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Di-μ-chloro-bis({[bis(trimethylsilyl)amino]-dichlorophosphoraniminato}trichlorotantalum(V))

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Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(Si–C) = 0.007 Å
R factor = 0.036
wR factor = 0.088
Data-to-parameter ratio = 26.2

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

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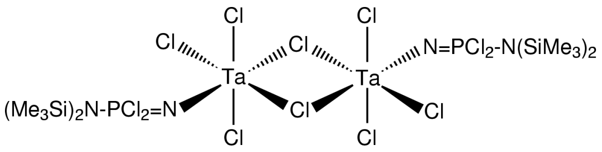
The title compound crystallizes as a centrosymmetric chlorine-bridged dimer, $[Cl_4Ta–N{=}PCl_2\text{-}N(SiMe_3)_2]_2$ or $[Ta_2Cl_8(C_6H_{18}Cl_2N_2PSi_2)_2]$, with one monomer in the asymmetric unit. The Ta atoms adopt a distorted octahedral geometry with the bridging Cl atom and the N atom of the phosphoraniminate ligand occupying axial positions. The Ta—N—P angle within the complex is 155.9 (2)°, with a Ta—N bond length of 1.827 (4) Å; similar P—N distances are observed within the NPN moiety [1.578 (4) and 1.600 (4) Å]. The P atom exists in a distorted tetrahedral geometry, while the silylated terminal N atom is close to planar [angle sum = 358.8 (3)°].

Comment

As part our investigations into the use of novel inorganic heterocycles as monomers for ring-opening polymerization (ROP) reactions (Manners, 1996; Gates & Manners, 1997), we explored the reaction of the silylated aminoiminophosphoranimine $(Me_3Si)_2NPCl_2{=}NSiMe_3$ with various metal halides to give four-membered *M*NPN rings (*M* = group 4 or 5 metal) (Rivard *et al.*, 2001, 2002). In the reaction of $TaCl_5$ with $(Me_3Si)_2NPCl_2{=}NSiMe_3$, we occasionally also obtained the linear isomer $[Cl_4Ta—N{=}PCl_2—N(SiMe_3)_2]_2$, (I).



(I)

Experimental

Under an atmosphere of N_2, one equivalent of $(Me_3Si)_2NPCl_2{=}N\text{-}SiMe_3$ (1.09 g, 3.12 mmol; Niecke & Bitter, 1976) was reacted with $TaCl_5$ (1.04 g, 2.90 mmol) at 298 K in 70 ml of dichloromethane. After 16 h, the volatiles were removed and the remaining white precipitate was washed with hexanes (2 × 50 ml) and recrystallized from dichloromethane (2 ml, 270 K) to give colourless blocks of (I). Yield: 0.11 g (6%). $^{31}P\{^1H\}$ NMR ($CDCl_3$): 19.1 (*s*) p.p.m.; ^1H NMR ($CDCl_3$): 0.66 (*s*) p.p.m.

Crystal data

$[Ta_2Cl_8(C_6H_{18}Cl_2N_2PSi_2)_2]$
M_r = 1198.05
Monoclinic, $P2_1/c$
a = 9.2497 (3) Å
b = 12.3549 (3) Å
c = 17.4418 (6) Å
β = 102.209 (12)°
V = 1948.15 (14) Å^3
Z = 2

D_x = 2.042 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 12 859 reflections
θ = 2.6–27.5°
μ = 6.66 mm^{-1}
T = 150 (1) K
Plate, colourless
0.20 × 0.20 × 0.15 mm

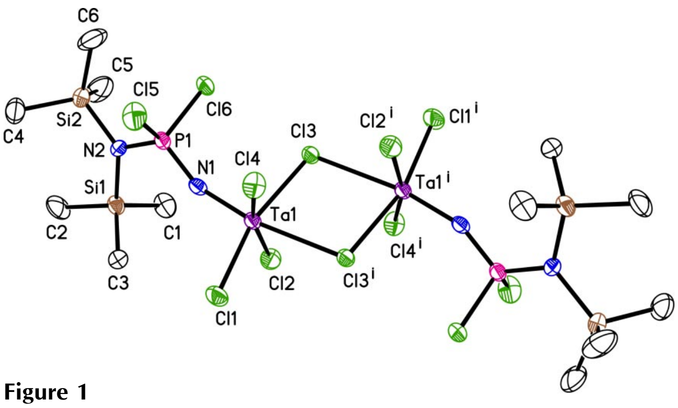


Figure 1
View of the centrosymmetric dimer of (I) with the crystallographic labelling scheme [symmetry code: (i) $1 - x$, $1 - y$, $-z$]. Displacement ellipsoids are at the 30% probability level. The H atoms are not shown.

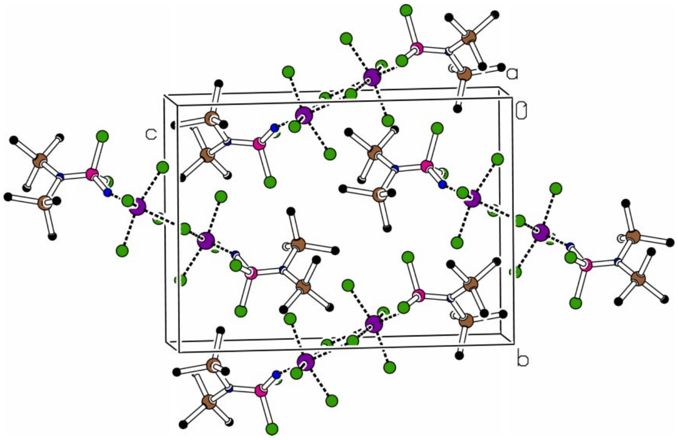


Figure 2
Packing diagram of (I) (Spek, 2002). The following are the atom colour codes: purple Ta, green Cl, pink P, brown Si, blue N and black C.

Data collection

Nonius KappaCCD diffractometer
φ scans and ω scans with κ offsets
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
$T_{\min} = 0.411$, $T_{\max} = 0.524$
11 340 measured reflections
4422 independent reflections
3734 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.050$
$\theta_{\max} = 27.5°$
$h = -11 \rightarrow 11$
$k = -15 \rightarrow 16$
$l = -18 \rightarrow 22$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.088$
$S = 1.03$
4422 reflections
169 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.045P)^2 + 0.0565P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 2.28$ e Å^{-3}
$\Delta\rho_{\min} = -1.40$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ta1—N1	1.827 (4)	Cl5—P1	1.9888 (17)
Ta1—Cl1	2.3204 (13)	Cl6—P1	1.9959 (16)
Ta1—Cl2	2.3346 (13)	P1—N1	1.578 (4)
Ta1—Cl4	2.3438 (12)	P1—N2	1.600 (4)
Ta1—Cl3	2.4688 (11)	Si1—N2	1.840 (4)
Ta1—Cl3^i	2.7177 (12)	Si2—N2	1.833 (4)
N1—Ta1—Cl1	102.65 (12)	Cl1—Ta1—Cl3^i	87.55 (4)
N1—Ta1—Cl2	97.35 (12)	Cl2—Ta1—Cl3^i	83.05 (4)
Cl1—Ta1—Cl2	90.27 (5)	Cl4—Ta1—Cl3^i	82.65 (4)
N1—Ta1—Cl4	96.55 (12)	Cl3—Ta1—Cl3^i	76.56 (4)
Cl1—Ta1—Cl4	90.09 (5)	Ta1—Cl3—Ta1^i	103.44 (4)
Cl2—Ta1—Cl4	165.66 (5)	Cl5—P1—Cl6	102.92 (8)
N1—Ta1—Cl3	93.24 (12)	P1—N1—Ta1	155.9 (2)
Cl1—Ta1—Cl3	164.11 (5)	P1—N2—Si2	121.0 (2)
Cl2—Ta1—Cl3	87.61 (4)	P1—N2—Si1	118.1 (2)
Cl4—Ta1—Cl3	88.13 (4)	Si2—N2—Si1	119.7 (2)
N1—Ta1—Cl3^i	169.78 (11)		

Symmetry code: (i) $1 - x, 1 - y, -z$.

All H atoms were placed in calculated positions, with C—H distances of 0.98 Å, and included in the refinement in riding motion approximation with $U_{\text{iso}} = 1.5U_{\text{eq}}$ of the carrier atom. The methyl groups were allowed to rotate but not to tip. The two largest electron-density peaks of 2.28 and 2.17 e Å^{-3} found in the final difference Fourier were within 1.0 Å of the Ta atom. The next largest peak was 0.81 e Å^{-3}.

Data collection: *COLLECT* (Nonius, 1997–2002); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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