Crystal structure of tantalum pentachloride, $(TaCl_5)_2$

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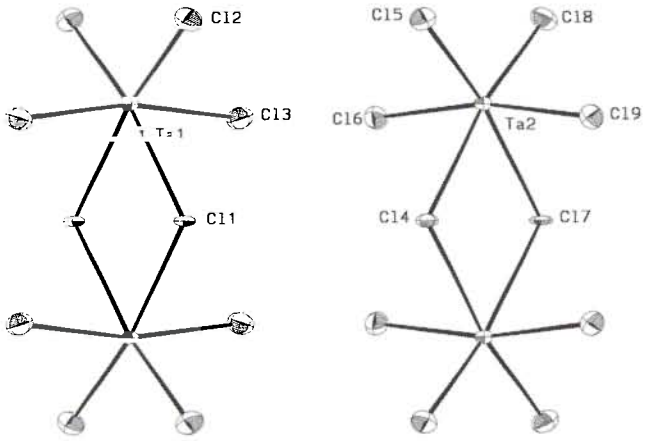

Abstract

$Cl_{10}Ta_2$, monoclinic, $C12/m1$ (No. 12), a = 18.278(3) Å, b = 17.766(5) Å, c = 5.850(1) Å, β = 90.62(2)°, V = 1899.5 Å^3, Z = 6, $R_{gt}(F)$ = 0.061, $wR(F^2)$ = 0.170, T = 193 K.

Source of material

0.11 g of Ta powder and 1 ml of S_2Cl_2 were frozen at 77 K in a glass ampoule which then was evacuated and sealed. The ampoule was heated at a rate of 0.5 K/min up to 475 K and left at that temperature for 14 days. Upon cooling at 0.1 K/min $(TaCl_5)_2$ and sulfur crystallized.

Discussion

As stated by Zalkin and Sands [1], $(TaCl_5)_2$ is isotypic with the modification they found for $(NbCl_5)_2$ and which was later refined [2]. The structure contains two crystallographically independent dimeric molecules. The Cl atoms form a hexagonal closest packing. This also applies to the structure of $(TaI_5)_2$, but it exhibits stacking disorder [3]. For $(NbCl_5)_2$ another modification with cubic closest packing of the Cl atoms is known [4]. For a general review of crystal structures of $(MX_5)_2$ molecules, including yet unkown (hypothetical) structures, see [5]. Recently, several packing varieties were found for $(MoCl_5)_2$ [6]. The average bond lengths are: Ta—Cl(bridge) 2.547(3) Å, Ta—Cl(eq) 2.225(4) Å, Ta—Cl(ax) 2.307(4) Å.

Table 1. Data collection and handling.

Crystal:	yellow column, size 0.20 × 0.43 × 1.25 mm
Wavelength:	Mo K_α radiation (0.71070 Å)
μ:	193.25 cm^{-1}
Diffractometer, scan mode:	Enraf-Nonius CAD4, ω
$2\theta_{max}$:	49.96°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	2600, 1721
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1485
$N(param)_{refined}$:	89
Programs:	HABITUS [7], SHELXL-97 [8], ZORTEP [9]

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

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ta(1)	4*g*	0	0.11061(5)	0	0.0112(6)	0.0047(6)	0.0173(6)	0	0.0016(3)	0
Ta(2)	8*j*	0.33335(3)	0.11067(3)	0.5228(1)	0.0109(5)	0.0058(5)	0.0166(5)	0.0000(2)	0.0004(3)	–0.0004(2)
Cl(1)	4*i*	0.0520(3)	0	0.2250(8)	0.015(2)	0.004(2)	0.018(2)	0	–0.000(2)	0
Cl(2)	8*j*	0.0560(2)	0.1915(2)	0.2408(7)	0.023(2)	0.016(2)	0.029(2)	–0.004(2)	–0.003(2)	–0.004(2)
Cl(3)	8*j*	0.1021(2)	0.0974(2)	–0.2265(7)	0.023(2)	0.014(2)	0.030(2)	0.002(2)	0.009(2)	0.001(2)
Cl(4)	4*i*	0.2806(3)	0	0.7446(8)	0.016(2)	0.005(2)	0.018(2)	0	0.006(2)	0
Cl(5)	8*j*	0.2774(2)	0.1913(2)	0.7611(7)	0.021(2)	0.015(2)	0.029(2)	0.002(2)	0.004(2)	–0.004(2)
Cl(6)	8*j*	0.2316(2)	0.0976(2)	0.2893(7)	0.016(2)	0.016(2)	0.026(2)	–0.001(2)	–0.003(2)	0.005(2)
Cl(7)	4*i*	0.3858(3)	0	0.3014(8)	0.019(3)	0.002(2)	0.020(2)	0	0.006(2)	0
Cl(8)	8*j*	0.3891(2)	0.1911(2)	0.2845(7)	0.023(2)	0.015(2)	0.027(2)	-0.004(2)	0.004(2)	0.002(2)
Cl(9)	8*j*	0.4349(2)	0.0981(2)	0.7560(7)	0.018(2)	0.018(2)	0.023(2)	–0.002(2)	–0.003(1)	–0.002(1)

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References

1. Zalkin, A.; Sands, D. E.: The crystal structure of $NbCl_5$. Acta Crystallogr. **11** (1958) 615-619.
2. Hönle, W.; v. Schnering, H. G.: Crystal structure of niobium pentachloride. Z. Kristallogr. **191** (1990) 139-140.
3. Müller, U.: Die Kristallstruktur von Tantalpentaiodid und ihre Fehlordnung. Acta Crystallogr. **B35** (1979) 2502-2509.
4. Cotton, F. A.; Kibala, P. A.; Matusz, M.; Sandor, R. B. W.: Structure of a second polymorph of niobioum pentachloride. Acta Crystallogr. **C47** (1991) 2435-2437.
5. Müller, U.: Strukturmöglichkeiten für Pentahalogenide mit Doppeloktaeder-Molekülen $(MX_5)_2$ bei dichtester Packung der Halogenatome. Acta Crystallogr. **A34** (1978) 256-267.
6. Beck, J.; Wolf, F.: Three new polymorphic forms of molybdenum pentachloride. Acta Crystallogr. **B53** (1997) 895-903.
7. Herrendorf, W.; Bärnighausen, H.: HABITUS, Programm zur Optimierung der Kristallgestalt für die Absorptionskorrektur. University of Karlsruhe, Germany 1993, 1996.
8. Sheldrick, G. M.: SHELXL-97, Program for crystal structure determination. University of Göttingen, Germany 1997.
9. Zsolnay, L.: ZORTEP, PC version of ORTEP (C. K. Johnson). University of Heidelberg, Germany 1993.