Crystal structure of diethyl ether-tetrachloro-diethylamido-tantalum(V), $TaCl_4(C_4H_{10}N)(C_4H_{10}O)$

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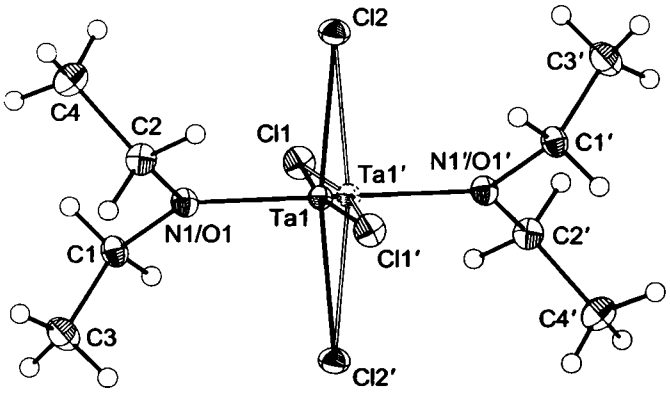

Abstract

$C_8H_{20}Cl_4NOTa$, monoclinic, $P12_1/n1$ (no. 14), $a = 7.701(2)$ Å, $b = 11.414(2)$ Å, $c = 9.021(2)$ Å, $\beta = 107.41(3)°$, $V = 756.7$ Å^3, $Z = 2$, $R_{gt(F)} = 0.020$, $wR_{ref(F^2)} = 0.047$, $T = 100$ K.

Source of material

Following the prescription [1], 230 µL of Me_3SiNEt_2 were added dropwise to a solution of 0.42 g $TaCl_5$ in 20 mL diethyl ether. The yellow solution was allowed to stir at room temperature for 2 h. Afterwards the solvent was removed in vacuo, which lead to an orange solid. This solid was dissolved in fresh diethyl ether again and stored at 0 °C for 12 h, −30 °C for 24 h and −65 °C for 24 h. A broken piece of the orange, needle-shaped crystals, which were selected from the cold mother solution into a high viscosic oil under a constant flow of argon, was mounted inside the oil onto a nylon loop for X-ray diffraction.

Experimental details

For powder diffraction a glass-capillary of 0.3 mm diameter was filled with grinded crystals. Data were collected at room temperature with Cu $K\alpha$ radiation. The lattice parameters were also obtained at RT from LeBail-fit [2] of the powder diffraction results: $a = 7.6925(3)$ Å, $b = 11.5183(7)$ Å, $c = 9.0491(5)$ Å, $\beta = 106.613(4)°$; $\chi^2 = 2.85$, $R_{Bragg} = 0.029$, Si as external standard. The positions of the hydrogen atoms were located from Fourier difference maps and refined by least square methods, applying restrains of isotropic displacement parameters 1.5 times of the attached carbon atom. The tantalum atom was split into two positions due to the deviation of the maximum and minimum libration amplitudes about a factor of approximately four, if Ta would be refined on the primary 2*a* position (0,0,0).

Discussion

The title compound was prepared in the course of our investigation on single source precursors for TaON. It shows a characteristic octahedral surrounding of tantalum by four chlorine, one diethyl amido ligand and one diethyl ether as conventional σ-donor ligand. The crystal structure shows disorder with respect to the positions of the Ta atom, the ether and the amido ligand which was handled by a split position refinement, yielding occupation factors of 0.5, each.

Considering the split model, the Ta—N and Ta—O bond lengths (1.930(1) Å and 2.334(2) Å, respectively) are in acceptable agreement with those found for other Ta compounds (e.g. 1.895 Å and 2.213 Å, respectively, [3]). The other distances and angles fit very well to the respective values. The disorder might be coped with reducing of the symmetry to space group $P2_1$ or Pn. However, refinements with these lower space groups did not lead to an ordering.

Table 1. Data collection and handling.

Crystal:	orange fragment, size 0.30 × 0.40 × 0.50 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	79.48 cm^{-1}
Diffractometer, scan mode:	Bruker AXS SMART APEX CCD, ω
$2\theta_{max}$:	68.98°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	11371, 3073
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2986
$N(param)_{refined}$:	103
Programs:	SHELXTL [4], DIAMOND [5]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1A)	4*e*	0.274(3)	0.050(2)	0.825(3)	0.020
H(1B)	4*e*	0.316(3)	0.180(2)	0.846(3)	0.020
H(2A)	4*e*	−0.115(3)	0.253(2)	0.901(3)	0.021
H(2B)	4*e*	−0.064(3)	0.269(2)	0.747(3)	0.021
H(3A)	4*e*	0.248(4)	0.122(3)	0.584(3)	0.035
H(3B)	4*e*	0.115(4)	0.223(2)	0.592(3)	0.035
H(3C)	4*e*	0.053(4)	0.095(2)	0.579(3)	0.035
H(4A)	4*e*	0.047(4)	0.428(3)	0.916(3)	0.036
H(4B)	4*e*	0.217(4)	0.367(3)	0.886(3)	0.036
H(4C)	4*e*	0.172(4)	0.343(2)	1.042(3)	0.036

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Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ta(1)	4*e*	0.5	0.00695(4)	0.01300(2)	–0.01238(3)	0.00866(7)	0.0132(1)	0.0120(1)	–0.00003(7)	0.00376(5)	–0.00048(7)
Cl(1)	4*e*		–0.31022(5)	0.04429(3)	0.88045(4)	0.0107(1)	0.0228(2)	0.0202(2)	0.0019(1)	0.0027(1)	0.0016(1)
Cl(2)	4*e*		0.00430(5)	0.13065(3)	1.20466(4)	0.0192(2)	0.0195(2)	0.0168(1)	–0.0003(1)	0.0072(1)	–0.0043(1)
O(1)	4*e*	0.5	0.0756(2)	0.1401(1)	0.8758(1)	0.0135(5)	0.0151(5)	0.0184(5)	0.0021(4)	0.0074(4)	0.0008(4)
N(1)	4*e*	0.5	0.0756	0.1401	0.8758	0.0135	0.0151	0.0184	0.0021	0.0074	0.0008
C(1)	4*e*		0.2218(2)	0.1284(1)	0.8008(2)	0.0139(6)	0.0193(6)	0.0185(6)	0.0006(5)	0.0082(5)	0.0012(5)
C(2)	4*e*		–0.0127(2)	0.2572(1)	0.8555(2)	0.0158(6)	0.0161(6)	0.0208(6)	0.0035(5)	0.0055(5)	0.0020(5)
C(3)	4*e*		0.1536(3)	0.1453(2)	0.6252(2)	0.0254(8)	0.0284(8)	0.0187(6)	–0.0004(6)	0.0095(6)	0.0012(6)
C(4)	4*e*		0.1175(3)	0.3552(2)	0.9335(2)	0.0256(8)	0.0183(7)	0.0269(8)	–0.0008(5)	0.0069(7)	–0.0021(6)

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