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Note

$TTBuPcCrCl_2H$ a sparingly soluble tetra-t-butyl-phthalocyaninato-chloro-chromium complex

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Abstract

An axially substituted chloro complex of tetra-t-butylphthalocyaninato-chromium was prepared by chromium insertion into metal-free tetra-t-butylphthalocyanine ($TTBuPcH_2$). By extracting the soluble components into acetonitrile and pentane a product with the composition $TTBuPcCrCl_2H$ was obtained. It was shown to contain anionic phthalocyanine moieties. In aqueous sodium hydroxide μ-oxo-bis(tetra-t-butylphthalocyaninato)chromium(III) is formed. Boiling pyridine replaces one of the Cl ligands yielding $TTBuPcCrCl\cdot 2py$. Thermogravimetric analysis showed the elimination of both pyridine molecules between 105 and 215 °C and Cl elimination at higher temperatures. $TTBuPcCrCl\cdot 2py$ is oxidized by thionyl chloride to $TTBuPc^{-I}Cr^{III}Cl_2$. Reaction with pyridine reforms $TTBuPcCl\cdot 2py$. All newly synthesized products were characterized by elementary analysis, IR, UV–Vis and FAB mass spectrometry.

Keywords: Chromium complexes; Phthalocyanine complexes; Chloro complexes; Pyridine complexes

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1. Introduction

Unsubstituted phthalocyaninato-chromium(II) (PcCr) crystallizes out of boiling chloronaphthalene in the pure β-modification [1]. An analogous procedure for the preparation of t-butyl substituted phthalocyaninato-chromium failed. Attempts to isolate a pure TTBuPcCr complex by column chromatography were unsuccessful. The product could not be eluted with non-polar solvents from Al_2O_3 or silica gel. Elution with coordinating solvents like pyridine or dimethylformamide produced complexes, which oligomerized in higher concentrated solutions, probably by condensation reactions of axially coordinated OH^-. Such difficulties did not occur with the salt-like chloro complex. We report the preparation of an ionic tetra-t-butylphthalocyaninato-chloro-chromium complex of well defined composition. On account of its low solubility in non-polar solvents it can be separated from the non-ionic by-products. An analytically pure product was obtained without chromatographic separations. It is recommended as a basis for the preparation of other tetra-t-butylphthalocyaninato-chromium complexes.

2. Experimental

2.1. *4-t-Butylphthalodinitrile*

This compound, the starting material for the preparation of $TTBuPcH_2$, was obtained by the Rosenmund-von-Braun reaction, following a Japanese patent [2]. If the reaction is carried out at a slightly lower temperature than described in the patent, the formation of TTBuPcCu can be suppressed. We further found that it is necessary to add some pyridine to the reaction mixture in order to obtain good yields.

2.2. *$TTBuPcH_2$*

This was prepared by a modification of the original synthesis [3]. 1.2 g (52 mmol) of sodium were dissolved in 100 ml anhydrous and deaerated pentanol-1 and a solution of 10 g (54 mmol) of 4-t-butylphthalodinitrile in 20 ml of anhydrous pentanol-1 was added dropwise, while stirring vigorously. Then the reaction mixture was slowly heated to 130 °C. During this procedure the color changed from yellow to a brownish black. After 4 h of refluxing and 12 h of stirring at room temperature the reaction mixture was poured into 300 ml of methanol at 5 °C. The mixture was again stirred for 15 min and

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the greenish blue precipitate was filtered. It was washed with cold methanol until the filtrate became colorless. Finally it was washed with 10 ml of acetone. Yield 8.94 g (85%), ^1H NMR (200 MHz, $CDCl_3$, room temperature): δ 9.05 (8H, multiplet), 8.15 (4H, multiplet), 1.95 (36H, singlet), −2.2 (2H). MS (70 eV): $m/e = 738$ (100%, M^+), 723 (9.9%, $M^+ - CH_3$). *Anal.* Calc. for $C_{48}H_{50}N_8$: C, 78.1, H, 6.8; N, 15.1. Found: C, 78.0, H, 6.9, N, 14.9%.

2.3. *TTBuPcCrCl$_2$H*

A mixture of 327 mg (2.45 mmol) of anhydrous $CrCl_3$, a spatula of zinc dust, and 10 ml of freshly distilled quinoline was heated to 180 °C under an N_2 atmosphere. After 45 min of stirring, the solution became a yellowish brown. After the addition of 1.02 g (1.4 mmol) of thoroughly dryed $TTBuPcH_2$ the temperature was gradually raised to 240 °C within 2.5 h and the mixture subsequently stirred for 30 min at this temperature. After cooling down to room temperature 150 ml of toluene were added and the mixture was shaken four times with 6 M HCl to remove most of the quinoline. The toluene solution was evaporated to dryness and the residue was refluxed with 250 ml of 5 N HCl for 2 h. The cooled reaction mixture was filtered and washed with 200 ml of water. The non-ionic components were removed by extraction first with acetonitrile and then with pentane. Yield 0.32 g (26.3%) of a dark green powder. MS (neg. FAB, tetraglyme matrix): $m/e = 858$ (16%, M^+), 823 (22%, $M^+ - Cl$), 788 (100%, $M^+ - 2Cl$). *Anal.* Calc. for $C_{48}H_{49}N_8CrCl_2$: C, 67.0; H, 5.8; N, 13.0; Cr, 6.0; Cl, 8.2. Found: C, 67.1; H, 6.1; N, 11.9; Cr, 6.1; Cl, 8.1%.

2.4. *(TTBuPcCr)$_2$O·H$_2$O*

10 ml of 2 N NaOH were added to a suspension of 10 mg (0.01 mmol) of $TTBuPcCrCl_2H$ in 20 ml of benzene. In approximately 2 min the complex dissolved to a green solution. 10 min later the color changed to blue. The reaction mixture was stirred for another 10 min at room temperature and subsequently for 20 min at 50 °C. After vacuum evaporation of the solvent the residue was washed several times with water to clean the product from the adherent salts. Yield 8.5 mg (90%) of a blue–violet powder. MS (neg. FAB, tetraglyme matrix): $m/e = 1593$ (1.8%, M^+), 1576 (1.1%, $M^+ - O$), 789 (100%, $[M+H]^+ - TTBuPcCrO$). *Anal.* Calc. for $C_{96}H_{98}N_{16}Cr_2O_2$: C, 71.6; H, 6.1; N, 13.9; Cr, 6.4; O, 2.0. Found: C, 71.2; H, 6.3; N, 13.2; Cr, 6.4; O, 2.3%.

2.5. *TTBuPcCrCl·2py*

A solution of 50 mg (0.06 mmol) of $TTBuPcCrCl_2H$ in 50 ml pyridine was refluxed for 2 h. After vacuum evaporation of the pyridine, the residue was ground five times with 10 ml of H_2O to dissolve adherent pyridinium hydrochloride. Then the product was dried in vacuo (10^{-5} bar) at room temperature. Yield 51 mg (89%), dark green powder. MS (neg. FAB, tetraglyme matrix): $m/e = 823$ (38%, $M - py$), 788 (100%, $M - py - Cl$). *Anal.* Calc. for $C_{58}H_{58}N_{10}CrCl$: C, 70.9; H, 5.95; N, 14.25; Cr, 5.29; Cl, 3.61. Found: C, 70.3; H, 6.03; N, 13.92; Cr, 5.20; Cl, 3.65%.

2.6. *TTBuPc^{-I}Cr^{III}Cl$_2$*

100 mg of TTBuPcCrCl·2py were dissolved in 30 ml of benzene and poured into a distillation flask. The solution was deaerated in an N_2 atmosphere by ultrasound agitation. Then 1 ml of thionyl chloride was distilled into the solution from an $SOCl_2$/quinoline mixture (1:1). After 10 min of stirring at 5 °C, the solvent was distilled off in vacuo. Traces of adherent $SOCl_2$ were removed by briefly washing with water. Yield 72 mg (82%) of a violet–black powder. *Anal.* Calc. for $C_{48}H_{48}N_8CrCl_2$: Cr, 6.0; Cl, 8.2. Found: Cr, 5.5; Cl, 8.5%. The compound was stable for some time. After a few hours the aromatic $TTBuPc^{2-}$ system was reformed, but some 4-t-butylphthalimide was also formed in the decomposition reaction. For this reason we did not perform elementary analysis.

2.7. *Equipment*

UV–Vis: Varian 2300; Zeiss PMQ II. IR: Nicolet 5PC. NMR: Bruker AC 200; DTA: Mettler TA 1. MS: Finnegan MAT 90 (tetraglyme matrix). Electrolytic conductivities: Wayne-Kerr B 331. Elementary analysis: Heraeus CHN-O-Rapid. Magnetic balance: home made apparatus of the 2nd Institute of Physics, University of Cologne. Molecular mass: Knauer.

3. Results

3.1. *Insertion of Cr(III) into metal-free tetra-t-butylphthalocyanine*

Taube and Lunkenheimer [4] obtained phthalocyaninato-chloro complexes by reaction of H_2Pc with anhydrous chromium(III) chloride in boiling quinoline. The analogous treatment of $TTBuPcH_2$ yielded products containing varying amounts of chloride. However, most of the by-products could be removed by successively extracting with acetonitrile and pentane, because most t-butyl substituted phthalocyanines are highly soluble in organic solvents. The final product had a Cl:Cr ratio of 2:1. The same product was obtained by a procedure analogous to that described by Grunewald and Homborg [5]. Crude tetra-t-butylphthalocyaninato-chromium compounds were dissolved in conc. H_2SO_4, precipitated with water and treated first with KOH and then with HCl [6].

3.2. Characterization

The absorption spectrum in toluene showed the characteristic features of the Pc^{2-} moiety with Q and Soret bands (Table 1). The weak bands around 500 nm are assigned to charge transfer bands [7] and are characteristic for axial substitution. In the negative FAB mass spectrum, the most intense peak was found at $m/e=788$ (TTBuPcCr), weaker peaks at 823 and 858. Their isotopic pattern agreed with the compositions TTBuPcCrCl and $TTBuPcCrCl_2$, respectively. The magnetic moment of 3.5 ± 0.2 BM is consistent with chromium in the oxidation state +3 (d^3 configuration). These observations and the Cl:Cr ratio of 2:1 obtained from the elementary analysis point to a hexacoordinated chromium(III) center. This being the case, the complex must be negatively charged, $[TTBuPcCrCl_2]^-$. The ionic structure explains the low solubility in non-polar solvents.

Conductivity measurements in THF/CH_3CN (45/95 vol./vol.) showed the complex to be a weak electrolyte. A 0.98×10^{-4} M solution had a molar conductivity $\Lambda_m=58.6\ \Omega^{-1}\ cm^2\ mol^{-1}$ (20 °C). For comparison, Bu_4NCl of the same concentration had $\Lambda_m=261\ \Omega^{-1}\ cm^2\ mol^{-1}$. Ionophoresis showed the colored layer to move towards the anode. The chemical analysis allows only H^+ as the counter ion. Hence, the complex is analogous to $PcCrCl_2H$, described by Elvidge and Lever [8,9]. Their spectrum obtained in methanol agrees reasonably with the spectrum of our complex obtained in tetrahydrofuran (Table 1) with the exception of an additional band at 565 nm that we found in the spectrum of the TTBu complex. It is 670 cm^{-1} to the blue of the Q band (686 nm). We assign it to a vibronic sideband [10]. The Shpolskii spectrum of H_2Pc in n-paraffins showed an intense vibronic band at $\Delta\bar{\nu}=677\ cm^{-1}$ (n-octane) [11].

3.3. Reaction with water and hydroxide ion

In boiling water the bound chloride was partially removed. Complete removal could be achieved with diluted NaOH. A product was formed with a TTBuPc:Cr:O ratio of 1:1:1. This composition would correspond to TTBuPcCrOH. However, the freezing point depression in benzene (0.01 M of Cr) pointed to a dimer. The signal of the dimer was also found in the FAB mass spectrum ($m/e=1593$ ($C_{96}H_{96}N_{16}Cr_2O$)). The absorption spectrum (Table 1) showed a hypsochromic shift of the Q band with respect to the dichloro complex. Such a shift is characteristic of dimeric phthalocyanines [7]. In the series of catena-poly-μ-oxo-phthalocyaninato-silicium compounds, a similar position of the Q band (630 nm) was observed in the dimer [12]. In the IR spectrum a new band appeared at 775 cm^{-1}, which could be assigned to the asymmetric Cr–O–Cr vibration $(TPPCr)_2O$ $\nu_{as}=860\ cm^{-1}$ (TPP = tetraphenylporphyrin) [13]. Since the chemical analysis showed a Cr:O ratio of 1:1 we formulate the composition tentatively as $(TTBuPcCr)_2O\cdot H_2O$ in analogy to the corresponding TPPCr complex [14]. The unsubstituted phthalocyanine complex was formulated as $(PcCr)_2O\cdot 2H_2O$ [15].

3.4. Reaction with pyridine

On dissolving $TTBuPcCrCl_2H$ in pyridine, the absorption bands gradually shifted to longer wavelengths. The process was accelerated briefly heating the solution to 90 °C (see Table 1). On a preparative scale, the pyridine adduct was obtained by boiling for 2 h. It had the composition TTBuPcCrCl · 2py. The FAB mass spec-

Table 1
UV–Vis data of tetra-t-butylphthalocyaninato-chromium complexes

Compound	Medium	λ (nm) (log ε)						
$TTBuPcCrCl_2H$								
	THF	686(5.41)	656(4.54)	618(4.58)		497(4.06)	483(4.03)	353(4.79)
	toluene	715sh 696	660sh	618	520 509		490	360
	py(1)[a]	684(5.28)	655(4.65)	616(4.66)		484(4.54)	370(4.74)	351(4.80)
	py(2)[b]	697(5.24)	670(4.66)	627(4.66)	509(4.55)	503(4.57)	371(4.80)	359(4.84)
$(TTBuPcCr)_2O\cdot H_2O$								
	toluene	629(4.47)				495(3.86)		340(4.65)
TTBuPcCrCl · 2py								
	toluene	693(5.21)	670(4.55)	623(4.55)	507(4.36)	500(4.41)	372(4.69)	359(4.75)
$TTBuPc^{-I}Cr^{+III}Cl_2$								
	benzene	787(4.24)	735sh	706(4.33)	543(4.44)	442(4.29)	382sh	352(4.49)

[a] Freshly prepared solution in pyridine.
[b] Heated briefly to 90 °C.

trum showed peaks only for TTBuPcCrCl ($m/e=823$) and TTBuPcCr ($m/e=788$), but no peak corresponding to a complex containing pyridine. The pyridine is obviously not very strongly coordinated. DTA experiments showed two broad endothermic peaks: one between 105 and 215 °C, the other started at 225 °C but was not yet complete at 300 °C. Weight loss was 16.3% at 215 °C and 19.1% at 300 °C. The first has to be assigned to the dissociation of two pyridine molecules (weight loss calc. 16.1%) and the other to the dissociation of Cl (weight loss calc. 19.68%). Samples heated to 215 and 300 °C contained 4.3% and 0.4% Cl, respectively (calc. for TTBuPcCrCl: 4.3% Cl). The IR bands characteristic for pyridine were found at 1580, 1444 and 634 cm^{-1}. They were not split, as it was found in the case of (Pc)Co(py)Cl·py [16]. The band at 634 cm^{-1} is characteristic for coordinated pyridine [17].

3.5. Oxidation

Oxidation of the pyridine adduct with thionyl chloride produced a blackish purple product, which dissolved in cyclohexane and benzene giving a purple color and in pyridine a green color. The solid decomposed in air within a few hours. The UV–Vis spectrum of the benzene solution was the same as that described for ring oxidized phthalocyanines. Its spectrum in benzene agreed within 30 nm with that of a solid sample of the unsubstituted analogue [18]. Reduction with hydrazine reformed the TTBuPc^{2-} chromophore (Fig. 1). The Cl and Cr content agreed with the composition TTBuPc^{-I}Cr^{+III}Cl$_2$.

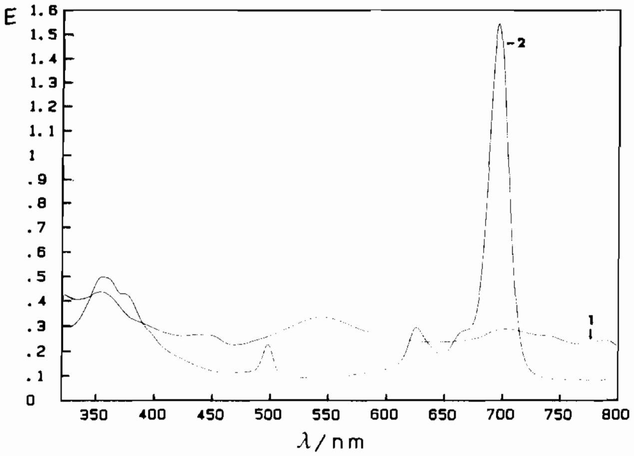

Fig. 1. Absorption spectrum of (1) TTBuPc^{-I}CrCl$_2$ in benzene (6.21 mg l^{-1}); spectrum (2) obtained after addition of hydrazine.

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