O98—H981···O51	0.83 (6)	2.03 (6)	2.810 (8)	158 (6)
O98—H982···O31^{i}	0.82 (5)	2.78 (6)	3.258 (8)	119 (4)
O98—H982···O92	0.82 (5)	2.11 (5)	2.912 (10)	166 (6)

Symmetry codes: (i) $x, y-1, z$; (ii) $x, 1+y, z$; (iii) $x-1, 1+y, z$; (iv) $x-1, y, z$; (v) $x, y, z-1$; (vi) $1+x, y, z$; (vii) $1+x, y-1, z$; (viii) $x, y, 1+z$.

H atoms were located from a difference map and their positions were refined. Restraints on oxygen-bound H atoms involved one common U, a unique O—H distance for all H atoms and H—H distances in the water molecules restrained to the 1.58-fold of the O—H distance (corresponding to a 105° angle). The common O—H distance refined to 0.828 (14) Å.

Data collection: *IPDS Diffractometer Software* (Stoe & Cie, 1993). Cell refinement: *IPDS Diffractometer Software*. Data reduction: *IPDS Diffractometer Software*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976) and *PLATON* (Spek, 1982). Software used to prepare material for publication: *SHELXL*93.

This work was supported by Akzo, Wuppertal, Germany, and Südzucker AG, Obrigheim, Germany (gift of the levoglucosan sample).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: SK1042). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Burger, J. & Klüfers, P. (1995). *Chem. Ber.* **128**, 75–79.
Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Gatehouse, B. M. & Poppleton, B. J. (1970). *Acta Cryst.* B**26**, 1761–1765.
Habermann, N., Jung, G., Klaassen, M. & Klüfers, P. (1992). *Chem. Ber.* **125**, 809–814.
Habermann, N., Klaassen, M. & Klüfers, P. (1993). *Carbohydr. Res.* **241**, 9–23.
IUPAC-IUB Joint Commission on Biological Nomenclature Recommendations 1980 (1982). *Eur. J. Biochem.* **126**, 433–437.
Jeffrey, G. A. & Saenger, W. (1991). In *Hydrogen Bonding in Biological Structures*. Berlin, Heidelberg, New York: Springer-Verlag.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Klaassen, M. & Klüfers, P. (1994). *Z. Anorg. Allg. Chem.* **620**, 1631–1634.
Klüfers, P. & Mayer, P. (1996). *Acta Cryst.* C**52**, 2970–2972.
Park, Y. J., Kim, H. S. & Jeffrey, G. A. (1971). *Acta Cryst.* B**27**, 220–227.
Sheldrick, B. (1977). *Acta Cryst.* B**33**, 3003–3005.
Sheldrick, G. M. (1985). *SHELXS*86. *Program for the Solution of Crystal Structures*. University of Göttingen, Germany.
Sheldrick, G. M. (1993). *SHELXL*93. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Spek, A. L. (1982). *The EUCLID Package. Computational Crystallography*, edited by D. Sayre, p. 528. Oxford: Clarendon Press.
Stoe & Cie (1993). *Scanner Stoe IPDS Diffractometer Software*. Version 1.08. Stoe & Cie, Darmstadt, Germany.
Takagi, S. & Jeffrey, G. A. (1977). *Acta Cryst.* B**33**, 3033–3040.
Takagi, S. & Jeffrey, G. A. (1978). *Acta Cryst.* B**34**, 2006–2010.

Acta Cryst. (1996). C**52**, 2975–2977

Tetrachloro[2-(phenylamino)pyridinato]-titanate(IV) with a 2-(Phenylamino)-pyridinium Counterion

MIKA POLAMO* AND MARKKU LESKELÄ

Inorganic Chemistry Laboratory, Department of Chemistry, University of Helsinki, PO Box 55 (A. I. Virtasen aukio 1), FIN-00014 University of Helsinki, Finland. E-mail: polamo@kumpu.helsinki.fi

(Received 8 July 1996; accepted 2 August 1996)

Abstract

The title salt, 2-(phenylamino)pyridinium tetrachloro[2-(phenylamino)pyridinato-N,N']titanate(IV), $(C_{11}H_{11}N_2)$-$[TiCl_4(C_{11}H_9N_2)]$, is a product of the reaction of titanium tetrachloride and 2-(phenylamino)pyridine. The coordinated deprotonated aminopyridine forms a four-membered chelate ring. Titanium has a pseudo-octahedral coordination sphere. A second 2-(phenylamino)pyridine residue behaves as a proton acceptor and is a counterion in the solid state.

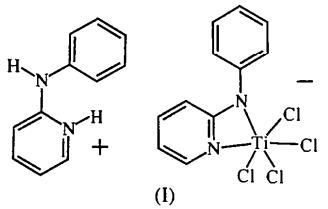
Comment

Amido complexes of early transition metals are commonly synthesized *via* transmetallation reactions. Over 60 years ago, tetrakis(diphenylamido)titanium was obtained as a product of the reaction of potassium diphenylamide and $TiCl_4$ (Dermer & Fernelius, 1934). Lithium reagents have most commonly been used in the syntheses of both homoleptic (Bradley & Thomas, 1960) and heteroleptic amido complexes, such as mixed-halide complexes of the type $(R_2N)_yTiX_{4-y}$ (y = 1–3; R = Me, Et; X = Cl, Br, I) (for review see Bürger & Neese, 1970). Various amido complexes have also been prepared by refluxing $TiCl_4$ with primary or secondary amines (Cowdell & Fowles, 1960).

It has been shown recently that both the chloro(dimethylamido)bis(aminopyridinato)titanium and chlorotris(aminopyridinato)titanium complexes can be prepared with high yields using $[TiCl_2(Me_2N)_2(thf)_2]$ (thf is tetrahydrofuran) as a starting material (Kempe & Arndt, 1996). This method is particularly useful because lithium aminopyridinates were reported to form the desired transition metal complexes with only very low yields. A limitation of the amine-exchange reaction is that only monochloro complexes, such as chlorotris[2-(phenylamino)pyridinato]titanium and chloro(dimethylamido)bis[2-(phenylamino)pyridinato]titanium, can be obtained.

In our attempt to find synthetic routes to dichloroaminopyridinate complexes, four equivalents of 2-

phenylaminopyridine and titanium(IV) chloride were refluxed in toluene. The excess of the amine ligand was used as a HCl acceptor. The reaction took place only partially: a six-coordinate tetrachloro[2-(phenylamino)-pyridinato]titanate(IV) anion containing a TiN_2C chelate ring was formed and a second 2-aminopyridine ligand behaved as a proton acceptor and remained as a counter-ion to give the title structure, (I).



(I)

The solid-state structure of (I) thus consists of a 2-(phenylamino)pyridinium cation and a tetrachloro[2-(phenylamino)pyridinato]titanate(IV) anion. Titanium has distorted pseudo-octahedral coordination. The main reason for the distortion is the narrow N—Ti—N angle [63.1 (2)°] in the four-membered chelate ring. Other *cis* angles vary between 85.33 (14) and 108.93 (8)°. Ti—N(amido) [1.966 (5) Å] and Ti—N(py) [2.189 (5) Å] distances are similar to those found in chloro(dimethylamido)bis[2-(phenylamino)pyridinato]titanium (Kempe & Arndt, 1996) in which the Ti—N(amido) bonds are 2.007 (4) and 2.101 (4) Å and the Ti—N(py) bonds are 2.144 (4) and 2.257 (5) Å. Ti—Cl distances in the title complex vary between 2.238 (2) and 2.384 (2) Å, whereas a value of 2.3492 (7) Å was found in chloro(dimethylamido)bis[2-(phenylamino)pyridinato]titanium. The structure of the counterion needs little comment. The angle between the pyridyl and phenyl planes [67.4 (2)°] is similar to the corresponding angle found in the complex with phenylaminopyridine coordinated to titanium [70.0 (2)°].

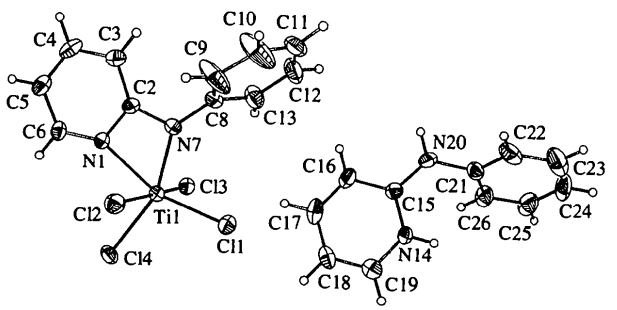


Fig. 1. A perspective view of the cation and anion drawn with 30% probability ellipsoids.

Experimental

2-(Phenylamino)pyridine (8.58 g, 50.4 mmol) was dissolved in toluene (40 ml) and the solution was cooled to 253 K. Titanium(IV) chloride (1.45 ml, 13.2 mmol) was added. The temperature of the solution was increased to 313 K over a period of 45 min. After 1 h at 313 K, the reaction mixture was filtered. Dark-red prismatic crystals suitable for single-crystal measurements were obtained at room temperature after 15 h. All reaction steps were carried out under an argon atmosphere using standard Schlenk techniques. The crystal used for X-ray measurements was mounted on a glass fiber using the oil-drop method (Kottke & Stalke, 1993).

Crystal data

$(C_{11}H_{11}N_2)[TiCl_4(C_{11}H_9N_2)]$
M_r = 530.12
Triclinic
$P\bar{1}$
a = 9.580 (15) Å
b = 9.652 (12) Å
c = 14.625 (19) Å
α = 94.18 (13)°
β = 90.27 (15)°
γ = 118.44 (9)°
V = 1184 (3) Å^3
Z = 2
D_x = 1.486 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 20 reflections
θ = 3–18°
μ = 0.830 mm^{-1}
T = 193 (1) K
Block
0.45 × 0.35 × 0.20 mm
Dark red

Data collection

Rigaku AFC-7*S* diffractometer
2θ-ω scans
Absorption correction:
ψ scans (North, Phillips & Mathews, 1968)
T_{min} = 0.77, T_{max} = 0.85
3546 measured reflections
3546 independent reflections

2476 observed reflections [$I > 2\sigma(I)$]
θ_{max} = 25°
$h = -11 \rightarrow 11$
$k = -11 \rightarrow 11$
$l = -17 \rightarrow 0$
3 standard reflections
monitored every 200 reflections
intensity decay: 1.3%

Refinement

Refinement on F^2
$R(F)$ = 0.0667
$wR(F^2)$ = 0.1359
S = 1.053
3546 reflections
280 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0461P)^2 + 2.1081P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = −0.007
$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.42 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
Ti1	1.05596 (13)	1.33899 (12)	0.26665 (8)	0.0392 (3)
Cl1	1.0850 (2)	1.1233 (2)	0.27438 (12)	0.0493 (4)
Cl2	1.2699 (2)	1.4528 (2)	0.16628 (11)	0.0520 (5)
Cl3	0.8508 (2)	1.2535 (2)	0.37295 (11)	0.0441 (4)
Cl4	1.2208 (2)	1.5315 (2)	0.37970 (11)	0.0510 (4)
N1	0.9769 (6)	1.4967 (5)	0.2124 (3)	0.0397 (12)
C2	0.8830 (7)	1.3803 (7)	0.1486 (4)	0.0411 (15)

C3	0.7920 (8)	1.4060 (8)	0.0839 (4)	0.056 (2)
C4	0.8034 (9)	1.5535 (9)	0.0868 (5)	0.063 (2)
C5	0.9009 (8)	1.6724 (8)	0.1531 (4)	0.054 (2)
C6	0.9881 (7)	1.6390 (7)	0.2139 (4)	0.044 (2)
N7	0.8989 (6)	1.2512 (6)	0.1628 (3)	0.0419 (13)
C8	0.8164 (7)	1.1053 (7)	0.1074 (4)	0.042 (2)
C9	0.8540 (11)	1.0891 (11)	0.0191 (5)	0.112 (4)
C10	0.7756 (12)	0.9451 (13)	−0.0308 (6)	0.125 (5)
C11	0.6556 (10)	0.8214 (9)	0.0021 (6)	0.069 (2)
C12	0.6202 (10)	0.8352 (9)	0.0903 (6)	0.080 (3)
C13	0.7014 (9)	0.9757 (8)	0.1436 (5)	0.064 (2)
N14	0.7558 (6)	0.5339 (5)	0.3904 (3)	0.0413 (12)
C15	0.6405 (7)	0.5464 (7)	0.3451 (4)	0.0419 (15)
C16	0.6564 (8)	0.6968 (8)	0.3370 (5)	0.054 (2)
C17	0.7888 (10)	0.8248 (8)	0.3756 (5)	0.064 (2)
C18	0.9079 (9)	0.8087 (8)	0.4212 (5)	0.057 (2)
C19	0.8885 (8)	0.6623 (8)	0.4287 (4)	0.050 (2)
N20	0.5147 (6)	0.4150 (6)	0.3071 (4)	0.0536 (15)
C21	0.4717 (7)	0.2561 (7)	0.3279 (5)	0.047 (2)
C22	0.4528 (8)	0.1442 (10)	0.2593 (6)	0.074 (2)
C23	0.3991 (11)	−0.0126 (12)	0.2799 (9)	0.103 (4)
C24	0.3711 (10)	−0.0456 (10)	0.3678 (10)	0.099 (4)
C25	0.3931 (9)	0.0658 (10)	0.4365 (7)	0.082 (3)
C26	0.4423 (8)	0.2192 (8)	0.4177 (6)	0.062 (2)

Table 2. *Selected geometric parameters (Å, °)*

Ti1—N7	1.966 (5)	N1—C2	1.348 (7)
Ti1—N1	2.189 (5)	C2—N7	1.356 (7)
Ti1—Cl1	2.238 (2)	N7—C8	1.426 (7)
Ti1—Cl4	2.326 (2)	N14—C15	1.344 (7)
Ti1—Cl3	2.373 (2)	N14—C19	1.363 (7)
Ti1—Cl2	2.384 (2)	C15—N20	1.343 (7)
N1—C6	1.324 (7)	N20—C21	1.443 (8)
N7—Ti1—N1	63.1 (2)	Cl4—Ti1—Cl2	87.19 (8)
N7—Ti1—Cl1	95.6 (2)	Cl3—Ti1—Cl2	173.91 (8)
N1—Ti1—Cl1	158.37 (14)	C6—N1—C2	121.0 (5)
N7—Ti1—Cl4	155.5 (2)	C6—N1—Ti1	149.1 (4)
N1—Ti1—Cl4	92.47 (14)	C2—N1—Ti1	89.8 (4)
Cl1—Ti1—Cl4	108.93 (8)	N1—C2—N7	107.5 (5)
N7—Ti1—Cl3	91.1 (2)	N1—C2—Ti1	58.5 (3)
N1—Ti1—Cl3	91.06 (14)	N7—C2—Ti1	49.0 (3)
Cl1—Ti1—Cl3	92.71 (8)	C2—N7—C8	122.8 (5)
Cl4—Ti1—Cl3	88.07 (7)	C2—N7—Ti1	99.6 (4)
N7—Ti1—Cl2	91.7 (2)	C8—N7—Ti1	137.6 (4)
N1—Ti1—Cl2	85.33 (14)	N20—C15—N14	119.4 (6)
Cl1—Ti1—Cl2	92.45 (8)		

The determination of the unit cell was not straightforward. All the crystals selected, including the one used for data collection, suffered from wide peak profiles with high, and sometimes asymmetric, backgrounds. The reliability of the unit-cell parameters is thus rather poor. Data were not corrected for decay (1.3%). All non-H atoms were refined anisotropically. H atoms were refined on calculated positions with displacement parameters 1.3 times those of their host atoms. Additional refinements were carried out in order to confirm that the correct locations had been chosen for the heterocyclic N atom and the site of ammonium protonation in the aminopyridine cation. In these refinements, an N atom was placed at the positions of the C16, C22 or C26 atoms and an additional proton was located on N20 instead of on N14. All these additional refinements resulted in less satisfying displacement factors and *R* values than the solution presented here.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993*a*). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1993*b*). Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXL*93.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1287). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Bradley, D. C. & Thomas, I. M. (1960). *J. Chem. Soc.* pp. 3857–3861.

Bürger, H. & Neese, H.-J. (1970). *Chimia*, **24**, 209–236.

Cowdell, R. T. & Fowles, W. A. (1960). *J. Am. Chem. Soc.* **82**, 2522–2526.

Dermer, O. C. & Fernelius, W. C. (1934). *Z. Anorg. Allg. Chem.* **221**, 83–97.

Kempe, R. & Arndt, P. (1996). *Inorg. Chem.* **35**, 2644–2649.

Kottke, T. & Stalke, D. (1993). *J. Appl. Cryst.* **26**, 615–619.

Molecular Structure Corporation (1993*a*). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corporation (1993*b*). *TEXSAN. Single Crystal Structure Analysis Software*. Version 1.6c. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Sheldrick, G. M. (1990). *SHELXTL/PC*. Version 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (1993). *SHELXL*93. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Acta Cryst. (1996). C**52**, 2977–2980

Trichlorobis[2,6-di(phenylamino)-pyridinato-*N*,*N*′]tantalum(V) Toluene Solvate (1/1)

MIKA POLAMO

Inorganic Chemistry Laboratory, Department of Chemistry, University of Helsinki, PO Box 55 (A. I. Virtasen aukio 1), FIN-00014 University of Helsinki, Finland. E-mail: polamo@kumpu.helsinki.fi

(*Received 5 June 1996; accepted 13 September 1996*)

Abstract

The title compound, $[TaCl_3(C_{17}H_{14}N_3)_2].C_7H_8$, is formed when 2,6-bis(phenylamino)pyridine and tantalum(V) chloride are refluxed in toluene. The organic ligand loses an amino proton and forms a σ bond with the metal atom, while its pyridine N atom acts as a donor. A small chelate ring is thus formed. The two bidentate ligands and three Cl atoms afford a seven-coordinate central atom.

Comment

Although many crystal structures of aminopyridines are known, few results of complexation studies have