

Articles

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Synthesis, Reactivity, and X-ray Crystal Structure of Dichloro(phthalocyaninato)titanium(IV)

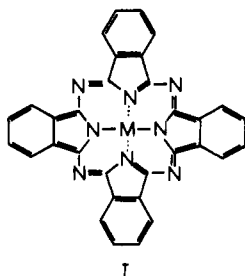
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Received April 9, 1984

A new synthesis of dichloro(phthalocyaninato)titanium(IV), $[C_{32}H_{16}N_8Cl_2Ti]$ ($PcTiCl_2$), has been performed from phthalodinitrile and titanium tetrachloride in α -chloronaphthalene. Substitution reactions of the chloride ions in $PcTiCl_2$ lead to the formation of complexes of formula $PcTiX$, where X = catecholate ($C_6H_4O_2^{2-}$), oxalate ($C_2O_4^{2-}$), and peroxide (O_2^{2-}) groups. These compounds have also been obtained by using $PcTiO$ as starting material. Interconversion of all these species has been examined and their structure discussed on the basis of their chemical and physical behavior. Single crystals of the title compound were obtained under controlled conditions, and its X-ray crystal structure has been solved. Crystals of $PcTiCl_2$ are triclinic ($P\bar{1}$) with $a = 8.744$ (9) Å, $b = 12.244$ (4) Å, $c = 12.835$ (4) Å, $\alpha = 79.73$ (3)°, $\beta = 95.32$ (6)°, $\gamma = 103.27$ (6)°, and $Z = 2$. The two chlorine atoms are bound to the titanium atom in a cis position (Cl-Ti-Cl angle 82.4°) with respect to the plane of the phthalocyanine molecule, with the metal considerably displaced out of the plane of the N_4 chromophore (Ct N_4 -Ti distance 0.84 Å) toward the two chlorine atoms (average Ti-Cl and Ti-N bond distances 2.087 and 2.317 Å, respectively). The Cl-Ti-Cl moiety appears to choose an intermediate position between the eclipsed and the staggered conformation relative to the Ti-N₄ bond system. The structural conformation of $PcTiCl_2$ is discussed in relation to the structure of similar species already known from the literature.

Introduction

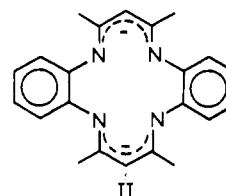
In contrast with the continuous effort produced to extend the fundamental and applied chemistry of the large number of reported metal phthalocyanines,² the chemistry of titanium phthalocyanine compounds appears not to have been proportionately developed, especially if account is taken of the consistent investigation carried out on many of the other known first transition series metal phthalocyanines (I).^{2a,b} Only a few titanium-containing



I
(M = bivalent metal ion)

phthalocyanine compounds are mentioned in the literature, namely $PcTiCl_3$,³ $PcTiCl_2$,⁴ prepared from $TiCl_3$ and phthalodinitrile, and $PcTiO$,³⁻⁵ structurally characterized recently⁶ (here and throughout the text Pc designates the phthalocyaninato dianion, $C_{32}H_{16}N_8^{2-}$). As such, the latter is one of the few authentic titanyl complexes that has been verified by single-crystal X-ray diffraction studies, the others being Ti(IV) porphyrins.^{7,8} A compound of formula $C_{32}H_{15}N_8ClTi(OH)_2$ has also been briefly mentioned.⁹ We

describe here the synthesis, reactivity, and X-ray crystal structure of $PcTiCl_2$. The X-ray work confirms the cis arrangement of the chlorine atoms suggested by the chemical behavior shown by $PcTiCl_2$ in its reactions with catechol and oxalic acid. Recently, a variety of Ti(IV) complexes of the $[C_{22}H_{22}N_4]^{2-}$ macrocycle (II) have been reported.¹⁰ Among those was the $(C_{22}H_{22}N_4)TiCl_2$



species, which also exhibits a cis arrangement of the chlorides. A detailed comparison of the above two molecular structures is presented and the discussion extended to include other similar macrocyclic species containing the MX_2 moiety (M = Ti, Sn; X = Cl, Br).¹¹⁻¹⁴

Experimental Section

Materials. Practical grade phthalodinitrile was recrystallized from toluene prior to use. α -Chloronaphthalene was distilled before using. All other chemicals were reagent grade and were used without further purification. Solvents were stored over 4-Å molecular sieves and degassed prior to using.

$PcTiCl_2$. A 1.0-g sample of phthalodinitrile was dissolved in 10.0 mL of hot α -chloronaphthalene, and 0.5 g of $TiCl_4$ was introduced via a syringe while maintaining a N_2 atmosphere. The reaction mixture was then heated at 220 °C for 10 h with stirring. After the solution was cooled and filtered, the solid obtained was washed with methanol until the filtrate was free from color; yield 60%. Anal. Calcd for $C_{32}H_{16}N_8TiCl_2$: C, 60.85; H, 2.55; N, 17.75. Found: C, 60.5; H, 2.4, N, 17.80.

- (1) Permanent address: Department of Chemistry, Florida State University, Tallahassee, FL 32306.
- (2) (a) L. J. Boucher, "Coordination Chemistry of Macrocyclic Compounds", G. E. Melson, Ed., Plenum Press, New York, 1979, p 461; (b) K. Kasuya and M. Tsutsui, *Coord. Chem. Rev.* **32**, 67 (1980); (c) P. Sayer, M. Gouterman, and C. R. Connell, *Acc. Chem. Res.*, **15**, 73 (1982).
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- (4) D. P. Block and E. G. Meloni, *Inorg. Chem.* **4**, 111 (1965).
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- (10) V. L. Goedken and J. A. Ladd, *J. Chem. Soc., Chem. Commun.*, 142 (1982).
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- (13) D. M. Collins, W. R. Scheidt, and J. L. Hoard, *J. Am. Chem. Soc.*, **94**, 6689 (1972).
- (14) D. Rogers and R. S. Osborn, *J. Chem. Soc., Chem. Commun.*, 840 (1971).

Table I. Crystallographic Data for $(C_{32}H_{16}N_8)TiCl_2$

formula: $(C_{32}H_{16}N_8)Cl_2Ti$
 mol wt: 631.342
 space group: $P\bar{1}$
 a , Å: 8.744 (9)
 b , Å: 12.244 (4)
 c , Å: 12.835 (4)
 α , deg: 79.73 (3)
 β , deg: 95.32 (6)
 γ , deg: 103.27 (6)
 V , Å³: 1314 (1)
 Z : 2
 d (calcd), g cm⁻³: 1.60
 d (obsd), g cm⁻³: 1.58 (2) by flotation
 cryst color and dimens, mm: dark purple prisms,
 0.03 × 0.15 × 0.25
 radiation: graphite-monochromated Mo K α , $\lambda = 0.71069$ Å
 diffractometer: Nicolet P2₁
 abs coeff, (μ), cm⁻¹: 5.9
 scan speed, deg min⁻¹: variable
 2θ scan range, deg: $3^\circ \leq 2\theta \leq 50^\circ$
 scan tech: θ - 2θ
 data collcd: $h, \pm k, \pm l$ (total 4770)
 scan width, deg: 2.0
 no. of unique data: 4770
 no. of unique data with $I > 2\sigma(I)$: 2158
 std reflns: 2/30
 LS parameters: 387
 data/parameters: 5.58
 R , % (F_o): 7.85
 R_w , % (F_o): 9.02

PcTiO. This compound was obtained by hydrolysis of $PcTiCl_2$ in water-saturated CH_2Cl_2 for a few hours. Its physical properties were identical with those previously reported for this complex.⁴

PcTi(C₆H₄O₂). This compound was prepared from $PcTiCl_2$ as follows: A 1.0-g sample of $PcTiCl_2$ was suspended (partially dissolved) in 10.0 mL of α -chloronaphthalene, and 0.250 g of catechol was added. Rapid evolution in HCl and a color change from blue-green to deep green were observed by heating the reaction mixture at 200 °C for 10 min. The suspension was then cooled and the catecholate complex separated by filtration from the solution, washed abundantly with methanol, and air-dried; yield 90%. An alternative procedure is to use $PcTiO$ as the starting material in place of $PcTiCl_2$; yield 90%. Anal. Calcd for $C_{38}H_{20}N_8O_2Ti$: C, 68.3; H, 3.0; N, 16.75. Found: C, 68.1; H, 3.1; N, 16.5.

PcTi(C₂O₄). A 1.0-g sample of either $PcTiCl_2$ or $PcTiO$ was added to a hot solution of 10.0 mL of α -chloronaphthalene containing 1.0 g of oxalic acid. The mixture was heated at 240 °C for 30 min, with constant stirring, and then cooled to room temperature. The solid oxalato complex that formed was separated by filtration from the solution, washed with methanol until the solution was colorless, and then dried in air; yield 95%. Anal. Calcd for $C_{34}H_{16}N_8O_4Ti$: C, 63.00; H, 2.5; N, 17.25. Found: C, 62.7; H, 2.3; N, 17.0.

PcTiO₂. A 1.0-g sample of either $PcTiCl_2$ or $PcTiO$ was finely dispersed in 10 mL of a CH_2Cl_2/CH_3CN mixture (1:1) containing 0.1 g of 30% aqueous H_2O_2 . The suspension was stirred vigorously for 1 h at room temperature and then filtered, and the solid obtained was washed with methanol and air-dried. In this preparation care has to be taken to vigorously stir the suspension in order to ensure the complete conversion of the starting material into the desired product. Heating of the reaction mixture must be avoided to prevent partial decomposition of the complexes. Anal. Calcd for $C_{32}H_{16}N_8O_2Ti$: C, 64.9; H, 2.7; N, 18.9. Found: C, 64.4; H, 2.45; N, 18.65.

Physical Measurements. IR spectra of the solid materials were recorded in the region 4000–200 cm⁻¹ with the Perkin-Elmer 621 spectrophotometer by suspending the samples as Nujol mulls between NaCl or CsI plates.

Growth of Single Crystals. Single crystals of $PcTiCl_2$ were grown directly from dilute solutions of the reaction mixture of $TiCl_4$ and phthalodinitrile (200 mg of phthalodinitrile and 50 mg of $TiCl_4$ in 10 mL of α -chloronaphthalene). When the reaction is allowed to proceed without stirring at approximately 190 °C, followed by careful controlled cooling of the reaction mixture, bluish purple, rectangularly shaped single crystals were obtained. The crystals were filtered from the solution, washed, and dried as with the bulk compound.

X-ray Data Collection. Crystallographic investigation of single crystals obtained from the reaction mixture with Weissenberg photography indicated that the crystals were triclinic. A suitable crystal was then

Table II. Positional Parameters ($\times 10^4$) for the Atoms of $(C_{32}H_{16}N_8)Cl_2Ti$

atom	x/a	y/b	z/c
Ti(1)	4974 (4)	3191 (2)	2612 (2)
Cl(1)	5245 (6)	1445 (3)	3581 (3)
Cl(2)	7531 (6)	3757 (3)	3265 (3)
N(1)	2900 (15)	3002 (8)	3378 (7)
N(2)	4981 (14)	4885 (7)	2696 (7)
N(3)	5759 (16)	3894 (8)	1124 (7)
N(4)	3505 (16)	2074 (7)	1682 (7)
N(5)	3378 (16)	4713 (8)	4167 (7)
N(6)	6831 (16)	5847 (8)	1321 (7)
N(7)	5110 (15)	2248 (8)	219 (7)
N(8)	1412 (16)	1237 (8)	2909 (8)
C(1)	1724 (21)	2056 (10)	3495 (9)
C(2)	717 (21)	2057 (11)	4317 (10)
C(3)	-626 (22)	1284 (11)	4746 (12)
C(4)	-1340 (22)	1566 (12)	5556 (11)
C(5)	-703 (24)	2600 (12)	5952 (11)
C(6)	612 (21)	3385 (12)	5531 (10)
C(7)	1310 (20)	3070 (10)	4726 (9)
C(8)	2639 (20)	3677 (10)	4097 (9)
C(9)	4390 (19)	5279 (10)	3489 (8)
C(10)	5095 (18)	6501 (9)	3451 (9)
C(11)	4826 (20)	7268 (10)	4078 (9)
C(12)	5639 (23)	8412 (11)	3785 (11)
C(13)	6582 (22)	8721 (10)	2935 (11)
C(14)	6845 (22)	7967 (11)	2294 (11)
C(15)	6026 (21)	6842 (11)	2609 (9)
C(16)	6020 (19)	5827 (9)	2147 (9)
C(17)	6717 (18)	4948 (9)	858 (8)
C(18)	7576 (17)	5042 (9)	-94 (9)
C(19)	8642 (21)	5906 (11)	-636 (9)
C(20)	9275 (20)	5672 (11)	-1509 (9)
C(21)	8805 (20)	4590 (11)	-1832 (9)
C(22)	7700 (20)	3760 (10)	-1311 (9)
C(23)	7079 (19)	3949 (10)	-414 (8)
C(24)	5955 (20)	3273 (9)	331 (9)
C(25)	3983 (20)	1722 (9)	819 (9)
C(26)	2966 (20)	636 (10)	672 (10)
C(27)	2941 (23)	-61 (11)	-89 (11)
C(28)	1725 (23)	-1060 (12)	-11 (11)
C(29)	663 (23)	-1343 (13)	782 (11)
C(30)	711 (22)	-631 (11)	1549 (12)
C(31)	1843 (20)	352 (10)	1433 (9)
C(32)	2224 (20)	1251 (9)	2103 (10)

transferred to a Nicolet P2₁ diffractometer, and the unit cell dimensions were determined from accurately centered high-angle reflections. The crystal data, data collection, and refinement details are summarized in Table I. Intensity data were measured, at room temperature, with a scan angle of $(2.0 + 0.35 \tan \theta)^\circ$ to account for α_1 and α_2 splitting, and a variable scan speed with a maximum scan time of 180 s was used to collect the data. These were corrected for Lorentz and polarization effects, but no absorption correction was applied, given the low value of μ and the crystal dimensions. Furthermore, a ψ scan on two reflections showed a maximum deviation of 5%.

Direct methods were used to locate the Ti, Cl, and some of the atoms of the Pc ring, assuming $P\bar{1}$ as the space group. Subsequent Fourier maps based on the phasing of these atoms were used to locate the remaining atoms of the structure. Least-squares refinement then proceeded, minimizing the function $R_w = [\sum_i (w_i |F_o - F_c|)^2] / \sum_i (w_i F_o^2)$, where $w = 1/\sigma$.

The agreement factor for isotropic refinement of all non-hydrogen atoms was $R = 9.7\%$. Refinement proceeded with anisotropic thermal parameters for all non-hydrogen atoms and led to $R = 7.85\%$ at convergence. Positions of the hydrogen atoms of the Pc ring were fixed at their calculated positions with fixed isotropic thermal parameters of 4 \AA^2 in the final cycles of refinement. The final difference map showed no peaks higher than 0.5 e \AA^{-3} , located near the Cl atoms. Neutral atomic scattering factors (f' and f'' values) were taken from ref 15. Computations were performed on a HP-1000 computer by using the set of crystallographic programs available in our research area.¹⁶ Final agreement factors are given in Table I, and the final fractional coordi-

(15) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

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Table IX. Selected Structural Parameters for PcTiCl_2

Bond Distances, Å			
Ti-Cl(1)	2.324 (4)	Ti-N(2)	2.095 (8)
Ti-Cl(2)	2.309 (6)	Ti-N(3)	2.060 (11)
Ti-N(1)	2.089 (13)	Ti-N(4)	2.105 (12)
Bond Angles, deg			
Cl(1)-Ti-Cl(2)	82.4 (2)	N ₁ -Ti-Cl ₂	127.8 (3)
N(1)-Ti-N(2)	78.7 (4)	N ₂ -Ti-Cl ₁	145.1 (3)
N(1)-Ti-N(3)	135.7 (4)	N ₂ -Ti-Cl ₂	80.7 (3)
N(1)-Ti-N ₄	82.7 (4)	N ₃ -Ti-Cl ₁	127.0 (3)
N(2)-Ti-N ₃	82.5 (4)	N ₃ -Ti-Cl ₂	87.4 (3)
N ₂ -Ti-N ₄	129.6 (4)	N ₄ -Ti-Cl ₁	79.4 (3)
N ₃ -Ti-N ₄	79.1 (4)	N ₄ -Ti-Cl ₂	143.7 (3)
N ₁ -Ti-Cl ₁	88.0 (3)		

nates, in Table II. The main structural parameters are given in Table IX.

Results and Discussion

Synthesis and Reactivity of PcTiCl_2 . The reaction of phthalodinitrile and TiCl_4 in α -chloronaphthalene leads to a highly crystalline pure PcTiCl_2 . In a previous report⁹ the reaction of TiCl_4 with molten phthalodinitrile apparently resulted in the formation of an ill-characterized product formulated differently. The synthesis of PcTiCl_2 was also previously performed by reacting TiCl_3 with phthalodinitrile, and it was claimed that Ti(III) was the source of the electrons necessary for the formation of the phthalocyaninato anion, TiCl_4 resulting as an unreactive byproduct.⁴ This is highly unlikely in view of the facile reactivity of TiCl_4 with phthalodinitrile in α -chloronaphthalene. The highly crystalline PcTiCl_2 is moderately stable to air. X-ray crystals showed no evidence of decomposition after 1 month of exposure to the atmosphere. However, the finely divided material is hydrolyzed by moist organic solvents, and solutions of the complex are extremely sensitive to trace amounts of water, producing the corresponding previously well-characterized PcTiO .³⁻⁵ The IR spectrum of PcTiCl_2 is very similar to that of the oxo species, with the exception of the absence of the band at 972 cm^{-1} assigned to the Ti=O stretch and the presence of two moderately strong absorptions in the far-IR region at 395 and 350 cm^{-1} . These absorptions suggested a cis arrangement of the chloride ions and have been assigned to the symmetric and antisymmetric Ti-Cl modes, respectively. The reactivity of PcTiCl_2 , and of PcTiO as well, with good oxygen donor chelates was in keeping with this suggestion, which was definitely confirmed by the single-crystal X-ray structure determination of PcTiCl_2 (vide infra).

The most noteworthy reactions of PcTiCl_2 and PcTiO are the displacement of the ancillary ligands by strongly chelating oxygen donor ligands. Either complex reacts with potentially bidentate ligands such as catechol or oxalic acid to produce complexes of formula PcTiX (X = catecholato and oxalato anions) with the release of HCl and H_2O , respectively. With the exception of the well-characterized peroxide derivatives of porphyrins, no other examples are reported in the porphyrin and phthalocyanine literature where the available coordination sites are cis. Cis coordination has particular significance because it is a prerequisite for many catalytic processes.

The observed 1:1 stoichiometry in PcTiX species and the absence of any O-H absorptions in the IR region, together with the proven cis geometry of the starting PcTiCl_2 , all strongly support the proposal of cis chelation. For both chelates, the complexes are identical, with either the oxo or dichloride used as starting material. The IR spectrum contained the characteristic absorptions of coordinated oxalate and catecholato and were devoid of the absorptions that had been assigned to the TiCl_2 and Ti=O moieties. Like most phthalocyanine complexes the species PcTiX show poor solubility in all solvents, except hot α -chloronaphthalene. Both chelate complexes appear to be stable in solution with little tendency to react with moisture to form PcTiO . As expected, both react with anhydrous HCl in nonpolar organic solvents to re-form the original cis complex, as confirmed by its IR spectrum. The actual conformation of these chelates, i.e., a staggered or eclipsed conformation of the oxygen atoms with respect to the four co-

ordinated nitrogen atoms, is unknown. Solubility limitations precluded high-resolution ^1H NMR studies. A low barrier to rotation would lead to nonequivalency of the phthalocyanine benzenoid H atoms.

High thermal stability under an inert atmosphere is a characteristic common to many four-coordinate metallophthalocyanine complexes. PcTiO is also sufficiently thermally stable that it too may be sublimed. Although the catecholato complex is thermally stable to $300\text{ }^\circ\text{C}$, appreciable decomposition occurred at the sublimation temperature of $330\text{ }^\circ\text{C}$, although the IR spectrum of the sublimate showed that much of the compound sublimed unchanged. PcTiCl_2 and PcTiO cosublime, thus preventing their separation or purification by this technique.

Reaction of either PcTiCl_2 or PcTiO with aqueous H_2O_2 in $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ mixtures leads to the formation of the peroxo complex, PcTiO_2 . This formulation is primarily based on the IR spectrum, which has a new absorption at 900 cm^{-1} and is missing the characteristic Ti=O stretching mode at 972 cm^{-1} . The new absorption appears very near a skeletal mode of the phthalocyanine ring at 910 cm^{-1} , which is present in all the complexes studied. The observed absorption intensity and position of the 900-cm^{-1} band are characteristic of the $\nu_{\text{O-O}}$ stretch that is observed in other well-characterized Ti(IV)- O_2^{2-} complexes in the very narrow range $900\text{--}895\text{ cm}^{-1}$.^{8,17} The peroxide complex is less stable both in solution and in the solid state than the other PcTi^{IV} complexes. Changes of the IR spectrum are discernible after a few days from the preparation of the compound and consist mainly of the gradual disappearance of the 900-cm^{-1} absorption and the appearance of the Ti=O band. Examination of the solid "aged" compound under a high-power microscope reveals inhomogeneity developing in the form of small, white crystallites of phthalimide appearing on the surface of the material. Heating a dispersion of the peroxide complex in α -chloronaphthalene solvent with triphenylphosphine regenerates PcTiO .

The possibility of preparing the μ -oxo species [PcTi-O-TiPc^{2+}] was suggested by strong Ti(IV)-O-Ti(IV) bonding in a number of complexes, as indicated by the relatively short Ti-O distances, $1.78\text{--}1.85\text{ \AA}$, observed in their crystal structures.^{17c,18} Finely dispersed PcTiO in a $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ mixture treated with HClO_4 does yield a new material. The IR spectrum of this new product indicates that the phthalocyanine ligand is intact, the 970-cm^{-1} Ti=O absorption is absent, and a new band appears at 820 cm^{-1} , in addition to the normal ClO_4^- bands expected for the μ -oxo salt, $[(\text{PcTi-O-TiPc})](\text{ClO}_4)_2$. The 820-cm^{-1} band is tentatively assigned to the asymmetric Ti-O-Ti stretch and is found in the same location for another μ -oxo Ti(IV) complex.¹⁰ The reaction is reversible in the sense that wet organic solvents made basic with amines regenerate the PcTiO complex. We were unsuccessful in purifying the compound adequately for analytically pure samples. The reaction appears complicated by the fact that the strongly acidic conditions required to protonate the titanil oxygen may also be sufficiently acidic to protonate the azamethine bridgehead linkages of the phthalocyanine ring as well.

Crystal Structure of PcTiCl_2 . The crystal structure of PcTiCl_2 consists of discrete molecules of six-coordinate Ti(IV) surrounded by the four N atoms of the phthalocyaninato ligand and the two chlorine atoms in a cis arrangement. The Ti(IV) is displaced 0.84 \AA above the N_4 plane toward the coordinated Cl atoms with average Ti-N and Ti-Cl bond distances of 2.087 and 2.317 \AA , respectively. A view of the molecule, approximately normal to the plane of the phthalocyanine ligand, together with the labeling scheme is shown in Figure 1. A side view is shown in Figure 2. Average important parameters are summarized in Table X, together with those of related Ti(IV) and Sn(IV) structures, which are reported for comparison purposes. In particular, the two

- (17) (a) R. Guillard, M. Fontesse, P. Fournari, C. LeComte, and J. Protas, *J. Chem. Soc., Chem. Commun.*, 161 (1976); (b) H. Mimoun, M. Postel, F. Casabianca, J. Fisher, and A. Mitschler, *Inorg. Chem.*, **21**, 1303 (1982); (c) Mühlebach, K. Müller, and G. Schwarzenbach, *Inorg. Chem.*, **9**, 2381 (1970).
 (18) M. M. Olmstead, P. P. Power, and M. Viggiano, *J. Am. Chem. Soc.*, **105**, 2927 (1983) and references cited therein.

Table X. Comparison of Bonding Parameters of $[\text{PcTiCl}_2]$ with Related Complexes

complex	distance, Å				ref
	av Ti-N	Ti from N_4 plane	Ti-Cl	N-Ct	
PcTiCl_2	2.087	0.84	2.317	1.910	this work
$(\text{C}_{22}\text{H}_{22}\text{N}_4)\text{TiCl}_2$	2.042	0.91	2.410	1.828	10
$(\text{OEPMe}_2)\text{TiO}^a$	2.110	0.58		2.029	7
PcTiO , α and β (av of polymorphs)	2.067	0.63		1.969	6
$(\text{OEP})\text{TiO}^b$	2.114	0.55		2.041	8
$(\text{OEP})\text{TiO}_2$	2.109	0.62		2.015	8
$(\text{TPP})\text{TiBr}_2^c$	2.062	0.00	2.454 (Br)	2.062	11
$(\text{salen})\text{TiCl}_2^d$	2.141	0.00	2.346		12
	(Ti-O = 1.835 Å)				
$(\text{TPP})\text{SnCl}_2$	2.098	0.00	2.420	2.098	13
PcSnCl_2	2.050	0.00	2.448	2.050	14

^a OEPMe_2 = α, γ -dimethyl- α, γ -dihydrooctaethylporphyrin. ^b OEP = octaethylporphyrin. ^c TPP = tetraphenylporphyrin. ^d salen = N, N' -ethylenebis(salicylideneamine).

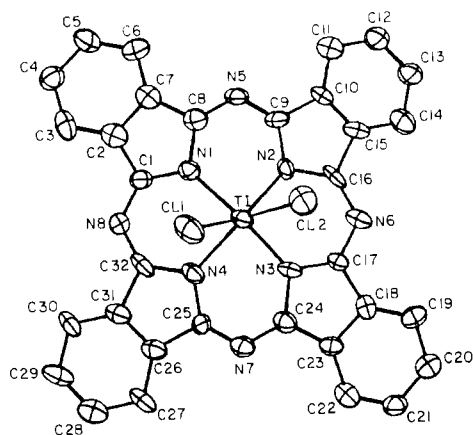


Figure 1. Molecular structure and labeling scheme for PcTiCl_2 as viewed normal to the Pc ring. Thermal ellipsoids are drawn at the 50% probability level.

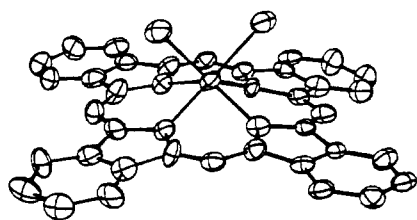


Figure 2. Side view of the PcTiCl_2 molecule illustrating the position of the Cl atoms relative to the Pc ring. Thermal ellipsoids are drawn at the 50% probability level.

tin(IV) dichloride complexes of TPP and Pc ligands are of interest also because of the d^{10} electronic configuration of the central metal atom and the implied absence of crystal field effects.

Two relevant features are present in the molecular structure of PcTiCl_2 : (1) the out-of-plane displacement of Ti(IV) from the N_4 core of the phthalocyanine ligand and the consequent cis arrangement of the chlorine atoms; (2) the intermediate orientation of the TiCl_2 moiety between the eclipsed and the staggered positions with respect to the four Ti-N bonds.

At first sight it appears that displacement of the metal atom from the N_4 plane and cis arrangement of the chlorine atoms in PcTiCl_2 are not in line with what is normally observed since, as shown in Table X, with the exception of $(\text{C}_{22}\text{H}_{22}\text{N}_4)\text{TiCl}_2$, all other similarly formulated halogen-containing complexes are trans (with the obvious in-plane location of the central metal). Even PcSnCl_2 has a trans arrangement of the chlorides, which is exactly the reverse of what would be expected in terms of their ionic radii ($\text{Sn(IV)} = 0.71 \text{ \AA}$, $\text{Ti(IV)} = 0.68 \text{ \AA}$). Flexibility of the N_4 donor system (rather limited for the phthalocyanine and porphyrin ligands because of the high conjugation and consequent rigidity of these chromophores) and the degree of covalency of the metal-nitrogen bonds are undoubtedly additional factors influ-

encing the position of the metal relative to the N_4 plane and the associated cis or trans arrangement of the remaining sites about the metal ion. The interrelated influence of these factors is shown particularly well in the structure of PcSn^{19} where Sn(II), potentially a strongly covalent bivalent metal ion, is so grossly oversized for the phthalocyanine site that it is displaced 1.11 \AA from the N_4 atom plane with Sn(II)-N distances of 2.25 \AA . The higher covalent character of the Sn(IV)-N bond compared to that of the Ti(IV)-N bond evidently facilitates the coplanar arrangement of the Sn(IV)- N_4 system in PcSnCl_2 . Thus, Sn(IV) in entering the N_4 plane achieves an overall minimum energy, optimizing bonding orbital overlap, at the expense of considerable strain in expanding the phthalocyanine core ring size from an unstrained N-Ct distance of 1.92^{20} - 2.050 \AA . Evidently in PcTiCl_2 , the more ionic Ti(IV) is considerably less sensitive to the orbital mismatching that accompanies the large displacement (0.84 \AA) from the N_4 plane and the observed cis arrangement becomes energetically more favorable.

Further insight can be gathered from the detailed structural information available on PcTiCl_2 and the similar complexes reported in Table X. The Ti(IV) structures most closely related to that of PcTiCl_2 are the α and β polymorphs of PcTiO , the titanil and peroxy complexes of OEP, and the dichloride complex containing the $\text{C}_{22}\text{H}_{22}\text{N}_4^{2-}$ macrocycle. Of these, the OEP complexes have the largest N-Ct distance (2.015 - 2.041 \AA) and also the longest Ti-N distance, 2.11 \AA . The two polymorphs of PcTiO have essentially the same average Ti-N distance (2.067 \AA), the latter being slightly shorter, though perhaps without chemical significance, than the average Ti-N distance in PcTiCl_2 (2.087 \AA). Noteworthy, the shortest Ti-N distance is observed for $(\text{C}_{22}\text{H}_{22}\text{N}_4)\text{TiCl}_2$. This may be attributable to mainly two factors: First, the N atoms of the $\text{C}_{22}\text{H}_{22}\text{N}_4^{2-}$ ligand are probably more basic than those of the phthalocyanine and porphyrin analogues. Second, the ligand in $(\text{C}_{22}\text{H}_{22}\text{N}_4)\text{TiCl}_2$ is more flexible than for example in PcTi complexes, where the constraints of the rigid macrocycle force the N donor pairs to be oriented only along the plane of the phthalocyanine chromophore.

It is evident from Figure 1 that the chlorides are not perfectly staggered with respect to the Ti- N_4 coordination bonds. When viewed normal to the phthalocyanine plane, the chlorides are rotated about 10° from perfect staggering. This does not appear to be the result of nonbonding contacts due to packing forces, but rather to an electronic effect. It has been shown that the eclipsed arrangement of O_2^{2-} in $\text{Ti}(\text{OEP})\text{O}_2$ is the result of bonding interactions between the Ti(IV) d_{xy} and π^* orbitals of O_2^{2-} .²¹ Orbitals of the same symmetry are available on the two chloride atoms, but calculations show that these interactions are much weaker due to the longer Ti-Cl distances and the more ionic nature

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of the chlorides.²² Thus, the observed intermediate conformation is a compromise between the optimum bonding situation occurring for an eclipsed conformation and minimum nonbonding steric repulsions between the chloride and nitrogen atoms for the staggered conformation.

Acknowledgment. V.L.G. was an invited visiting professor to the Chemistry Department of the University of Rome. We are

(22) C. Mealli and V. L. Goedken, to be submitted for publication.

most grateful to the Research Area of Rome (CNR, Montelibretti) for providing both kind hospitality and research facilities for conducting this work.

Supplementary Material Available: Tables of anisotropic thermal parameters (Table III), H atom coordinates and isotropic thermal parameters (Table IV), bond distances (Table V) and bond angles (Table VI), observed and calculated structure factors (Table VII), and distances of atoms from the phthalocyanine N₄ least-squares plane (Table VIII) (18 pages). Ordering information is given on any current masthead page.

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Synthesis, Structure, Spectroscopic Properties, and Electrochemical Behavior of Group 4[†] Metal Derivatives Containing Bulky Aryloxy Ligands¹

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Received April 12, 1984

Use of the sterically demanding ligand 2,6-di-*tert*-butylphenoxide (OAr') allows the isolation of a number of mononuclear, mixed halo-aryloxides of titanium, zirconium, and hafnium. The products can be grouped into three types. The dihalides Ti(OAr')₂X₂ (X = Cl, Br) are deep red solids extremely soluble in all hydrocarbon solvents. Molecular weight measurements indicate a monomeric structure in benzene. The monohalides M(OAr')₃Cl (M = Ti, Zr, Hf) and Ti(OAr')₃X (X = Br, I) are monomeric in solution, and ¹H NMR data show that restricted rotation about the M-O-Ar' bonds occur, leading to nonequivalent *tert*-butyl groups at low temperature. X-ray diffraction studies on HfCl(OAr')₃ and TiI(OAr')₃ show the compounds to be isostructural with an extremely congested metal coordination sphere. The paramagnetic, blue complex Ti(OAr')₃ can be obtained in good yield from TiCl₃(NMe₃)₂ and excess LiOAr' in benzene. Crystal data for HfCl(OAr')₃ at -165 °C: *a* = 17.521 (5) Å, *b* = 11.155 (2) Å, *c* = 10.686 (2) Å, α = 104.71 (1)°, β = 99.51 (1)°, γ = 83.82 (1)°, *Z* = 2, and *d*_{calcd} = 1.387 g cm⁻³ in space group P $\bar{1}$. Crystal data for TiI(OAr')₃ at -164 °C: *a* = 17.327 (8) Å, *b* = 11.088 (5) Å, *c* = 10.928 (4) Å, α = 106.09 (2)°, β = 100.29 (2)°, γ = 82.54 (2)°, *Z* = 2, and *d*_{calcd} = 1.328 g cm⁻³ in space group P $\bar{1}$. An investigation of the electrochemistry of these compounds shows that the dihalides Ti(OAr')₂X₂ (X = Cl, Br) undergo reversible one-electron reductions to the corresponding monoanions while for the more sterically crowded Ti(OAr')₃X (X = Cl, Br, I) reduction products are halide dependent.

Introduction

The use of sterically bulky ligands has made considerable impact on a number of important areas of inorganic and organometallic chemistry. The importance of the size of tertiary phosphines (as quantified by cone angles) on a number of stoichiometric and catalytic reactions has been well documented,² while the use of the large C₅Me₅ ligand has recently led to the development of novel chemistry in a number of areas.³⁻⁷ Early work by Bradley and others showed that use of bulky ligands such as the bis(trimethylsilyl)amide group can allow the isolation of complexes with unusually low coordination numbers,⁸ such complexes giving insight into the electronic structures of transition-metal complexes.⁹

We and others have recently been focusing our attention on the chemistry associated with sterically bulky oxygen donor ligands, and in particular we have been systematically investigating the use of 2,6-dialkylphenoxides as ancillary ligands.¹⁰⁻¹⁵ There has recently been a renaissance in the study of early-transition-metal alkoxide chemistry prompted by a number of developments. Alkoxide groups have played an important part in the development of the chemistry associated with metal-metal multiple bonds¹⁶ while both theoretical¹⁷ and synthetic¹⁸ studies have shown that such groups are essential for certain organometallic reactions such as olefin metathesis. The structural similarities between transition metal alkoxides and metal oxides has been pointed out,¹⁹ and it has been proposed that the study of their reactivity can give insight into chemistry occurring at catalytic metal oxide surfaces.²⁰ One important aspect of metal alkoxide chemistry stems from the

ability of the alkoxide ligand to act as either a terminal, doubly, or triply bridging group, allowing ready oligomerization to form condensed systems in which the metal attains a higher coordination number.²¹ Somewhat fine control of this in some cases unwanted process can be achieved by the choice of the steric properties of

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[†]The group notation is being changed in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is being eliminated because of wide confusion. Group I becomes groups 1 and 11, group II becomes groups 2 and 12, group III becomes groups 3 and 13, etc.

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