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Notes

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The Chemistry of Dichloro[phthalocyaninato(2−)]titanium(IV)

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In the course of our study of coordination polymers we investigated the titanium analog of the [phthalocyaninato(2−)]germanium and -silicon polymers reported by Joyner and Kenney.[1] At the time we undertook this study there were no details on titanium derivatives of phthalocyanine in the literature, but recently Taube has reported the synthesis of TiPcCl and its conversion to TiPcO[2] and Shklover, *et al.*, have reported the synthesis of $Ti(C_{32}H_{15}ClN_8)(OH)_2$.[3] We also have isolated TiPcO, but from another intermediate, $TiPcCl_2$, and wish to report at this time on the synthesis of $TiPcCl_2$ and some of its reactions.

Dichloro[phthalocyaninato(2−)]titanium(IV) was made by the reaction shown in eq. 1. This reaction is very convenient in that the titanium(III) furnishes the

$$2TiCl_3 + 4C_6H_4(CN)_2 \longrightarrow TiPcCl_2 + TiCl_4 \qquad (1)$$

electrons necessary to convert phthalonitrile to the phthalocyanine anion and in that the titanium(IV) not incorporated into $TiPcCl_2$ is readily removed by volatilization. Consequently the preparation of $TiPcCl_2$ proceeds smoothly in a homogeneous medium, and a clean product is obtained in good yield. This is a more convenient route to titanium(IV) derivatives of phthalocyanine than either of the previously published procedures, the reaction of $TiCl_3$ with Li_2Pc and subsequent oxidation[2] or the reaction of $TiCl_4$ with o-$C_6H_4(CN)_2$.[3]

Although $TiPcCl_2$ does not appear to react readily with water because it is not wet by water, an infrared study showed that it hydrolyzes in air. The band at 808 cm.$^{-1}$ in $TiPcCl_2$ gradually disappears, and the band at 972 cm.$^{-1}$ in $(TiPcO)_x$ grows, as samples of $TiPcCl_2$ sit in the atmosphere. Thus it is necessary to protect $TiPcCl_2$ from moisture. The chloride ions are relatively easy to replace in general, as shown by ready conversion to other derivatives of $TiPc^{2+}$.

All our attempts to convert $TiPcCl_2$ to $TiPc(OH)_2$ failed; in every case the product corresponded to $(TiPcO)_x$. This is in marked contrast to the germanium and silicon systems in which the dihydroxy compounds were first isolated and subsequently polymerized by thermal dehydration.[1] It is probable that the oxide is a high-molecular-weight polymer analogous to $(GePcO)_x$ and $(SiPcO)_x$ since there is no evidence for hydroxyl absorption in its infrared spectrum.

The intractability of $(TiPcO)_x$ could well be due to a rigid backbone, *i.e.*, the bulky $TiPc^{2+}$ units when held together by O^{2-} anions should interfere considerably with each other's movement, so we sought to introduce some flexibility into the system by using a chain of atoms between the titanium atoms instead of just a single oxygen atom. One approach was to make a phosphonate derivative by the reaction of $TiPcCl_2$ with phenylphosphonic acid. Although the products isolated did not prove to be high polymers, their analyses suggest an impure oligomer containing five or six units with a phosphonic acid end group, *i.e.*, $H[OP(C_6H_5)O_2TiPc]_{5-6}OP(C_6H_5)O_2$. These products, too, are insoluble in a wide range of solvents and do not melt, so that purification and definitive characterization as a polymer is not possible. Higher reaction temperatures and longer reaction times did not lead to a substantially greater degree of polymerization.

Several attempts to make polymers of the type $(TiPcOSiR_2O)_x$ with $R_2 = (C_6H_5)_2$, $(CH_3)_2$, or $(C_6H_5)(CH_3)$ by the reaction of $TiPcCl_2$ with $R_2Si(OH)_2$, $R_2Si(ONa)_2$, $R_2Si(C_2H_3O_2)_2$, or $R_2Si(OC_2H_5)_2$ under various conditions were unsuccessful. It is interesting that the prototype reaction between $TiPcCl_2$ and $NaOSi(C_6H_5)_3$ goes quite smoothly in refluxing benzene to yield $TiPc[OSi(C_6H_5)_3]_2$, one of the few phthalocyanines that melts rather than sublimes and that is soluble in an organic solvent.

None of the infrared absorption bands common to the titanium(IV) derivatives of phthalocyanine reported here appears diagnostic. They all occur in the spectra for various of the other metallic derivatives of phthalocyanine reported in the literature.[4]

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(1) R. D. Joyner and M. E. Kenney, *J. Am. Chem. Soc.*, **82**, 5790 (1960); *Inorg. Chem.*, **1**, 717 (1962).

(2) R. Taube, *Z. Chem.*, **3**, 194 (1963). Pc is used here, as has become customary, to represent the phthalocyanine anion, $C_{32}H_{16}N_8{}^{2-}$.

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Experimental

Reagents.—All chemicals used were the best quality commercially available. Titanium(III) chloride was obtained from Stauffer Chemical Co., the o-$C_6H_4(CN)_2$ was Eastman Kodak White Label grade recrystallized twice from benzene, $(C_6H_5)_3SiOH$ was obtained from General Electric Co., and $(C_6H_5)P(O)(OH)_2$ from Eastman Kodak Co.

$TiPcCl_2$.—About 5 g. of $TiCl_3$ was weighed by difference in a nitrogen-containing dry bag.[5] An amount of o-$C_6H_4(CN)_2$ equivalent to two times the number of moles of $TiCl_3$ taken and 150 ml. of 1-chloronaphthalene were added to the flask while the system was protected from the atmosphere with a blanket of nitrogen. The mixture was then heated with stirring under nitrogen. At 180° a red liquid (presumably an addition compound of $TiCl_4$ with 1-chloronaphthalene[6]) began to distil and continued to come over as the temperature rose to 252°, the boiling point of 1-chloronaphthalene. After the liquid distilling over was no longer red, the mixture was refluxed another 0.5 hr. and then allowed to cool to room temperature. All subsequent handling was also done under nitrogen. The mixture was filtered to yield a dark bluish purple solid which was washed with six 75-ml. portions of dry benzene and three 75-ml. portions of diethyl ether and then dried, first with a stream of nitrogen and then by pumping. Yields were 95–98%.

Anal. Calcd. for $C_{32}H_{16}Cl_2N_8Ti$: C, 60.9; H, 2.6; Cl, 11.2; N, 17.8; Ti, 7.6. Found: C, 60.6; H, 2.9; Cl, 11.1; N, 17.6; Ti, 7.9.

$(TiPcO)_x$.—A mixture of 2.0 g. of $TiPcCl_2$, 1 ml. of triethylamine, and 150 ml. of 95% ethanol was refluxed for 4–5 hr. and then allowed to cool to room temperature. When cool, the mixture was filtered, and the dark blue residue was washed well with 95% ethanol and then with diethyl ether. The dried product corresponded to a quantitative yield of TiPcO.

Anal. Calcd. for $C_{32}H_{16}N_8OTi$: C, 66.7; H, 2.8; N, 19.4; Ti, 8.3. Found (two runs): C, 66.4, 66.4; H, 3.8, 2.6; N, 19.6, 19.7; Ti, 8.3, 7.7.

$[TiPcOP(C_6H_5)O_2]_x$.—To 2 g. of $TiPcCl_2$ and 0.5 g. of $C_6H_5PO(OH)_2$ was added under nitrogen flush 100 ml. of benzene dried over Linde 4A Molecular Sieves. Then 25 ml. of pyridine was added, and the mixture was refluxed with stirring under nitrogen overnight, cooled, and filtered. After the residue was washed with benzene, methanol, and diethyl ether, it was dried in an oven at 100° to give 2.22 g. of blue-green solid.

Anal. Calcd. for $C_{38}H_{21}N_8O_3PTi$: C, 63.7; H, 3.0; N, 15.6; P, 4.3; Ti, 6.7. Found (two runs): C, 62.9, 63.0; H, 3.3, 4.2; N, 15.2, 14.8; P, 4.5, 4.3; Ti, 8.6, 6.7.

$TiPc[OSi(C_6H_5)_3]_2$.—A 1.9-g. sample of triphenylsilanol was placed in a flask with 100 ml. of benzene and excess sodium metal cut into small pieces. Nitrogen was passed through the flask while the mixture was refluxed with stirring for 1 hr. The mixture was then allowed to cool and filtered under nitrogen into another flask containing 2.0 g. of $TiPcCl_2$. The new mixture was refluxed with stirring overnight, cooled, and filtered. The residue was then extracted for 24 hr. with the filtrate in a Soxhlet extractor. After the extracting solvent had cooled, it was filtered to yield a solid which was washed sparingly with methanol and diethyl ether and dried. There resulted 1.53 g. (44% yield) of green solid which melted at 340°.

Anal. Calcd. for $C_{68}H_{46}N_8O_2Si_2Ti$: C, 73.5; H, 4.2; N, 10.1; Si, 5.1; Ti, 4.3. Found: C, 73.0; H, 4.7; N, 10.3; Si, 4.7; Ti, 4.4.

Spectra.—Infrared spectra were determined for Nujol mulls on a Perkin-Elmer Model 221 infrared spectrophotometer. Lines common to the spectra ($cm.^{-1}$) were 1607 ± 4 m, 1500 ± 8 m, 1408 ± 8 m, 1330 ± 2 s, 1284 ± 4 m, 1156 ± 1 m, 1117 ± 2 ms, 1070 ± 3 ms, 1056 ± 2 ms, 896 ± 4 m, 774 ± 2 m, 750 ± 3 m, and 724 ± 3 m. Additional bands were observed as follows. $TiPcCl_2$: 1038 m, 998 w, 969 vw, 891 m, 879 w, 839 w, 808 m, 783 m, 779 m, 721 m, 681 vw; $(TiPcO)_x$: 972 m, 967 m, 837 w, 803 w; $[TiPcOP(C_6H_5)O_2]_x$: 1138 m, 1007 s, 969 m, 823 w, 693 m, 665 m; $TiPc[OSi(C_6H_5)_3]_2$: 1590 m, 1429 m, 1305 ms, 1104 m, 1043 s, 998 w, 971 w, 944 w, 886 vs, 800 w, 766 w, 736 m, 711 m, 707 m, 697 s.

Thermogravimetric Analysis.—The standard thermogravimetric analysis procedure developed in our laboratories[7] (nitrogen atmosphere, 5°/min. heating rate) showed weight losses starting at 385° for $TiPcCl_2$, 475° for $(TiPcO)_x$, 400 to 460° for $[TiPcOP(C_6H_5)O_2]_x$, and 350° for $TiPc[OSi(C_6H_5)_3]_2$.

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[6] Similar to $TiCl_4 \cdot C_{14}H_{10}$, etc. See H. L. Krauss and H. Hüttmann, *Z. Naturforsch.*, **18b**, 976 (1963).

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Metal Ion–Solvent Reactions.
I. Kinetics of the Oxidation of Ruthenium(II) by Water

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Controlled-potential electrolysis has made possible the preparation of powerful oxidizing or reducing agents without the introduction of other reaction products.[1] Such electrolytically-generated species of unusual oxidation states, produced under circumstances which leave little doubt as to their identity, may react with other oxidation–reduction species present in solution to give information about the kinetics of homogeneous electron-transfer processes.[2] Since an understanding of possible oxidation–reduction reactions between ionic species and the solvent is necessary before this method can be applied to studies of more complicated systems, an examination of the oxidation of ruthenium(II) in aqueous media was undertaken.

The rate of oxidation of ruthenium(II) was monitored by following the change in the height of the absorption peak at 690 mμ attributed to the species $RuCl_4^{2-}$. The ruthenium(II) concentration was calculated using the molar absorptivity, estimated at 1100 by Jørgensen.[3] The oxidation was found to be a pseudo-first-order process in deaerated acid-chloride media. First-order rate constants calculated from experimental runs carried out by varying the initial concentrations of ruthenium(II) in 2.5 *M* KCl (pH 1.5) at 30.0° are summarized in Table I. Since first-order rate constants are independent of the absolute concentration of the reacting species, any uncertainties in the value of the

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