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Crystal structure of (benzoylacetonato-κ^2*O*,*O*′)dichloridodimethoxidotantalum(V), $C_{12}H_{15}Cl_2O_4Ta$

Leandra Herbst*, Hendrik G. Visser and Andreas Roodt

Department of Chemistry, University of the Free State, P.O. Box 339, Bloemfontein 9300, South Africa

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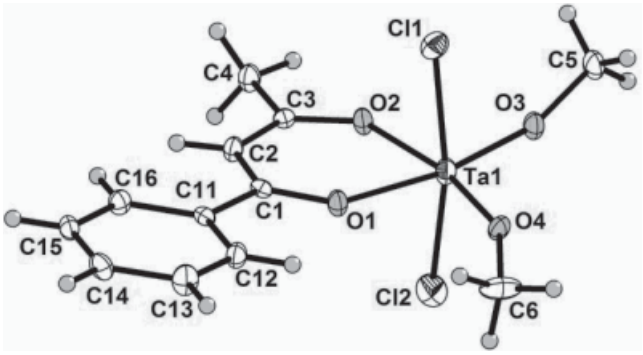

Abstract

$C_{12}H_{15}Cl_2O_4Ta$, monoclinic, $P2_1/c$ (no. 14), a = 15.318(5) Å, b = 12.194(4) Å, c = 7.982(5) Å, β = 93.990(4)°, V = 1487.3 Å^3, Z = 4, $R_{gt}(F)$ = 0.0296, $wR_{ref}(F^2)$ = 0.0639, T = 100 K.

Table 1. Data collection and handling.

Crystal:	yellow plates, size 0.154×0.301×0.402 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	77.54 cm^{-1}
Diffractometer, scan mode:	Bruker APEX-II CCD, φ and ω
$2\theta_{max}$:	56°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	24935, 3600
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 3468
$N(param)_{refined}$:	172
Programs:	SHELX [19], SAINT [20], DIAMOND [21], WinGX [22]

Source of material

$TaCl_5$ (0.1326 g; 0.37 mmol) was carefully dissolved in absolute methanol (5 ml) (caution: exothermic reaction) and benzoylacetone (0.061 g; 0.37 mmol) was slowly added to the solution. The yellow solution was stirred for one hour at room temperature and the covered solution was left to stand at 252 K for 24 hours after which yellow crystals, suitable for X-ray diffraction were obtained. (Yield: 0.1094 g, 62%). **UV/Vis**: λ^{MeOH}_{max} = 314 nm, ε = 179 cm^{-}·M^{-1}; **IR**: ν_{CO} 1524.8 cm^{-1}. **^{1}H NMR** (600 MHz, Methanol-d_4): δ = 8.04 (m, Ph-5H), 3.32 (s, OMe-6H), 2.20 (s, Me-3H), 2.03 (s, 1H). **^{13}C NMR** (600 MHz, Methanol-d_4): δ = 194.09, 182.75, 134.64, 132.16, 128.64, 126.69, 48.52, 26.11, 24.37.

Experimental details

The methyl and aromatic H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C–H = 0.95 and 0.98 Å and U_{iso}(H) = 1.5U_{eq}(C) and 1.2U_{eq}(C), respectively. The highest peak (3.19 e·Å^{-3}) is located 0.77 Å from Ta1 and the deepest hole (–1.86 e·Å^{-3}) is situated 0.66 Å from Ta1.

* Correspondence author (e-mail: herbstl@ufs.ac.za)

Discussion

β-Diketones, more specifically acetylacetone-type ligands, are strong chelating agents that find applications in homogenous catalysis and the separations industry [1-5]. This study forms part of ongoing research to investigate the interaction of transition metals used in the nuclear industry, specifically zirconium, hafnium, niobium and tantalum, with *O*,*O*′- and *N*,*O*-bidentate ligands [6-14]. The [$TaCl_2(CH_3O)_2$(*phacac*)] (*phacac*H = benzoylacetone) complex crystallized in a monoclinic spacegroup $P2_1/c$, with four molecules per unit cell. The asymmetric unit consists of a tantalum(V) metal centre surrounded by two methoxido groups, two chlorido ligands and one *O*,*O*′-bonded benzoylacetonato ligand. The octahedral environment around the tantalum metal centre is slightly disordered with Ta–O distances varying between 1.837(3) and 2.085(3) Å, while the Ta–Cl distances are 2.3799(15) and 2.4136(13) Å, respectively. The O–Ta–O angles in the equatorial plane are 80.81(12)° for the *phacac* bite angle, with the *trans* O_{phacac}–Ta–OMe angle being 166.73(13) and 170.20(13)° for O1–Ta–O3 and O2–Ta–O4, respectively. The *trans* Cl–Nb–Cl angle is 169.39(4)°. An equatorial plane defined through O1, O2, O3 and O4, shows that the tantalum metal centre is slightly elevated above the plane by 0.046(3) Å, which also illustrates the distorted octahedral geometry of the molecule. All the bond distances and angles are similar to other relevant tantalum(V) structures [15-18].

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

Atom	Site	x	y	z	U_{iso}
H(2)	4*e*	0.7662	0.2412	0.4405	0.022
H(4A)	4*e*	0.9554	0.2590	0.7208	0.034
H(4B)	4*e*	0.8780	0.3381	0.6657	0.034
H(4C)	4*e*	0.9343	0.2854	0.5301	0.034
H(5A)	4*e*	0.9696	–0.1121	1.1401	0.041
H(5B)	4*e*	0.8712	–0.1275	1.1770	0.041
H(5C)	4*e*	0.9103	–0.0093	1.1644	0.041
H(6A)	4*e*	0.6866	–0.3214	0.7247	0.057
H(6B)	4*e*	0.7259	–0.2849	0.5573	0.057
H(6C)	4*e*	0.6434	–0.2250	0.6187	0.057
H(12)	4*e*	0.5939	–0.0536	0.4116	0.025
H(13)	4*e*	0.4684	–0.0443	0.2354	0.032
H(14)	4*e*	0.4356	0.1133	0.0813	0.027
H(15)	4*e*	0.5282	0.2627	0.1068	0.023
H(16)	4*e*	0.6537	0.2560	0.2846	0.023

Table 3. 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}
C(1)	4*e*	0.7168(3)	0.0923(4)	0.4852(5)	0.018(2)	0.018(2)	0.011(2)	0.001(2)	0.004(2)	–0.001(2)
C(2)	4*e*	0.7759(3)	0.1791(3)	0.5068(6)	0.020(2)	0.014(2)	0.020(2)	–0.001(2)	–0.002(2)	0.003(2)
C(3)	4*e*	0.8484(3)	0.1783(3)	0.6216(5)	0.017(2)	0.016(2)	0.015(2)	0.003(2)	0.002(2)	–0.001(2)
C(4)	4*e*	0.9095(3)	0.2737(4)	0.6358(6)	0.024(2)	0.019(2)	0.023(2)	–0.004(2)	–0.003(2)	0.004(2)
C(5)	4*e*	0.9116(3)	–0.0826(4)	1.1210(6)	0.036(3)	0.023(2)	0.022(2)	–0.001(2)	–0.012(2)	0.003(2)
C(6)	4*e*	0.6978(4)	–0.2600(5)	0.6541(8)	0.039(3)	0.036(3)	0.041(3)	–0.011(2)	0.009(2)	–0.023(3)
C(11)	4*e*	0.6378(3)	0.0997(3)	0.3670(5)	0.016(2)	0.018(2)	0.011(2)	0.000(2)	0.001(2)	–0.001(2)
C(12)	4*e*	0.5810(3)	0.0101(4)	0.3508(6)	0.025(2)	0.016(2)	0.021(2)	–0.001(2)	–0.002(2)	0.004(2)
C(13)	4*e*	0.5060(3)	0.0157(4)	0.2451(7)	0.026(2)	0.022(2)	0.031(3)	–0.009(2)	–0.008(2)	0.002(2)
C(14)	4*e*	0.4861(3)	0.1102(4)	0.1530(6)	0.021(2)	0.027(2)	0.018(2)	–0.003(2)	–0.005(2)	0.002(2)
C(15)	4*e*	0.5415(3)	0.1994(4)	0.1683(5)	0.023(2)	0.019(2)	0.016(2)	0.001(2)	–0.002(2)	0.003(2)
C(16)	4*e*	0.6169(3)	0.1954(4)	0.2745(6)	0.021(2)	0.017(2)	0.021(2)	–0.004(2)	0.000(2)	0.002(2)
O(1)	4*e*	0.7271(2)	0.0012(3)	0.5651(4)	0.023(2)	0.017(2)	0.019(2)	–0.003(1)	–0.006(1)	0.004(1)
O(2)	4*e*	0.8668(2)	0.0977(3)	0.7234(4)	0.022(2)	0.018(2)	0.019(2)	–0.003(1)	–0.004(1)	0.005(1)
O(3)	4*e*	0.8877(2)	–0.0813(3)	0.9461(4)	0.023(2)	0.020(2)	0.022(2)	0.001(1)	–0.005(1)	0.004(1)
O(4)	4*e*	0.7524(2)	–0.1847(2)	0.7441(4)	0.027(2)	0.013(1)	0.023(2)	–0.001(1)	–0.003(1)	0.000(1)
Cl(1)	4*e*	0.71647(7)	0.03444(8)	0.9399(1)	0.0208(5)	0.0162(5)	0.0252(5)	–0.0007(4)	0.0000(4)	–0.0013(4)
Cl(2)	4*e*	0.91084(9)	–0.1106(1)	0.5535(2)	0.0401(7)	0.0330(7)	0.0259(6)	0.0053(5)	0.0054(5)	0.0029(5)
Ta(1)	4*e*	0.81438(1)	–0.05461(1)	0.75852(2)	0.0192(1)	0.01433(9)	0.0170(1)	–0.00032(6)	–0.00309(6)	0.00328(6)

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