Two Phthalocyanine Units 'Stapled' by Carbon–Carbon σ Bonds in a New Sandwich-type Molecule: {5,5′;19,19′-Bi[phthalocyaninato(2−)]}titanium(IV). Synthesis, *X*-Ray Crystal Structure, and Properties†

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{5,5′;19,19′-Bi[phthalocyaninato(2−)]}titanium(IV)–1-chloronaphthalene(1/1), [TiL]·$C_{10}H_7Cl$, is obtained by the reaction of [Ti(pc)Cl_2] (pc = phthalocyaninato dianion, $[C_{32}H_{16}N_8]^{2-}$) with Na_2(pc) in 1-chloronaphthalene at 190 °C. An *X*-ray single-crystal structure (monoclinic, space group *C*2/*c*, *a* = 16.327(3), *b* = 18.568(4), *c* = 19.022(4) Å, β = 94.50(1)°, *Z* = 4) indicates for this complex a sandwich-type structure with the titanium atom in the centre of the molecule and the two phthalocyaninato units 'stapled' by two inter-ring C–C σ bonds [C(11)–C(11′) 1.556(6) and C(31)–C(31′) 1.575(6) Å]. Due to the staggered orientations of the two macrocyclic rings (relative rotation 45°) the planes of the two inner N_4 systems (each of which is slightly distorted from planarity) form a square-antiprism, with an average interplane distance of 2.32 Å (much shorter than that found in similar 'unstapled' complexes), and Ti–N bond distances in the range 2.17—2.26 Å. The complex shows high thermal stability and can be oxidized by nitric acid to give the species [TiL]NO_3. The complexes [TiL] and [TiL]NO_3 show differing solid-state electrical conductivity properties.

Metal phthalocyanines have been intensively investigated as molecular electrical conductors or semiconductors.[1] Among the various species examined, sandwich-like bis(phthalocyaninato)metal complexes of formula M$(pc)_2$ (pc = phthalocyaninato dianion, $[C_{32}H_{16}N_8]^{2-}$; M = Sn^{IV},[2,3] a lanthanide, or an actinide[4,5]) include the well authenticated 'intrinsic semiconductor' Lu$(pc)_2$,[6] and generally achieve semiconducting properties when doped with electron acceptors or donors.[6a] The M$(pc)_2$ complexes (M = a lanthanide) are also interesting because they show electrochromic properties and have a potential for a variety of practical applications such as visual displays, full-colour imaging, *etc.*[7]

There have been no examples so far reported of bis(phthalocyaninato) metal complexes in which the 'sandwiched' atom is a first-row transition-series metal. We have recently described the synthesis and properties of [Ti(pc)Cl_2][8] and found this complex to exhibit a *cis* configuration with the titanium significantly displaced out of the plane of the N_4 chromophore (0.84 Å) towards the two chlorine atoms. It seemed suitable as a starting material for the formation of a sandwich-type molecule with a very short distance between the two phthalocyanine units, due also to the compact electron core of Ti^{IV} and its strong Lewis acidity.

The present paper reports the synthesis, *X*-ray crystal structure, and properties, of [TiL]·$C_{10}H_7Cl$ (L = {5,5′;19,19′-bi[phthalocyaninate(2−)]}) and briefly describes the oxidized species $[TiL]^+$ obtained as nitrate [TiL]NO_3, which shows a solid-state electrical conductivity much higher than its precursor.

Experimental

[Ti(pc)Cl_2],[8] Na_2(pc),[9] and $[Sn(pc)_2]$[2] were prepared by literature methods.

Preparation of {5,5′;19,19′-*Bi*[*phthalocyaninato*(2−)]}*titanium*(IV)–1-*chloronaphthalene*(1/1), [TiL]·$C_{10}H_7Cl$.—The salt Na_2(pc) (3.1 g, 5.56 mmol) and [Ti(pc)Cl_2] (3.72 g, 5.29 mmol) were heated under vacuum at 150 °C for 3 h. 1-Chloronaphthalene (70 cm^3) was then added, and the reaction mixture heated at 190 °C for 90 min. The hot mixture was filtered to separate NaCl and a mixture of H_2pc and [TiO(pc)] formed as by-products. On cooling, yellow-orange crystals of [TiL]·$C_{10}H_7Cl$ precipitated from the solution (917 mg, 16%). (Found: C, 72.00; H, 3.45; Cl, 3.10; N, 17.75; Ti, 3.95. Calc. for $C_{74}H_{39}ClN_{16}Ti$: C, 71.95; H, 3.20; Cl, 2.85; N, 18.15; Ti, 3.90%). Addition of hexane to the mother-liquor gave further complex but which was usually deficient in 1-chloronaphthalene.

The complex [TiL]·$C_{10}H_7Cl$ can be sublimed under vacuum (10^{-2} mmHg, ≈1.3 Pa) at 450—460 °C to give [TiL]. Crystals formed by sublimation under the above specified conditions were too small for single-crystal *X*-ray studies.

Single crystals suitable for *X*-ray investigation however were obtained from 1-chloronaphthalene by dissolving the complex in the hot solvent in an ampoule closed under vacuum. Slow cooling to room temperature and reiteration of temperature variation frequently results in the formation of crystals of [TiL]·$C_{10}H_7Cl$ up to 1 cm long.

X-*Ray Crystallography for* [TiL]·$C_{10}H_7Cl$.—Intensity data were collected at room temperature on a single-crystal four-circle diffractometer. Data reduction, structure solution, and refinement were carried out on a GOULD 32/77 computer using SHELX 76.[10] Crystal data and details of the parameters associated with data collection and structure refinement are

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† {5,5′;19,19′-Bi[phthalocyaninato(2−)]}titanium(IV)–1-chloronaphthalene(1/1).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Table 1. Experimental data for the *X*-ray diffraction analysis

Formula	$C_{64}H_{32}N_{16}Ti{\cdot}C_{10}H_7Cl$
Crystal system	Monoclinic
Space group	*C*2/*c*
Cell parameters[a]	
a/Å	16.327(3)
b/Å	18.568(4)
c/Å	19.022(4)
β/°	94.50(1)
U/Å^3	5 748.9(2.0)
Z	4
D_c/g cm^{-3}	1.428
M	1 235.6
Crystal size (mm)	0.20 × 0.32 × 0.48
μ/cm^{-1}	21.87
Diffractometer	Siemens AED
Diffraction geometry	Equatorial
Scan type	θ—2θ
Scan speed/° s^{-1}	0.05
Scan width/°	$(\theta - 0.65) - [\theta + (0.65 + \Delta\theta)]$; $\Delta\theta = [(\lambda\alpha_2 - \lambda\alpha_1)/\lambda]\tan\theta$
Radiation	Ni-filtered Cu-K_α (λ = 1.541 78 Å)
2θ Range/°	6—140
Reflections measured	$\pm h\ k\ l$
Unique total data	5 658
Unique observed data	3 270 [$I > 2\sigma(I)$]
Number of variables	442
Overdetermination ratio	7.4
Max. Δ/σ on last cycle	0.1 for complex, 1.0 for solvent
$R = \Sigma\lvert\Delta F\rvert/\Sigma\lvert F_o\rvert$	0.065
$R' = \Sigma w^{\frac{1}{2}}\lvert\Delta F\rvert/\Sigma w^{\frac{1}{2}}\lvert F_o\rvert$	0.069
Goodness of fit = $[\Sigma w\lvert\Delta F\rvert^2/(N_o - N_v)]^{\frac{1}{2}}$[b]	1.880

[a] Unit-cell parameters were obtained by least-squares analysis of the setting angles of 25 carefully centred reflections chosen from diverse regions of reciprocal space. [b] N_o = Number of observations, N_v = number of variables.

given in Table 1. The reduced cell quoted was obtained with use of TRACER.[11] For intensities and background, individual reflection profiles were analysed.[12] The structure amplitudes were obtained after the usual Lorentz and polarization corrections. Data were corrected for absorption using ABSORB.[13] The function minimized during the full-matrix least-squares refinement was $\Sigma w|F|^2$. A weighting scheme based on counting statistics[10] was applied. Anomalous scattering corrections were included in all structure-factor calculations.[14b] Scattering factors for neutral atoms were taken from ref. 14 for non-hydrogen atoms and from ref. 15 for hydrogen atoms. Among the low-angle reflections no correction for secondary extinction was deemed necessary.

The structure was solved by the heavy-atom method starting from a three-dimensional Patterson map. Refinement was first isotropic, then anisotropic for the non-H atoms, except for the atoms of the 1-chloronaphthalene solvent molecule which was found to be affected by a severe disorder. Several peaks were found spread around a centre of symmetry. Any attempt to give them a chemical meaning was unsuccessful. In addition, it was not possible to distinguish which peak was chlorine. The best fit was found considering 19 'partial' carbon atoms with site occupation factors of 0.75 for C(16S), 0.5 for C(1S) and C(4S), and 0.25 for all the others, and refining them isotropically. The site occupation factors were derived from the height of the peaks on difference maps and correspond to a complex : solvent molar ratio of 1 : 1. In spite of disorder the accuracy of the structural analysis is rather good as indicated by the low *R* and estimated standard deviations (e.s.d.s). All the hydrogen atoms of the complex molecule were located in a difference map and introduced in the refinement as fixed contributors (U_{iso} = 0.08 Å^2). The final difference map showed no unusual features, with no significant peak above the general background.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Oxidation of $[TiL]{\cdot}C_{10}H_7Cl$.—*With* 10% HNO_3. The complex $[TiL]{\cdot}C_{10}H_7Cl$ (480 mg) was suspended in aqueous 10% HNO_3 (10 cm^3) and the mixture stirred at room temperature for 2 h. The microcrystalline greenish black solid obtained was separated from the solution by filtration, washed abundantly with water and ethanol, and dried under vacuum (420 mg) (Found: C, 66.9; H, 2.75; N, 20.85. $C_{64}H_{32}N_{17}O_3Ti$ requires C, 67.75; H, 2.85; N, 21.15%).

With 65% HNO_3. The complex $[TiL]{\cdot}C_{10}H_7Cl$ (80 mg) was suspended in 65% HNO_3 (10 cm^3) and the mixture stirred at room temperature for 15 min. After filtration, the greenish black solid residue was washed abundantly with water, then with ethanol, and dried under vacuum. The i.r. spectrum of this material is practically identical to that exhibited by the complex obtained by oxidation of $[TiL]{\cdot}C_{10}H_7Cl$ with 10% HNO_3.

Reduction of $[TiL]NO_3$.—The complex $[TiL]NO_3$ (100 mg) was suspended with $NaBH_4$ (100 mg) in CH_3OH (7 cm^3) and stirred at room temperature for 30 min. After filtration, the solid obtained was washed with ethanol and dried under vacuum. It was identified by its i.r. spectrum as [TiL] (Found: C, 70.70; H, 2.90; N, 20.15. $C_{64}H_{32}N_{16}Ti$ requires C, 71.65; H, 3.00; N, 20.90%).

Treatment of $[TiL]{\cdot}C_{10}H_7Cl$ *with* 37% *aqueous* HCl.—The complex $[TiL]{\cdot}C_{10}H_7Cl$ (100 mg) was suspended in 37% aqueous HCl (5 cm^3) and the mixture refluxed for 2 h under stirring. After cooling, the solid residue was separated from the mother-liquor by filtration, washed with water, then with ethanol, and dried under vacuum. Elemental analyses and the i.r. spectrum of the solid obtained identified the material as [TiL].

Treatment of $[TiL]{\cdot}C_{10}H_7Cl$ *with* 96% H_2SO_4.—The complex $[TiL]{\cdot}C_{10}H_7Cl$ (100 mg) was dissolved in 96% H_2SO_4 (10 cm^3) giving a brownish yellow solution which was then poured into iced water dropwise. The suspension formed was filtered and the recovered solid was washed abundantly with water and ethanol and dried under vacuum. It was identified as [TiL] by its i.r. spectrum.

Physical Measurements.—I.r. spectra were recorded with a Perkin-Elmer 983 instrument by using Nujol mulls or KBr pellets and CsI windows. Room-temperature susceptibility measurements were carried out on a permanent magnet (7 000 G, 0.7 T) by using the Gouy method and a $NiCl_2$ solution as calibrant. E.s.r. spectra were obtained on a Varian V 4502-4 spectrometer (*X*-band).

Results and Discussion

X-Ray Crystal Structure of $[TiL]{\cdot}C_{10}H_7Cl$.—*X*-Ray data for $[TiL]{\cdot}C_{10}H_7Cl$ are given in Tables 1—3. Table 4 summarizes some of the structural features of [TiL] in comparison with similar $[M(pc)_2]$ complexes.

The side view of the sandwich-type structure of [TiL] given in Figure 1 shows that the two saucer-shaped phthalocyaninato units surround the Ti^{IV}, which is located in the centre of the molecule. Due to the staggered orientation of the two ligands (relative rotation 45°), the inner N_4 systems are arranged around the metal ion in the form of a square antiprism.

Table 2. Fractional atomic co-ordinates for $[TiL]\cdot C_{10}H_7Cl$

Atom	*X/a*	*Y/b*	*Z/c*
Ti	0.500 00	0.275 35(7)	0.250 00
N(1)	0.464 91(21)	0.236 42(21)	0.139 86(17)
N(2)	0.455 60(23)	0.105 75(21)	0.158 22(18)
N(3)	0.423 50(21)	0.180 41(19)	0.261 45(17)
N(4)	0.329 84(25)	0.206 53(22)	0.349 58(20)
N(5)	0.388 28(21)	0.314 27(20)	0.301 96(17)
N(6)	0.396 65(23)	0.444 09(21)	0.283 83(18)
N(7)	0.456 03(22)	0.369 98(20)	0.191 28(17)
N(8)	0.462 66(24)	0.343 71(23)	0.067 99(18)
C(1)	0.465 26(27)	0.274 49(29)	0.078 30(21)
C(2)	0.466 47(27)	0.224 55(29)	0.017 71(22)
C(3)	0.469 03(32)	0.238 93(31)	−0.054 58(23)
C(4)	0.468 06(34)	0.178 04(36)	−0.097 76(24)
C(5)	0.464 79(35)	0.108 72(33)	−0.072 00(26)
C(6)	0.460 67(32)	0.095 39(29)	0.000 21(24)
C(7)	0.462 94(28)	0.156 10(28)	0.043 21(23)
C(8)	0.460 51(27)	0.162 38(27)	0.120 91(22)
C(11)	0.454 92(28)	0.112 19(25)	0.233 41(22)
C(12)	0.401 58(28)	0.053 47(27)	0.259 93(23)
C(13)	0.394 45(32)	−0.018 57(28)	0.243 45(25)
C(14)	0.335 62(36)	−0.058 85(30)	0.276 07(29)
C(15)	0.286 94(35)	−0.026 03(35)	0.324 80(33)
C(16)	0.292 96(32)	0.046 08(31)	0.340 53(29)
C(17)	0.351 32(29)	0.085 78(29)	0.306 58(24)
C(18)	0.368 79(27)	0.162 69(26)	0.306 88(23)
C(21)	0.338 48(26)	0.276 20(29)	0.343 51(20)
C(22)	0.287 40(28)	0.324 77(29)	0.382 40(22)
C(23)	0.227 88(31)	0.309 37(31)	0.429 65(24)
C(24)	0.190 88(35)	0.368 62(38)	0.457 25(28)
C(25)	0.210 11(36)	0.438 48(35)	0.439 01(30)
C(26)	0.268 73(32)	0.453 77(29)	0.391 12(26)
C(27)	0.307 41(29)	0.393 52(29)	0.364 78(23)
C(28)	0.369 72(27)	0.387 79(26)	0.312 28(21)
C(31)	0.455 40(26)	0.438 77(25)	0.230 98(22)
C(32)	0.439 17(28)	0.497 15(29)	0.177 15(24)
C(33)	0.422 95(32)	0.569 76(28)	0.184 38(26)
C(34)	0.406 77(34)	0.609 14(29)	0.122 68(32)
C(35)	0.406 64(34)	0.576 78(33)	0.055 79(28)
C(36)	0.421 43(31)	0.503 77(32)	0.049 83(24)
C(37)	0.437 91(28)	0.463 64(27)	0.111 24(24)
C(38)	0.452 53(28)	0.387 57(27)	0.123 38(23)
C(1S)	0.228 71(145)	0.169 86(143)	0.049 21(160)
C(2S)	0.254 90(162)	0.295 09(184)	0.083 54(211)
C(3S)	0.275 24(380)	0.367 95(362)	−0.068 37(369)
C(4S)	0.252 19(83)	0.278 29(99)	0.045 00(122)
C(5S)	0.231 61(224)	0.158 84(233)	0.140 14(243)
C(6S)	0.239 48(180)	0.210 85(218)	0.104 70(201)
C(7S)	0.266 17(145)	0.331 54(157)	0.055 76(161)
C(8S)	0.254 23(92)	0.283 80(103)	0.122 60(123)
C(9S)	0.260 69(150)	0.399 14(139)	−0.009 40(133)
C(10S)	0.205 88(285)	0.146 82(230)	0.145 01(295)
C(11S)	0.277 48(318)	0.348 79(335)	−0.085 78(307)
C(12S)	0.246 58(159)	0.254 46(182)	0.154 28(174)
C(13S)	0.257 82(144)	0.258 35(175)	−0.079 93(156)
C(14S)	0.259 23(161)	0.291 57(171)	−0.002 60(226)
C(15S)	0.212 27(188)	0.160 78(173)	0.175 37(143)
C(16S)	0.227 68(70)	0.224 98(79)	0.174 04(68)
C(17S)	0.261 96(130)	0.303 69(160)	−0.027 04(147)
C(18S)	0.265 34(155)	0.334 62(166)	0.016 28(177)
C(19S)	0.262 20(153)	0.245 87(161)	−0.178 56(134)

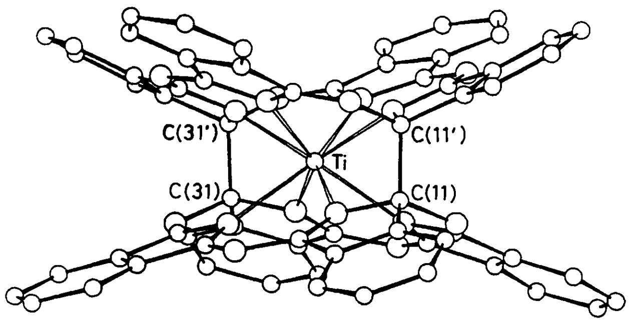


Figure 1. Side view of [TiL]

The most interesting and peculiar feature of the structure is the presence of two C–C σ bonds [C(11)–C(11′), C(31)–C(31′)] which 'staple' together the two phthalocyaninato units at opposite sites of titanium. This fact is unique to the present structure, since, to our knowledge, there are no examples in the literature of such an inter-ligand connection within the molecule for similar 'sandwiched' systems of formula $[M(pc)_2]$ [3,7a,16–18] (Table 4) or similar porphyrin complexes $[M(L)_2]$ (where L is a porphyrinate dianion).[19] A single inter-ligand C–C bond between two non-cyclic quadridentate chelating systems has been reported by C. Floriani and co-workers[20] for the bimetallic complex $[\{Ni(salphen)\}_2]$ [salphen = *NN′*-*o*-phenylenebis(salicylideneiminate)]. By contrast to the present titanium complex, bond formation and breaking for the salphen dimer implies a two-electron redox process. It is surprising that the tin complex $[Sn(pc)_2]$ is 'normal',[3] *i.e.* it does not show the inter-ligand C–C bonds found for the titanium complex, a fact which is not explained simply on the basis of the ionic radii of Sn^{IV} and Ti^{IV} since they are practically identical (0.71 and 0.68 Å respectively).[21] Certainly, the 'stapled' form of the two phthalocyaninato moieties in [TiL] must be the result of the combined influence of the small ionic radius of Ti^{IV} and its strong Lewis acidity.

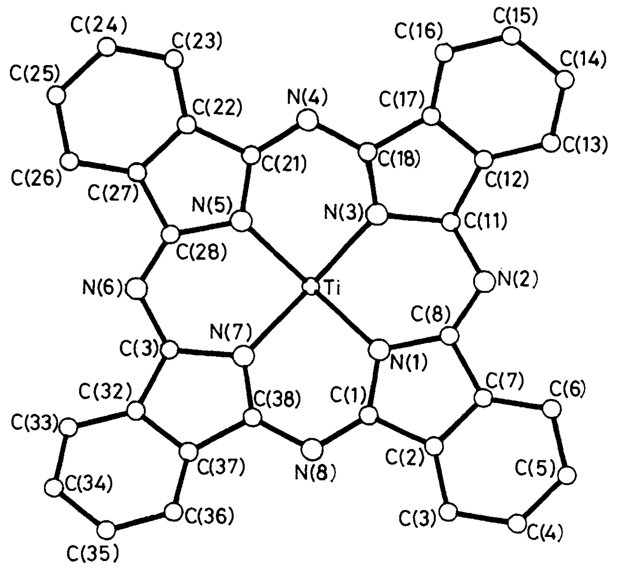


Figure 2. A phthalocyanine unit showing atom labelling

The inter-ligand bond distances are just a little longer [C(11)–C(11′) 1.556(6), C(31)–C(31′) 1.575(6) Å] than expected for normal C–C σ bonds [1.530(15) Å].[22] Each one of the C(11), C(11′), C(31), and C(31′) atoms forms four σ bonds, thus partially breaking the π-electron delocalization otherwise fully extended on each of the two macrocyclic rings. Figure 2 shows one of the two equivalent phthalocyanine units with the designations of the atoms as a guide to the numbering scheme. The two possible

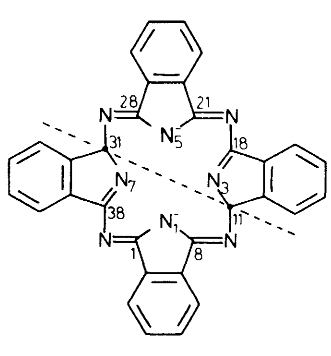
Table 3. Selected bond distances (Å) and angles (°) for [TiL]·$C_{10}H_7Cl$

Ti–N(1)	2.247 6(33)	C(6)–C(7)	1.391 5(71)
Ti–N(3)	2.181 2(37)	C(7)–C(8)	1.486 2(61)
Ti–N(5)	2.260 4(36)	C(11)–C(12)	1.506 9(67)
Ti–N(7)	2.173 6(37)	C(12)–C(13)	1.376 7(72)
N(1)–C(1)	1.368 2(56)	C(12)–C(17)	1.391 0(68)
N(1)–C(8)	1.421 6(63)	C(13)–C(14)	1.400 2(79)
N(2)–C(8)	1.274 6(61)	C(14)–C(15)	1.406 4(86)
N(2)–C(11)	1.436 2(54)	C(15)–C(16)	1.373 8(87)
N(3)–C(11)	1.481 6(58)	C(16)–C(17)	1.401 8(75)
N(3)–C(18)	1.331 9(57)	C(17)–C(18)	1.456 2(72)
N(4)–C(18)	1.344 6(62)	C(21)–C(22)	1.467 3(68)
N(4)–C(21)	1.307 4(67)	C(22)–C(23)	1.403 9(68)
N(5)–C(21)	1.373 4(58)	C(22)–C(27)	1.366 0(75)
N(5)–C(28)	1.415 4(61)	C(23)–C(24)	1.378 6(86)
N(6)–C(28)	1.271 4(60)	C(24)–C(25)	1.385 2(94)
N(6)–C(31)	1.446 3(58)	C(25)–C(26)	1.401 2(80)
N(7)–C(31)	1.484 3(58)	C(26)–C(27)	1.396 8(74)
N(7)–C(38)	1.329 1(55)	C(27)–C(28)	1.484 3(65)
N(8)–C(1)	1.300 3(68)	C(31)–C(32)	1.500 4(66)
N(8)–C(38)	1.352 1(60)	C(32)–C(33)	1.382 9(75)
C(1)–C(2)	1.480 6(66)	C(32)–C(37)	1.398 4(67)
C(2)–C(3)	1.404 6(62)	C(33)–C(34)	1.390 4(77)
C(2)–C(7)	1.363 2(73)	C(34)–C(35)	1.407 0(81)
C(3)–C(4)	1.396 8(81)	C(35)–C(36)	1.383 2(85)
C(4)–C(5)	1.379 8(88)	C(36)–C(37)	1.393 9(68)
C(5)–C(6)	1.402 5(68)	C(37)–C(38)	1.448 0(71)
C(11)–C(11′)	1.555 5(62)	C(31)–C(31′)	1.574 6(58)
N(5)–Ti–N(7)	73.80(13)	C(13)–C(12)–C(17)	121.38(46)
N(3)–Ti–N(7)	122.41(13)	C(12)–C(13)–C(14)	117.83(47)
N(3)–Ti–N(5)	74.14(13)	C(13)–C(14)–C(15)	120.23(52)
N(1)–Ti–N(7)	74.41(13)	C(14)–C(15)–C(16)	122.10(54)
N(1)–Ti–N(5)	110.79(13)	C(15)–C(16)–C(17)	116.86(51)
N(1)–Ti–N(3)	74.16(13)	C(12)–C(17)–C(16)	121.56(48)

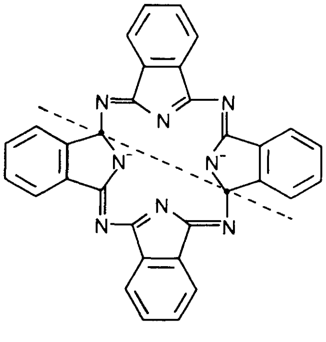
Table 4. Crystal data on bis(phthalocyanine) complexes

Complex	Average Ti–N (Å)	Distance between N_4 planes (Å)	Relative rotation (°)	Ref.
[TiL]	2.22	2.32	45	*
[Sn(pc)$_2$]	2.35	2.70	42	3
[U(pc)$_2$]	2.43	2.81	37	16
[Nd(pc)$_2$]	2.44	2.96	45	7*a*, 17
[Lu(pc)$_2$]	2.40	2.69	49	18

* This work.



(A)



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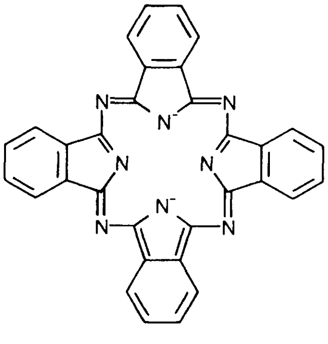
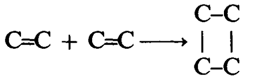


(C)

Figure 3. Different possible representations for the 'stapled' phthalocyanine framework [(A), (B)] and a 'normal' phthalocyanine molecular system [(C)]

alternative forms for each individual phthalocyaninato unit in [TiL] are given in Figure 3, where representations (A) and (B) take into account the different distribution of the 'double' and 'single' bonds within the macrocyclic framework. Accurate consideration of the bond distances listed in Table 3 definitely indicates (A) as the representation approached by the complex as shown by the following features of the structure: (*a*) the inner ring clearly locates 'double' and 'single' bonds on both sides of the dotted line passing through the C(11) and C(31) atoms (although aromaticity seems to be less perturbed at the peripheral benzene rings); (*b*) in accord with representation (A), two couples of opposite Ti–N bonds are formed, with shorter distances for Ti–N(3) and Ti–N(7) [average 2.177(4) Å] and longer for Ti–N(1) and Ti–N(5) [2.259(3) Å], the latter apparently associated with a more ionic character of the Ti–N bonds; (*c*) the average distance between the two inner N_4 planes (slightly distorted towards a tetrahedral configuration) is 2.32 Å. As can be seen from Table 4 this distance is much shorter than that found in any other [M(pc)$_2$] system (2.69—2.96 Å).

Furthermore, representation (A) has 18 double bonds, which differ from the 19 present in the 'normal' phthalocyaninato representation [structure (C)]. Therefore in the formation of [TiL] two π bonds are broken in the two phthalocyaninato units concommitant with formation of the two new inter-ligand C–C σ bonds. The isomerization process can be schematically represented as a cycloaddition reaction of the type shown below.



$$\mathrm{C{=}C + C{=}C \longrightarrow \begin{matrix} C{-}C \\ |\quad\;| \\ C{-}C \end{matrix}}$$

Stability, Spectroscopic and Magnetic Properties of [TiL]·$C_{10}H_7Cl$.—The complex [TiL]·$C_{10}H_7Cl$ is indefinitely stable to air. Thermogravimetric analysis in a nitrogen atmosphere (0.5 l min^{-1}) shows that the 1-chloronaphthalene is released between 100—200 °C. Complete elimination of 1-chloronaphthalene can also be achieved by heating at 200 °C under a vacuum (10^{-2} mmHg, ≈ 1.3 Pa) for 2 h, leaving the colour unchanged. The thermal stability observed for solid [TiL]

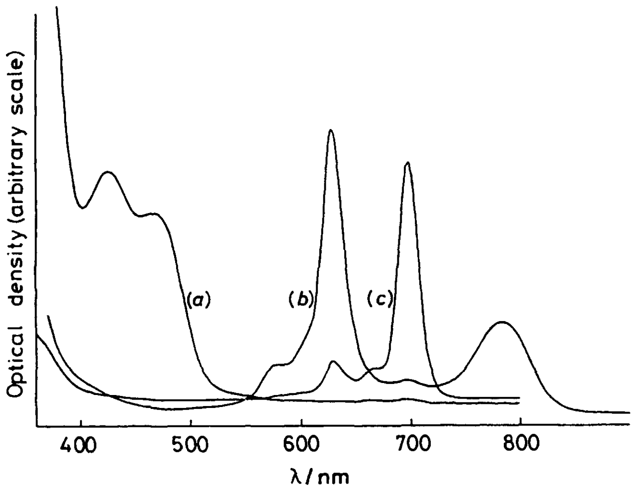


Figure 4. Visible solution spectra in 1-chloronaphthalene of [TiL] (*a*), [Sn(pc)$_2$] (*b*), and [Ti(pc)Cl$_2$] (*c*). The relative intensities of the three spectra are not directly comparable

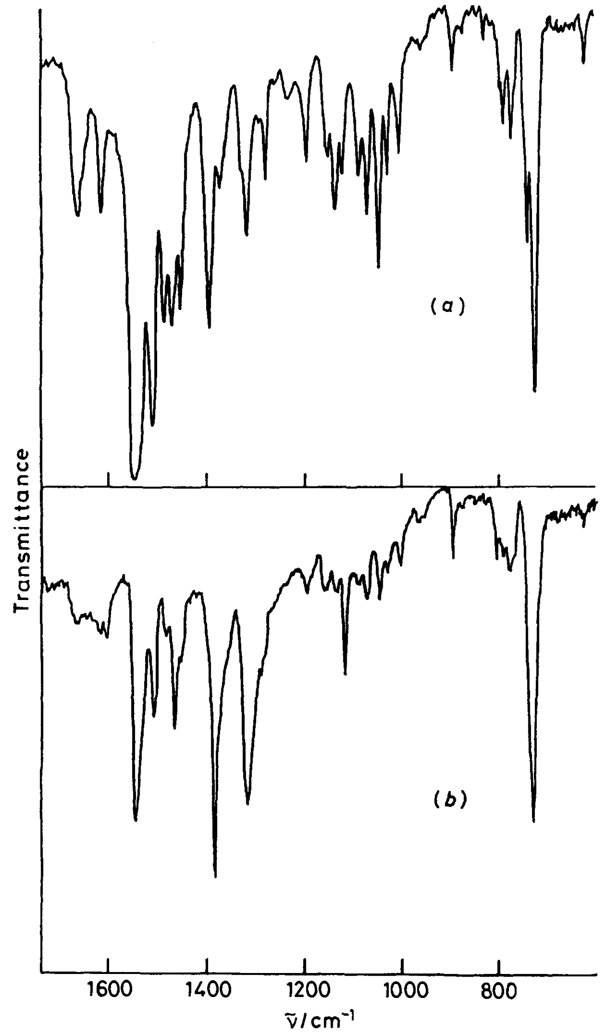


Figure 5. I.r. spectra of [TiL] (*a*) and [TiL]NO$_3$ (*b*) (KBr pellets)

seems to be comparable with that usually observed for 'normal' metal phthalocyanine systems. Heating under vacuum at 460 °C or under a rigorous nitrogen atmosphere at temperatures above 400 °C leaves [TiL] unchanged in its 'stapled' form. It can also be recovered unchanged after treatment with hot 37% aqueous HCl or on dissolution in 96% H_2SO_4 at room temperature followed by reprecipitation on addition to the solution of iced water. When heated in air at high temperatures (>400 °C), [TiL] breaks down irreversibly forming [TiO(pc)] and H_2pc, as clearly indicated by the i.r. spectrum of the mixture obtained and by comparison with that of a 1 : 1 reference mixture of the latter compounds.

The unusual yellow-orange colour of [TiL]·$C_{10}H_7Cl$, different from colours observed for 'normal' phthalocyanine systems (purple, green, or blue in the crystalline state, green or blue as microcrystalline powders and in solution), was considered to be indicative of a dramatic modification of the chromophore in the molecule, as confirmed by the *X*-ray crystal structure.

Both visible reflectance and solution spectra of [TiL] show similar features. The reflectance spectrum of [TiL] shows its most intense and broad absorption in the region 400—500 nm, with maxima roughly at 430 and 460 nm; additionally, shoulders at *ca.* 340 and 540 nm, and a peak of very weak intensity at *ca.* 665 nm are observed. The solution spectrum of [TiL] in 1-chloronaphthalene is shown in Figure 4 together with those of its precursor [Ti(pc)Cl$_2$] and a representative 'normal' phthalocyanine system [Sn(pc)$_2$]. Intense absorptions in the range 400—500 nm are observed with better defined maxima (at 424 and 475 nm) relative to the solid-state reflectance spectrum, whereas the weak absorptions above 500 nm (540 and 665 nm) are practically undetectable. As can be seen from Figure 4, the spectra of both [Ti(pc)Cl$_2$] and [Sn(pc)$_2$] show their most intense absorption (*Q*-band) in the region 600—700 nm (699 and 629 nm respectively), as is usual for 'normal' phthalocyanines, whereas no absorptions are present in the region 400—500 nm. The observed differences between the spectra of [TiL] and those of [Sn(pc)$_2$] and [Ti(pc)Cl$_2$] arise as a consequence of the partial disruption of the π-electron delocalization occurring in the 'stapled' [TiL] complex as revealed by *X*-ray crystallography.

Visible spectral data (Table 5) indicate that disruption of aromaticity in [TiL] also directly influences the intensity of the visible absorptions. Hence the solution spectrum of [TiL] in 1-chloronaphthalene shows absorption co-efficients (dm^3 mol^{-1} cm^{-1}) [$\varepsilon_{max.}$ 7 800 (424) and 6 600 (475 nm)] much lower than those found for the *Q*-bands in the spectra of [Sn(pc)$_2$] (ε = 117 000) and [Ti(pc)Cl$_2$] (ε = 172 000 dm^3 mol^{-1} cm^{-1}). These latter values are of the same order of magnitude as found for other sandwich-type [Ln(pc)$_2$] complexes (Ln = a lanthanide)[23] as well as for metal phthalocyanine derivatives in general. Thus, the lower intensity measured for the bands at 424 and 475 nm in the case of [TiL] can also be related to the peculiar chromophoric situation present in this complex. Quantitative spectra in pyridine for both [TiL] and [Sn(pc)$_2$] substantially accord with the spectra in 1-chloronaphthalene (Table 5).

The i.r. spectrum of [TiL], examined in the range 4 000—200 cm^{-1}, is particularly rich in absorptions in the region 1 700—600 cm^{-1} [Figure 5(*a*)] and is substantially different from the spectrum expected for the 'normal' phthalocyanine macrocyclic framework. A very intense absorption is present in the region of the carbon–carbon or carbon–nitrogen double bonds, located at 1 550 cm^{-1}. Bands of medium intensity are also found at 1 669 and 1 614 cm^{-1}, in a region (1 700—1 610 cm^{-1}) generally free from absorptions for 'normal' phthalocyanines. For samples of the complex crystallized from 1-chloronaphthalene the i.r. absorption found at *ca.* 680 cm^{-1} can be probably ascribed to the occluded solvent, although for some samples containing less than the expected (1 : 1) stoicheiometric amount of 1-chloronaphthalene, particularly those separated by addition of hexane to the 1-chloronaphthalene solutions, this band is usually of low relative intensity or not detectable.

Room-temperature magnetic susceptibility measurements on

Table 5. Visible spectral data for [TiL], $[Sn(pc)_2]$, and $[Ti(pc)Cl_2]$ given as λ/nm (ε/dm^3 mol^{-1} cm^{-1})

[TiL]			$[Sn(pc)_2]$		$[Ti(pc)Cl_2]$
a	*b*	*c*	*b*	*c*	*b*
340(sh)					360 (59 000)
430	424 (7 800)	425 (6 800)			
460	475 (6 600)	466 (5 200)			
540(sh)			578(sh) (23 000)	578	
			629 (117 000)	630	629 (41 000)
665		672 (800)			
			696 (17 000)	696	699 (172 000)
			782 (39 000)	782	

[a] Solid-state reflectance spectrum. [b] In 1-chloronaphthalene. [c] In pyridine.

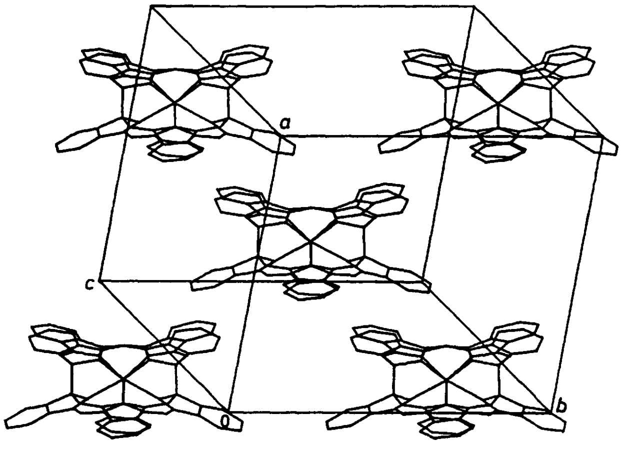


Figure 6. View of the arrangement of [TiL] molecules in the crystal lattice

several samples of $[TiL]\cdot C_{10}H_7Cl$ give $\mu_{eff.}$ values between 0.5 and 1.0. This low paramagnetism is almost certainly attributable to the presence of paramagnetic impurities. The low-temperature (77 K) e.s.r. spectrum of the solid shows the presence of a low-intensity signal at $g = 2$, observable only at high gain values, which can be confidently assigned to the presence of paramagnetic radical impurities, as is normal with metal phthalocyanines; indeed, comparable signals were also observed in the e.s.r. spectra of both $[Ti(pc)Cl_2]$ and $Na_2(pc)$.

Redox Behaviour of $[TiL]\cdot C_{10}H_7Cl$ *and Conductivity Measurements.*—Oxidation of $[TiL]\cdot C_{10}H_7Cl$ by aqueous 10% HNO_3 led to the formation of the monopositively charged species $[TiL]^{\cdot +}$, isolated as the nitrate $[TiL]NO_3$. The same product is also observed if 65% HNO_3 is used. The salt $[TiL]NO_3$ is air-stable and can be easily reconverted into [TiL] by reduction with $NaBH_4$.

Upon oxidation of $[TiL]\cdot C_{10}H_7Cl$ a marked decrease in intensity is observed for all the medium- or low-intensity absorptions present for [TiL] in the i.r. spectral region 1 700—600 cm^{-1}. The i.r. spectrum in Figure 5(*b*) also indicates that intense absorptions in the region 1 600—1 500 cm^{-1} are still present and a new sharp and intense peak at 1 383 cm^{-1} is observed which can be assigned to non-co-ordinated NO_3^-.

The room-temperature magnetic moment of $[TiL]NO_3$ is 1.75—2.00, indicative of the presence of one unpaired electron per molecule, as expected. Its e.s.r. spectrum at 77 K shows a signal at $g = 2.03$, typical of an organic radical cation, which under comparable experimental conditions is over one hundred times more intense than that observed for the non-oxidized material. The magnetic and e.s.r. data strongly suggest that oxidation is ligand centred, as is obvious since oxidation cannot occur at the central metal ion.

Figure 6 shows the arrangement of the [TiL] molecules in the crystal lattice. Intermolecular contacts of adjacent molecules are of the order of 3.55—3.56 Å, which is likely to preclude electrical conductivity in the solid state. Room-temperature conductivity measurements by the four-probe technique on single crystals of $[TiL]\cdot C_{10}H_7Cl$ confirm this, giving values for $\sigma < 10^{-8}\ \Omega^{-1}\ cm^{-1}$ at room temperature, and so the complex behaves as an insulator. Single crystals of $[TiL]NO_3$ have not been obtained so far. However, conductivity measurements on pressed pellets of the complex indicate that, compared with $[TiL]\cdot C_{10}H_7Cl$, σ increases approaching the range normally assigned to semiconductors (10^{-1}—$10^{-6}\ \Omega^{-1}\ cm^{-1}$). The electrical conductivity properties of $[TiL]NO_3$ and other derivatives of [TiL] are the subject of current study.

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