Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1302). Services for accessing these data are described at the back of the journal.

References

Biagini Cingi, M., Bandoli, G., Clemente, D. A. & Tiripicchio, A. (1980). *J. Appl. Cryst.* **13**, 197–198.

Ciccarese, A., Clemente, D. A., Fanizzi, F. P., Marzotto, A. & Valle, G. (1997). In preparation.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Mann, F. G. & Watson, H. R. (1958). *J. Chem. Soc.* pp. 2772–2780.

Marzotto, A., Clemente, D. A. & Valle, G. (1997). *Acta Cryst.* Submitted.

Niemeyer, H. M. (1979). *J. Mol. Struct.* **57**, 241–244.

Parkin, S., Moezzi, B. & Hope, H. (1995). *J. Appl. Cryst.* **28**, 53–56.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Acta Cryst. (1997). C**53**, 1583–1585

4-Methylpyridinium Pentachloro(4-methylpyridine-*N*)titanate(IV) Acetonitrile Solvate at 143 K

Karl Hensen,[a] Peter Pickel,[a] Alexander Lemke[a] and Michael Bolte[b]

[a]*Institut für Physikalische und Theoretische Chemie, J. W. Goethe-Universität Frankfurt, Marie-Curie-Straße 11, 60439 Frankfurt/Main, Germany, and* [b]*Institut für Organische Chemie, J. W. Goethe-Universität Frankfurt, Marie-Curie-Straße 11, 60439 Frankfurt/Main, Germany. E-mail: pickel@chemie.uni-frankfurt.de*

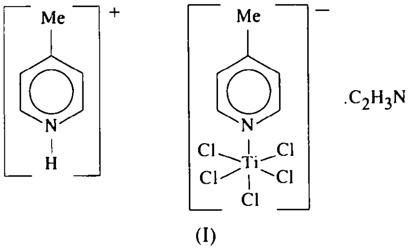
(*Received 6 May 1997; accepted 16 June 1997*)

Abstract

The structure of the title compound, $(C_6H_8N)[TiCl_5(C_6H_7N)].C_2H_3N$, consists of discrete complexes in which the Ti atom has a distorted pseudo-octahedral coordination with a 4-methylpyridinium cation as counterion. The 4-methylpyridine ligand and one chloro ligand occupy axial positions with the other four chloro ligands in the equatorial plane. The acetonitrile solvent molecule occupies a cavity in the structure.

Comment

Our group has been investigating the interactions of organic nitrogen bases with halogensilanes and methylhalogensilanes for a long time (Hensen & Wagner, 1976; Hensen, Zengerly, Pickel & Klebe, 1983; Hensen, Zengerly, Müller & Pickel, 1988; Hensen, Roßmann & Bensch, 1992; Fleischer, Hensen & Stumpf, 1996). Silicon and titanium tetrahalides are strong Lewis acids and form Lewis acid–Lewis base adducts with electron-pair donors (Emeléus & Rao, 1958; Rao, 1960; Mazo, Bobilev & Troyanov, 1987; Lemke, 1996). Thus, titanium tetrachloride forms complexes with pyridine and 4-methylpyridine in a 1:2 ratio. The structure of the title compound, (I), has been determined as part of our studies on the structure and properties of adducts of titanium tetrahalides and tertiary amines.



(I)

The three molecules lie on a crystallographic mirror plane perpendicular to the *a* axis forming layers parallel to the (100) plane. The distance between the layers is 3.59 Å, that is *a*/2. The Ti atom in the $[TiCl_5(4\text{-}Mepy)]^-$ anion is pseudo-octahedrally coordinated with a 4-methylpyridinium cation as a counterion. This is the first structure of a pseudo-octahedral titanium complex consisting of one nitrogen and five halogeno ligands. The Ti atom deviates by 0.132 (1) Å from the plane of the equatorial Cl atoms towards the axial Cl atom, so that all N—Ti—Cl_{eq} angles are smaller and all Cl_{ax}—Ti—Cl_{eq} angles are wider than 90°. While the bond lengths between Ti and the two equatorial Cl atoms differ significantly, 2.349 (1) and 2.291 (1) Å for Ti1—Cl2 and Ti1—Cl3, respectively, the axial Ti1—Cl1 bond [2.309 (2) Å] is in the same range as the Ti1—Cl2 bond. The torsion angles Cl2—Ti1—N1—C2 and Cl3—Ti1—N1—C2, with values of −136.23 (3) and −45.68 (3)°, respectively, show that the aromatic plane almost exactly bisects the equatorial Cl—Ti—Cl angle. There are two short N—H···Cl contacts: H11···Cl1 2.567 (5) Å and N11—H11···Cl1 140.9 (1)°, and H11···Cl2 2.730 (5) Å and N11—H11···Cl1 130.34 (8)°.

Our original aim was to determine the structure of the compound which is formed by titanium tetrachloride and 4-methylpyridine in a 1:2 ratio. However, slight moisture in the solvent, even though it was dried through a molecular sieve, causes part hydrolyzation of $TiCl_4(4\text{-}Mepy)_2$ which leads to the title compound, (I). The only structure that is similar to the title compound is the $[TiCl_5(thf)]^-$ anion (Sobota, Utko & Lis, 1984). In this structure, the Ti atom deviates by 0.174 Å from the plane of the equatorial Cl atoms towards the axial Cl atom, but in contrast to the title compound, the bonds from the Ti atom to the equatorial Cl atoms are significantly longer (2.296 to 2.318 Å) than the axial Ti—Cl bond (2.249 Å).

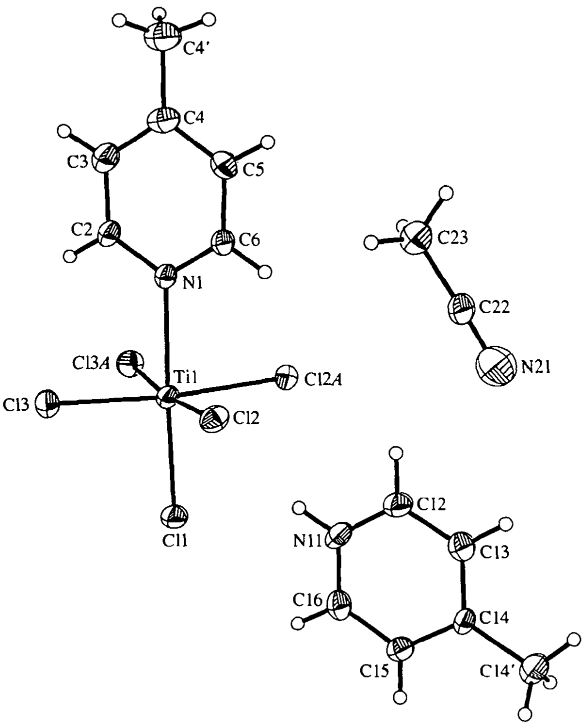


Fig. 1. Perspective view of the title compound with the atom numbering; displacement ellipsoids are drawn at the 50% probability level.

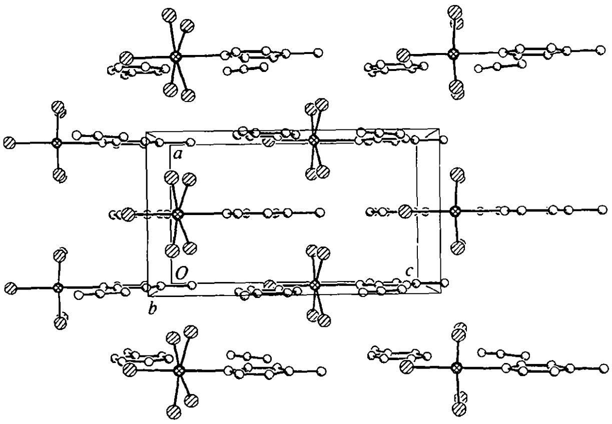


Fig. 2. Packing diagram of the unit cell of the title compound.

Experimental

All manipulations were carried out in a dry nitrogen atmosphere. Titanium tetrachloride (4.97 m*M*, 0.54 ml) was dissolved in 25 ml chloroform (which has been dried through a molecular sieve, 0.4 Å) and 4-methylpyridine (13.51 m*M*, 1.31 ml, distilled in the presence of calcium hydride) was added dropwise to the stirred solution, whereupon a yellow solid started to precipitate. The suspension was filtered under nitrogen, washed with chloroform and dried *in vacuo*. Subsequently the yellow solid was dissolved in acetonitrile. After six weeks, single crystals were obtained by gradual evaporation of the solvent.

Crystal data

$(C_6H_8N)[TiCl_5(C_6H_7N)].-C_2H_3N$
$M_r = 453.46$
Orthorhombic
$Pmn2_1$
$a = 7.1807\ (1)$ Å
$b = 10.8165\ (2)$ Å
$c = 12.6864\ (2)$ Å
$V = 985.35\ (3)$ Å^3
$Z = 2$
$D_x = 1.528$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 4007 reflections
$\theta = 1$–$25°$
$\mu = 1.113$ mm^{-1}
$T = 143$ K
Block
0.40 × 0.15 × 0.10 mm
Light yellow, transparent

Data collection

Siemens CCD three-circle diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996*a*)
$T_{\min} = 0.684$, $T_{\max} = 0.895$
7873 measured reflections

2130 independent reflections
1780 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.059$
$\theta_{\max} = 26.47°$
$h = -8 \rightarrow 8$
$k = -13 \rightarrow 13$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.074$
$S = 1.072$
2130 reflections
133 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0304P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.271$ e Å^{-3}
$\Delta\rho_{\min} = -0.366$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute configuration: Flack (1983)
Flack parameter = 0.05 (5)

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

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

	x	y	z	$U_{\rm eq}$
Ti1	0	0.27853 (8)	0.58243 (8)	0.0200 (2)
Cl1	0	0.31639 (13)	0.40334 (10)	0.0249 (3)
Cl2	0.22574 (11)	0.43162 (8)	0.61256 (7)	0.0242 (2)
Cl3	0.22801 (11)	0.13071 (8)	0.57405 (7)	0.0264 (2)
N1	0	0.2509 (4)	0.7575 (3)	0.0191 (9)
C2	0	0.1380 (4)	0.8000 (4)	0.0211 (12)
C3	0	0.1177 (5)	0.9067 (5)	0.0298 (12)
C4	0	0.2168 (5)	0.9774 (4)	0.0289 (13)
C4′	0	0.1980 (5)	1.0935 (5)	0.0412 (15)
C5	0	0.3341 (5)	0.9320 (4)	0.0287 (12)
C6	0	0.3471 (5)	0.8242 (4)	0.0231 (12)
N11	0	0.6178 (4)	0.4424 (3)	0.0290 (11)
C12	0	0.7126 (5)	0.5105 (4)	0.0310 (14)
C13	0	0.8309 (5)	0.4745 (4)	0.0289 (13)
C14	0	0.8551 (4)	0.3665 (4)	0.0213 (11)
C14′	0	0.9834 (5)	0.3250 (4)	0.0352 (14)
C15	0	0.7535 (5)	0.2980 (4)	0.0248 (13)
C16	0	0.6358 (5)	0.3388 (4)	0.0282 (13)
N21	0	0.8408 (6)	0.7408 (6)	0.084 (2)
C22	0	0.7703 (5)	0.8072 (5)	0.0389 (16)
C23	0	0.6787 (5)	0.8892 (5)	0.0312 (14)

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

Ti1—N1	2.241 (4)	Ti1—Cl1	2.3086 (15)
Ti1—Cl3	2.2910 (10)	Ti1—Cl2	2.3485 (10)
N1—Ti1—Cl3	87.30 (8)	Cl3^{i}—Ti1—Cl2	173.17 (6)
Cl3^{i}—Ti1—Cl3	91.23 (5)	Cl3—Ti1—Cl2	90.36 (3)
N1—Ti1—Cl1	177.45 (13)	Cl1—Ti1—Cl2	92.01 (4)
Cl3—Ti1—Cl1	94.48 (5)	Cl2—Ti1—Cl2^{i}	87.29 (5)
N1—Ti1—Cl2	86.15 (8)		

Symmetry code: (i) $-x, y, z$.

The data collection nominally covered over a sphere of reciprocal space by a combination of five sets of exposures; each set had a different φ angle for the crystal and each exposure covered 0.3° in ω. The crystal-to-detector distance was 5.95 cm. Coverage of the unique set is over 95% complete to at least 26° in θ. Crystal decay was monitored by repeating the initial frames at the end of data collection and analysing the duplicate reflections. All H atoms were located by difference Fourier synthesis and refined with fixed individual displacement parameters [$U(\mathrm{H}) = 1.5U_{\mathrm{eq}}(\mathrm{C_{methyl}})$, $U(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{C})$ or $U(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{N})$] using a riding model with C—H(methyl) = 0.98, C—H(aromatic) = 0.95 or N—H = 0.88 Å.

Data collection: *SMART* (Siemens, 1995). Cell refinement: *SMART*. Data reduction: *SAINT* (Siemens, 1995). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*96 (Sheldrick, 1996*b*). Molecular graphics: *XP* in *SHELXTL-Plus* (Sheldrick, 1991).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1120). Services for accessing these data are described at the back of the journal.

References

Emeléus, H. J. & Rao, G. S. (1958). *J. Chem. Soc.* pp. 4245–4250.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Fleischer, H., Hensen, K. & Stumpf, Th. (1996). *Chem. Ber.* **129**, 765–771.

Hensen, K., Roßmann, H. & Bensch, W. (1992). *Z. Anorg. Allg. Chem.* **610**, 145–150.

Hensen, K. & Wagner, H. B. (1976). *Chem. Ber.* **109**, 411–414.

Hensen, K., Zengerly, Th., Müller, Th. & Pickel, P. (1988). *Z. Anorg. Allg. Chem.* **558**, 21–27.

Hensen, K., Zengerly, Th., Pickel, P. & Klebe, G. (1983). *Angew. Chem.* Suppl. 9, pp. 973–984.

Lemke, A. (1996). Diplomarbeit, University of Frankfurt/Main, Germany.

Mazo, F. N., Bobilev, A. P. & Troyanov, S. I. (1987). *Vestn. Mosk. Univ. Khim.* **28**, 459–462.

Rao, G. S. (1960). *Z. Anorg. Allg. Chem.* **304**, 176–180.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1991). *SHELXTL-Plus.* Release 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (1996*a*). *SADABS. Program for Empirical Absorption Correction of Area Detector Data.* University of Göttingen, Germany.

Sheldrick, G. M. (1996*b*). *SHELXL96. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Siemens (1995). *SMART* and *SAINT. Area-Detector Control and Integration Software.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Sobota, P., Utko, J. & Lis, T. (1984). *J. Chem. Soc. Dalton Trans.* pp. 2077–2079.

Acta Cryst. (1997). C**53**, 1585–1588

trans-Dichloro(1,4,8,11-tetrazacyclotetradecane)cobalt(III) Chloride Tetrahydrate 0.47-Hydrochloride

Martha E. Sosa-Torres[a] and Rubén A. Toscano[b]

[a]*División de Estudios de Posgrado, Facultad de Química, Universidad Nacional Autónoma de México, Ciudad Universitaria, Coyoacán 04510, México, DF, México, and* [b]*Universidad Nacional Autónoma de México, Instituto de Química, Circuito Exterior, Ciudad Universitaria, Apartado Postal 70-213, México, DF, México. E-mail: mest@servidor.unam.mx*

(Received 6 November 1996; accepted 19 May 1997)

Abstract

The crystal and molecular structures of the title compound, $[\mathrm{CoCl_2(C_{10}H_{24}N_4)}]\mathrm{Cl.4H_2O.0.47HCl}$, have been determined and establish that the *trans*-$[\mathrm{CoCl_2(cyclam)}]^+$ cations crystallize as the *trans-RSSR* species. The Co atom occupies a crystallographic centre of symmetry and is in a tetragonally elongated octahedral coordinated array, comprising the four N atoms of the macrocycle and two Cl atoms. The chloride counterion exhibits statistical disorder, while one of the solvate water molecules also exhibits orientational disorder as a result of partial protonation. In the crystal packing, all possible hydrogen bonds are formed. The *trans*-$[\mathrm{CoCl_2(cyclam)}]^+$ cations are stacked into columns along the **b** direction forming channels which are occupied by the chloride counterion and the water molecules.

Comment

In studies of the details of the base-catalyzed substitution reactions of amine (aniono) cobalt(III) complexes, a number of systems have been found where the rate constants (k_2) for solvolysis of the amido conjugate base forms are of comparable magnitude with, or even significantly greater than, the rate constants (k_{-1}) for the reprotonation of these forms (Lichtig, Sosa & Tobe, 1984; Ahmed & Tobe, 1974; Marangoni, Panayotou & Tobe, 1973; Poon & Tobe, 1968). The *trans* stable isomer of the dichloro(cyclam)cobalt(III) complex was the first example (Poon & Tobe, 1968) for which it was shown that $k_{-1} << k_2$; in that study, the *RSSR* configuration had been assumed, but no X-ray study had been reported.

In addition to the geometric (*trans–cis*) isomerism in which the ligand is flat or folded, it is necessary to take into account further isomerism, arising from the configuration of the coordinated amine N atoms. Moreover, as far as we know, this is the first example of