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[*N*,*N*′-Diphenylureato(2−)][phthalocyaninato(2−)]titanium(IV)

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Key indicators

Single-crystal X-ray study
T = 193 K
Mean σ(C–C) = 0.005 Å
R factor = 0.042
wR factor = 0.091
Data-to-parameter ratio = 13.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

In the title complex, [Ti($C_{32}H_{16}N_8$)($C_{13}H_{10}N_2O$)], the geometry around the Ti atom is square pyramidal, with the four isoindoline N atoms forming the basal plane and the ureate group at the apical site. The crystal structure is formed by close packing of centrosymmetric dimers, consisting of slightly offset molecules related by a crystallographic center of inversion in a face-to-face manner.

Comment

Nowadays, great interest lies not only in building new metal phthalocyanine (Pc) molecules, but also in the prediction of their crystal and morphological structures and calculations of the physical properties, since different arrangements of the phthalocyanine molecules lead to materials with different physical properties and polymorphic modifications, referred to as physical isomers (Kadish *et al.*, 2003*a*). PcTiO is one of the most sensitive organic photoreceptors in electrophotographic printing (Law, 1993) and is often used in the manufacture of optical data storage devices, such as CD-ROM (Kuder, 1988). The crystal structure and different morphologies of PcTiO were studied by Hiller *et al.* (1982).

We became interested in the typical inorganic reaction patterns of PcTiO, aiming to synthesize its isoelectronic derivatives PcTi*X* [*X* = S, Se, *NR* (*NR*= *N*-organoimide) *etc.*] that have not been isolated in pure form to date. As one of the synthetic strategies for the replacement of the oxo functionality and generation of an imide group, we chose the metathesis of PcTiO with organic isocyanates according to the following scheme:

$$\mathrm{PcTi{=}O} + \mathrm{ArN{=}C{=}O} \longrightarrow \mathrm{PcTi{=}NAr} + \mathrm{CO_2}$$

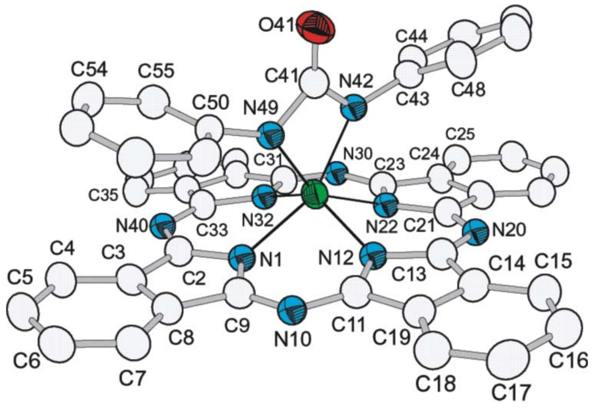
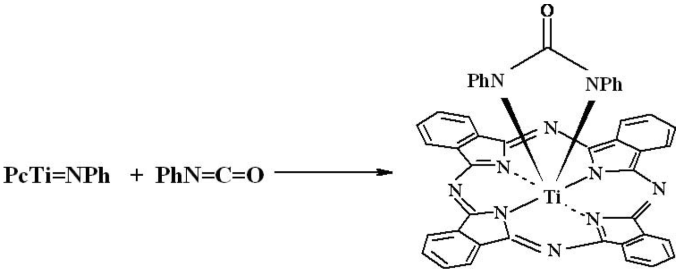


Figure 1
View of (I), with 50% probability displacement ellipsoids. H atoms have been omitted. C atoms are numbered sequentially around the rings.

This metathetical transformation depends very much on the steric bulk of the substituent *R* of the isocyanate. For small substituents such as phenyl, the imide complex could not be isolated in analytically pure form since it further reacts with a second equivalent of PhNCO. [2+2]-cycloaddition leads to the formation of the *N*,*N'*-ureato complex, (I).



(I)

The molecule of (I) consists of six-coordinate Ti^{IV} surrounded by four basal isoindoline rings of the *Pc* molecule and the ureato group in the apical position. The Ti atom is too large and unable to enter the cavity; it sits 'atop' or 'out-of-plane' from the N4 plane – so called extra-coordination. The macrocycle adapts to this special situation by deformation (Kadish *et al.*, 2003*b*).

The Ti atom is displaced from the mean plane of the isoindoline N atoms towards the ureato ligand by 0.79 **(s.u.?)** Å, corresponding to 0.70–0.72 Å in PcTiO (Hiller *et al.*, 1982) and 0.84 Å in $PcTiCl_2$ (Goedken *et al.*, 1985).

The crystal structure of (I) demonstrates that the presence of the apical ureato group at the central Ti atom modifies drastically the molecular packing of the phthalocyanine in the solid state, relative to the molecular packing of PcTiO (Hiller *et al.*, 1982). The crystal structure is formed by close packing of centrosymmetric dimers (Fig. 2), consisting of slightly offset molecules related by a crystallographic center of inversion in a face-to-face manner. Therefore, relevant consequences for the electronic and NLO properties would be expected for the title ureate–TiPc complex.

Experimental

Highly pure PcTiO was prepared according to the procedure reported by Yao *et al.* (1995). PcTiO was heated with an excess (10 equivalents) of phenyl isocyanate in chloronaphthalene (mixture of isomers, 90% α, 10% β, supplier Acros) or without solvent at 433 K for several hours. The product was washed extensively by extraction from refluxing MeCN and toluene, and dried under vacuum (10^{-3} mbar) at 393 K (blue–green, yield: 95%). Analysis for $C_{45}H_{26}N_{10}OTi$: MALDI-TOF MS (M^+ 770.6). Elemental analysis calculated: C 70.1, H 3.4, N 18.2, Ti 6.2%; found: C 69.6, H 3.6, N 18.0, Ti 6.0%. IR (KBr): 1690 ($\nu_{C=O}$); TGA (two endothermic thermal decompositions of the axial ureato group at 493–523 and 523–573K; weight loss calculated/found: 16 /19% and 27/28%; UV–vis in chloronaphthalene: 699 (*s*), 665.1 (*w*), 628.6 (*m*), 343 (*s*), 314.7–302.2. Single crystals were grown by the controlled cooling of a chloronaphthalene solution or the reaction medium from 433 to 298 K. Details of the synthesis of imide– and ureato–TiPc complexes by metathesis of different isocyanates with PcTiO will be discussed elsewhere (Sundermeyer *et al.*, 2005).

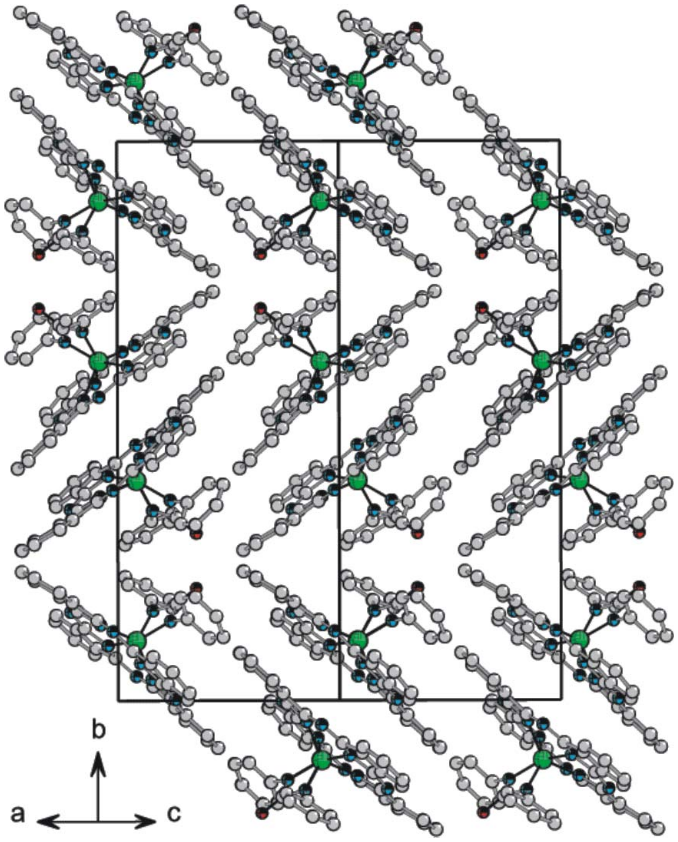


Figure 2
Packing diagram, viewed along the [101] direction.

Crystal data

$[Ti(C_{32}H_{16}N_8)(C_{13}H_{10}N_2O)]$
$M_r = 770.66$
Monoclinic, $P2_1/n$
$a = 11.8342\ (10)$ Å
$b = 26.0933\ (19)$ Å
$c = 12.4701\ (11)$ Å
$\beta = 116.845\ (6)^\circ$
$V = 3435.7\ (5)$ Å^3
$Z = 4$

$D_x = 1.49$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 10560 reflections
$\theta = 1.6$–16°
$\mu = 0.31$ mm^{-1}
$T = 193\ (2)$ K
Prism, black
$0.3 \times 0.12 \times 0.08$ mm

Data collection

Stoe IPDS-II diffractometer
ω scans
Absorption correction: multi-scan (Blessing, 1995)
$T_{min} = 0.923$, $T_{max} = 0.962$
25798 measured reflections
6900 independent reflections

3564 reflections with $I > 2\sigma(I)$
$R_{int} = 0.072$
$\theta_{max} = 26.3^\circ$
$h = -14 \rightarrow 14$
$k = -32 \rightarrow 32$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.091$
$S = 0.80$
6900 reflections
515 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0405P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.25$ e Å^{-3}
$\Delta\rho_{min} = -0.34$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.00083 (16)

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Table 1
Selected geometric parameters (Å, °).

C41—O41	1.217 (3)	N22—Ti1	2.105 (2)
C41—N42	1.389 (3)	N32—Ti1	2.060 (2)
C41—N49	1.393 (3)	N42—Ti1	2.001 (2)
N1—Ti1	2.113 (2)	N49—Ti1	1.972 (2)
N12—Ti1	2.069 (2)		
O41—C41—N42	130.0 (3)	N49—Ti1—N22	147.07 (9)
O41—C41—N49	129.0 (2)	N42—Ti1—N22	81.67 (8)
N42—C41—N49	101.1 (2)	N32—Ti1—N22	82.40 (8)
C41—N42—Ti1	96.02 (16)	N12—Ti1—N22	81.50 (9)
C41—N49—Ti1	97.17 (16)	N49—Ti1—N1	81.00 (8)
N49—Ti1—N32	108.59 (9)	N42—Ti1—N1	146.41 (8)
N42—Ti1—N32	109.04 (9)	N32—Ti1—N1	81.73 (9)
N49—Ti1—N12	105.29 (9)	N12—Ti1—N1	81.60 (9)
N42—Ti1—N12	105.45 (9)	N22—Ti1—N1	131.86 (8)
N32—Ti1—N12	139.10 (9)		

All H atoms were placed in calculated positions and refined using a riding model, with C—H = 0.95 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C).

Data collection: *X-AREA* (Stoe & Cie, 2003); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2001); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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