Crystal structure of bis(trichloro-bis(diethylamido)tantalum(V)), $[\text{TaCl}_3(\text{C}_4\text{H}_{10}\text{N})_2]_2$

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Abstract

$\text{C}_{16}\text{H}_{20}\text{Cl}_3\text{N}_2\text{Ta}$, triclinic, $P\bar{1}$ (no. 2), $a = 9.1629(6)$ Å, $b = 10.9357(7)$ Å, $c = 14.1722(9)$ Å, $\alpha = 83.705(1)^\circ$, $\beta = 87.790(1)^\circ$, $\gamma = 87.335(1)^\circ$, $V = 1409.2$ Å³, $Z = 4$, $\rho_{\text{calc}}(F) = 0.025$, $wR_{\text{ref}}(F^2) = 0.065$, $T = 100$ K.

Source of material

Following a published prescription [1], 1.55 mL of $\text{Me}_3\text{SiNEt}_2$ were added dropwise to a solution of 0.72 g TaCl_5 in 20 mL diethyl ether/toluene mixture (1:3). The orange solution was allowed to stir at room temperature for 24 h. Afterwards, the solvent was removed in vacuum, which leads to a ruby red solid. This solid was dissolved in dried pentane and stored at 0 °C for 12 h, -30 °C for 24 h and -65 °C for 24 h. A broken piece of a red, needle-shaped crystal, which was selected from the cold mother solution, was mounted using a nylon loop for X-ray diffraction.

Discussion

The title compound was prepared in the course of our investigations on single source precursors for tantalum nitrides and oxidenitrides [2–4]. The characteristic building unit of the molecular

structure is a bi-octahedral dimer, with all four of the terminal equatorial positions being occupied by diethyl amido groups. Due to the steric demand of the diethyl amido groups the apical chlorine atoms are moved towards each other. This leads to a characteristic bending, with Cl–Ta–Cl angles ranging between 165° and 172°, also known to occur in tantalum pentachloride [5]. The Ta–Cl and the Ta–N bond lengths are in acceptable agreement with those for other Ta compounds [2–4,6]. Also, the remaining distances and angles fit very well to the expectations. The asymmetric unit contains two crystallographically independent $[\text{TaCl}_3(\text{C}_4\text{H}_{10}\text{N})_2]_2$ molecules. Their centers of gravity form an approximate body centered arrangement within the unit cell.

Table 1. Data collection and handling.

Crystal:	red fragment, size 0.15 × 0.20 × 0.30 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	83.39 cm ⁻¹
Diffractometer, scan mode:	SMART APEX I, Bruker AXS, ω
$2\theta_{\text{max}}$:	68.12°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	22085, 11238
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2\sigma(I_{\text{obs}})$, 10717
$N(\text{param})_{\text{refined}}$:	373
Programs:	SHELXS-97 [7], SHELXL-97 [8], ATOMS [9]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U_{iso}
H(11A)	2i	1.161(4)	0.838(4)	0.211(3)	0.029
H(11B)	2i	1.202(4)	0.694(4)	0.225(3)	0.029
H(12A)	2i	1.009(5)	0.822(4)	0.356(3)	0.040
H(12B)	2i	1.172(5)	0.770(4)	0.372(3)	0.040
H(12C)	2i	1.041(5)	0.684(4)	0.373(3)	0.040
H(13A)	2i	0.849(4)	0.609(4)	0.172(3)	0.030
H(13B)	2i	0.929(4)	0.590(4)	0.274(3)	0.030
H(14A)	2i	1.082(5)	0.544(5)	0.099(4)	0.048
H(14B)	2i	1.005(5)	0.431(5)	0.167(3)	0.048
H(14C)	2i	1.139(6)	0.511(5)	0.185(4)	0.048
H(21A)	2i	0.694(4)	0.804(4)	0.233(3)	0.028
H(21B)	2i	0.579(4)	0.726(4)	0.196(3)	0.028
H(22A)	2i	0.565(5)	0.995(4)	0.167(3)	0.038
H(22B)	2i	0.463(5)	0.910(4)	0.240(3)	0.038
H(22C)	2i	0.448(5)	0.906(4)	0.135(3)	0.038
H(23A)	2i	0.679(5)	0.806(4)	-0.050(3)	0.036
H(23B)	2i	0.530(5)	0.808(4)	0.020(3)	0.036
H(24A)	2i	0.720(6)	0.586(5)	0.019(4)	0.054
H(24B)	2i	0.565(6)	0.601(5)	-0.026(4)	0.054
H(24C)	2i	0.576(6)	0.592(5)	0.084(4)	0.054
H(31A)	2i	0.625(4)	0.093(3)	0.307(3)	0.024
H(31B)	2i	0.533(4)	0.103(3)	0.398(3)	0.024
H(32A)	2i	0.839(5)	0.107(4)	0.399(3)	0.032
H(32B)	2i	0.756(4)	-0.013(4)	0.442(3)	0.032

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Table 2. Continued.

Atom	Site	x	y	z	U _{iso}
H(32C)	2i	0.748(4)	0.106(4)	0.491(3)	0.032
H(33A)	2i	0.805(4)	0.267(4)	0.281(3)	0.026
H(33B)	2i	0.732(4)	0.394(4)	0.284(3)	0.026
H(34A)	2i	0.649(4)	0.225(4)	0.161(3)	0.032
H(34B)	2i	0.729(5)	0.332(4)	0.131(3)	0.032
H(34C)	2i	0.572(5)	0.353(4)	0.165(3)	0.032
H(41A)	2i	0.372(4)	0.227(4)	0.263(3)	0.025
H(41B)	2i	0.225(4)	0.293(4)	0.256(3)	0.025

Table 2. Continued.

Atom	Site	x	y	z	U _{iso}
H(42A)	2i	0.267(5)	0.047(4)	0.342(3)	0.036
H(42B)	2i	0.221(5)	0.080(4)	0.232(3)	0.036
H(42C)	2i	0.121(5)	0.102(4)	0.322(3)	0.036
H(43A)	2i	0.185(4)	0.292(4)	0.516(3)	0.024
H(43B)	2i	0.135(4)	0.187(4)	0.459(3)	0.024
H(44A)	2i	0.072(5)	0.435(4)	0.400(3)	0.033
H(44B)	2i	-0.046(5)	0.354(4)	0.446(3)	0.033
H(44C)	2i	0.018(5)	0.343(4)	0.349(3)	0.033

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Ta(1)	2i	0.913249(9)	0.860070(8)	0.087749(6)	0.01601(4)	0.01298(4)	0.01475(4)	-0.00196(3)	-0.00104(3)	-0.00126(3)
Ta(2)	2i	0.469157(9)	0.355050(8)	0.422799(6)	0.01372(4)	0.01336(4)	0.01791(4)	0.00016(3)	-0.00070(3)	-0.00262(3)
Cl(11)	2i	1.16277(6)	0.95552(5)	0.03907(4)	0.0157(2)	0.0174(2)	0.0178(2)	-0.0010(2)	-0.0014(2)	0.0011(2)
Cl(12)	2i	0.88302(6)	1.01033(5)	0.19498(4)	0.0202(2)	0.0181(2)	0.0180(2)	-0.0002(2)	0.0004(2)	-0.0042(2)
Cl(13)	2i	0.96636(7)	0.75052(6)	-0.04487(4)	0.0322(3)	0.0182(2)	0.0197(2)	-0.0030(2)	0.0006(2)	-0.0060(2)
Cl(21)	2i	0.32372(6)	0.51543(5)	0.51814(4)	0.0133(2)	0.0182(2)	0.0262(3)	0.0004(2)	-0.0008(2)	-0.0070(2)
Cl(22)	2i	0.48977(7)	0.23422(6)	0.57051(4)	0.0225(2)	0.0194(2)	0.0193(2)	0.0004(2)	-0.0012(2)	-0.0011(2)
Cl(23)	2i	0.45069(7)	0.51461(5)	0.29573(4)	0.0231(2)	0.0161(2)	0.0234(2)	0.0000(2)	-0.0018(2)	0.0004(2)
N(1)	2i	0.9947(2)	0.7376(2)	0.1833(2)	0.0206(9)	0.0164(8)	0.0210(9)	-0.0007(7)	-0.0037(7)	-0.0016(7)
N(2)	2i	0.7143(2)	0.8060(2)	0.0928(2)	0.0195(9)	0.0194(9)	0.0187(8)	-0.0061(7)	-0.0021(7)	0.0011(7)
N(3)	2i	0.6106(2)	0.2637(2)	0.3501(2)	0.0157(8)	0.0154(8)	0.0203(9)	0.0012(6)	-0.0014(6)	-0.0035(7)
N(4)	2i	0.2979(2)	0.2737(2)	0.3894(2)	0.0148(8)	0.0178(8)	0.0201(9)	-0.0007(6)	0.0000(6)	-0.0031(7)
C(11)	2i	1.1217(3)	0.7605(3)	0.2395(2)	0.023(1)	0.026(1)	0.024(1)	-0.0020(9)	-0.0061(9)	0.0013(9)
C(12)	2i	1.0833(4)	0.7624(3)	0.3441(2)	0.042(2)	0.037(2)	0.021(1)	-0.011(1)	-0.008(1)	0.001(1)
C(13)	2i	0.9427(3)	0.6105(2)	0.2037(2)	0.031(1)	0.017(1)	0.027(1)	-0.0027(9)	-0.007(1)	0.0002(9)
C(14)	2i	1.0454(5)	0.5176(3)	0.1616(3)	0.062(2)	0.021(1)	0.037(2)	0.007(1)	-0.002(2)	-0.006(1)
C(21)	2i	0.6276(3)	0.8067(3)	0.1834(2)	0.018(1)	0.027(1)	0.025(1)	-0.0044(9)	-0.0005(8)	0.0046(9)
C(22)	2i	0.5151(3)	0.9135(3)	0.1817(2)	0.020(1)	0.040(2)	0.035(2)	0.002(1)	-0.004(1)	-0.004(1)
C(23)	2i	0.6276(4)	0.7683(3)	0.0156(2)	0.030(1)	0.033(1)	0.027(1)	-0.013(1)	-0.010(1)	0.004(1)
C(24)	2i	0.6228(5)	0.6279(4)	0.0219(3)	0.064(2)	0.035(2)	0.039(2)	-0.026(2)	-0.020(2)	0.002(1)
C(31)	2i	0.6212(3)	0.1269(2)	0.3697(2)	0.022(1)	0.0155(9)	0.022(1)	0.0016(8)	-0.0007(8)	-0.0035(8)
C(32)	2i	0.7519(3)	0.0795(3)	0.4286(2)	0.027(1)	0.026(1)	0.027(1)	0.009(1)	-0.005(1)	-0.001(1)
C(33)	2i	0.7169(3)	0.3110(2)	0.2747(2)	0.0165(9)	0.022(1)	0.025(1)	-0.0016(8)	0.0029(8)	-0.0020(9)
C(34)	2i	0.6624(3)	0.3035(3)	0.1755(2)	0.027(1)	0.030(1)	0.024(1)	0.003(1)	0.0029(9)	-0.000(1)
C(41)	2i	0.2797(3)	0.2286(2)	0.2957(2)	0.020(1)	0.023(1)	0.020(1)	-0.0016(8)	-0.0022(8)	-0.0040(8)
C(42)	2i	0.2153(3)	0.1028(3)	0.3003(2)	0.028(1)	0.031(1)	0.033(1)	-0.010(1)	0.002(1)	-0.013(1)
C(43)	2i	0.1633(3)	0.2714(2)	0.4510(2)	0.018(1)	0.022(1)	0.021(1)	-0.0019(8)	0.0004(8)	-0.0012(8)
C(44)	2i	0.0439(3)	0.3611(3)	0.4110(2)	0.019(1)	0.031(1)	0.032(1)	0.0044(9)	-0.0024(9)	-0.004(1)

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