted and octa-*tert*-butyl-substituted titanium bisphthalocyanines has been developed and their spectral characteristics have been studied.

In 1970 Kirin and Moskalev postulated[1] that a necessary condition for the formation of sandwich-like bisphthalocyanine metal complexes (Pc_2M) is that the radius of the phthalocyanine coordination space between the four internal nitrogen atoms should exceed the covalent radius of the metal (1.35 Å calculated from X-ray crystal data[2]); in addition, the metal oxidation state must be not less than +3. According to this concept there are 41 elements which satisfy this condition. To date sandwich-like bisphthalocyanines Pc_2M have in fact been obtained with most of these elements, all of which submit to this criterion. However, with some elements from this list such complexes have not been created. For example, our attempts to obtain a lead bisphthalocyanine were unsuccessful in spite of the fact that the covalent radius of lead(IV) ($r = 1.47$ A) is more than the radius of the phthalocyanine coordination space. At the same time, for titanium, which is absent in this list and which has covalent radius ($r = 1.32$ Å) less than the radius of the phthalocyanine coordination space, we created and separated in the individual state the first sandwich-type complexes of unsubstituted and octa-*tert*-butyl-substituted titanium bisphthalocyanines. This experimental result has cast doubt on the above-mentioned statement.

In our opinion some other factors influence the formation of the second macro-ring, among them a capacity to change coordination number and metal valence as well as displacement of the coordinated metal relative to the plane of the phthalocyanine ring. It was these arguments which were, perhaps, dominant in the preparation of Pc_2Ti. Earlier we showed[3] that the synthesis of sandwich-like bisphthalocyanines of tri- and tetravalent metals involves passage first through a corresponding monophthalocyanine stage. In this connection it should be expected that Pc_2Ti formation can proceed through a complex of titanium monophthalocyanine. According to the literature data[4,5] $PcTiCl_2$ exhibits a *cis* configuration with the titanium significantly displaced out of the plane of the phthalocyanine chromophore (0.84 Å) towards the two chlorine atoms. This seemed appropriate as a starting material for the formation of a sandwich-type



Pc_2Ti

molecule Pc_2Ti. In the case of PcPb the metal atom is displaced out of the plane of the phthalocyanine ring only in the distance range 0.37–0.40 Å and, moreover, for lead the divalent state is preferable and all attempts to oxidize it to lead(IV) lead only to the loss of metal from the complex.[6,7] These factors, perhaps, can explain the unsuccessful synthesis of Pc_2Pb in spite of the use of different synthetic methods.

Syntheses of unsubstituted titanium bisphthalocyanine (Pc_2Ti) and octa-*tert*-butyl-substituted titanium bisphthalocyanine ($\mathrm{Pc}^{t}_{2}\mathrm{Ti}$) were carried out by the slow addition of $TiCl_4$ to a solution of phthalocyanine (PcH_2) or tetra-*tert*-butylphthalocyanine ($\mathrm{Pc}^{t}\mathrm{H}_2$) (molar ratio 1:4) in DMSO in the presence of lithium salt. The reaction mixture was heated at 170–180 °C for 15–20 min. After being cooled the reaction mixture was diluted with 0.5 volumes of water, filtered from unreacted phthalocyanine and metal salts and then 2 volumes of water were added to the filtrate. The dark-blue compound precipitated was filtered and washed with water and acetone. Purification of titanium bisphthalocyanines was effected by TLC on aluminum oxide with benzene as solvent with subsequent vacuum drying (yield 35–40%). $\mathrm{Pc}^{t}_{2}\mathrm{Ti}$ was also prepared by the interaction of $TiCl_4$ with an eight-fold excess of 4-*tert*-butylphthalodinitryl in the presence of lithium salt; however, the yield of the product was reduced.[†]

Unlike $PcTiCl_2$ the bisphthalocyanine complex Pc_2Ti shows a specific absorption spectrum analogous to sandwich-like bisphthalocyanines and is characterized by the presence of a main absorption band at 620 nm and a less intense one at 772 nm. The introduction of *tert*-butyl groups into the phthalocyanine ring does not significantly influence the position of the absorption bands in the synthesized compound $\mathrm{Pc}^{t}_{2}\mathrm{Ti}$ (622 and 776 nm, respectively, Fig. 1), but the solubility of this complex in organic solvents is greatly increased (about two orders) in comparison with Pc_2Ti.

Earlier we noted[8] that the intensity ratio of the two absorption bands of the blue forms of the rare earth element (REE) bisphthalocyanines in the visible region and the distance between them depends strongly on the covalent radius of the complex-forming metal. So, an increase in the covalent radius reduces the distance between the bands and the long-wave band is gradually transformed to the shoulder. The same characteristic of the spectra is also observed for the phthalocyanines of the tetravalent metals protactinium, uranium and thorium.[9] However, in the case of the bisphthalocyanines of hafnium and zirconium (covalent radii 1.44 and 1.45 Å, respectively), as in the case of the bisphthalocyanines of the elements at the end of the REE series, the absorption in the region 700 nm shows a bathochromic shift and appears as a well-defined absorption band. Tin bisphthalocyanine, the covalent radius of which is equal to 1.41 Å, shows an even greater bathochromic shift of the long-wave band to 765 nm.[10,11] The first synthesized titanium bisphthalocyanine completes this row to date; it has a maximum long-wave band at 776 nm (Fig. 1). A likeness of the absorption spectrum of Pc_2Ti with the spectra of other tetravalent metal bisphthalocyanines allows us to consider it as a sandwich-like complex containing two equivalent phthalocyanine ligands, connected with an eight-coordinated titanium(IV) ion.

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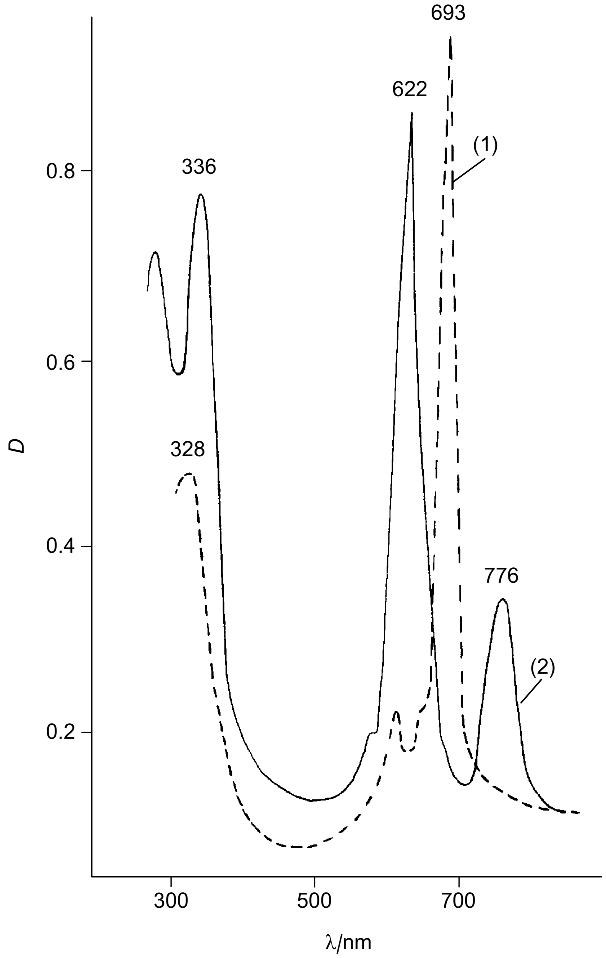

Fig. 1. Absorption spectra of $\mathrm{Pc}^{t}\mathrm{TiCl}_2$ (1) and $\mathrm{Pc}^{t}_{2}\mathrm{Ti}$ (2) in C_6H_6.

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[†] *Elemental analysis data* for Pc_2Ti. Found: C 71.48; H 2.87; N 21.22. Calc. for $C_{64}H_{32}N_{16}Ti$: C 71.64; H 3.01; N 20.89%; for $\mathrm{Pc}^{t}_{2}\mathrm{Ti}$, found: C 75.52; H 6.14; N 15.06. Calc. for $C_{96}H_{96}N_{16}Ti$: C 75.77; H 6.36; N 14.73%. Chlorine in both compounds was not detected.