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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71698 (6 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST1063]

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$(C_{18}H_{36}N_2O_6Na)_2[Ta_6Cl_{12}(CH_3O)_6]$.-6$CH_3OH$ with Partial Substitution of CH_3O^- by OH^-

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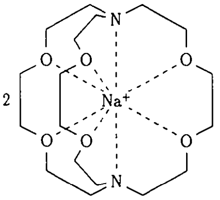
Abstract

Bis[(4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]-hexacosane-κ^2N,κ^6O)sodium] dodeca-μ-chlorohexamethoxy-1κO,2κO,3κO,4κO,5κO,6κO-*octahedro*-hexatantalate–methanol (1/6), $[Na(C_{18}H_{36}N_2O_6)]_2$-$[Ta_6Cl_{12}(CH_3O)_{5.4}(OH)_{0.6}]$.6$CH_3OH$, is built of $(C_{18}H_{36}N_2O_6Na)^+$ cations, $[Ta_6Cl_{12}(OCH_3/lOH)_6]^{2-}$ anions and solvating methanol molecules linked by hydrogen bridges to the anions. The octahedral $[Ta_6Cl_{12}]^{4+}$ cluster unit exhibits two slightly different Ta—Ta distances of 2.978 (1) and 2.987 (1) Å. All four crystallographically distinct Ta—Cl distances are identical within one standard deviation [2.447 (3) – 2.449 (3) Å]. For the terminal methoxy ligand a Ta—O distance of 2.05 (1) Å is observed. Because of the preparation procedure employed, we expected a partial substitution of OCH_3^- by OH^-, which was supported by the structure refinement as only 90% occupancy of the position of the C atom was observed.

Comment

In the course of experiments aimed at the preparation of $[Ta_6Cl_{12}]^{4+}$ clusters with the anions of thermally labile alcohols as outer ligands we attempted to adapt the method developed by Perchenek & Simon (1993) for $[Mo_6Cl_8]^{4+}$ systems to the redox labile $[Ta_6Cl_{12}]^{n+}$ unit ($2 \leq n \leq 4$). We prepared the title compound (I) as a starting material and determined its structure by single-crystal X-ray diffraction for proper characterization.



$[Ta_6Cl_{12}(OCH_3)_{5.4}(OH)_{0.6}]^{2-} \cdot 6CH_3OH$

(I)

The centre of the $[Ta_6Cl_{12}(OCH_3/OH)_6]^{2-}$ anion occupies position 3(*b*) with site symmetry $\bar{3}$ in the hexagonal setting of space group $R\bar{3}$ (No. 148). The octahedron is slightly elongated along the $\bar{3}$ axis passing through the triangles Ta-Ta^{i}-Ta^{ii} and Ta^{iii}-Ta^{iv}-Ta^{v}. The Ta—Ta distance of 2.978 (1) Å within the regular triangles compares with a distance of 2.987 (1) Å between these triangles. Twelve Cl atoms generated from two crystallographically different positions bridge all the edges of the Ta_6 octahedron. Despite the small distortion of the octahedron, all Ta—Cl distances are identical (2.448 ± 0.001 Å) within the precision of the structure determination. Six methanol molecules are connected to the anion *via* O(1)···H(9)—O(2) hydrogen bonds [O(1)···O(2) = 2.684 (15) Å], as similarly observed in the structure of $(C_{18}H_{36}N_2O_6Na)_2[Mo_6Cl_8(CH_3O)_6]$.-6$CH_3OH$, which contains an $[Mo_6Cl_8(CH_3O)_6]^{2-}$ anion (Perchenek & Simon, 1993). The anionic unit is, in certain details, *e.g.* point symmetry and degree of distortion, very similar to that in $[Na_2(CH_3OH)_9]$-$[Ta_6Cl_{12}(CH_3O)_6]$.3CH_3OH (Brničević, McCarley, Hilsenbeck & Kojić-Prodić, 1991), where methanol molecules are also coordinated to each OCH_3^- ligand by hydrogen bonds.

The Na atom occupies position 6(*c*) in the cation with site symmetry 3 for the whole cation. The six O and two N atoms of the cryptand are coordinated to the Na ion to form a distorted cube, as observed in many other cases.

The arrangement of ions can be derived easily from a rhombohedrally distorted anti-calcium fluoride-type structure.

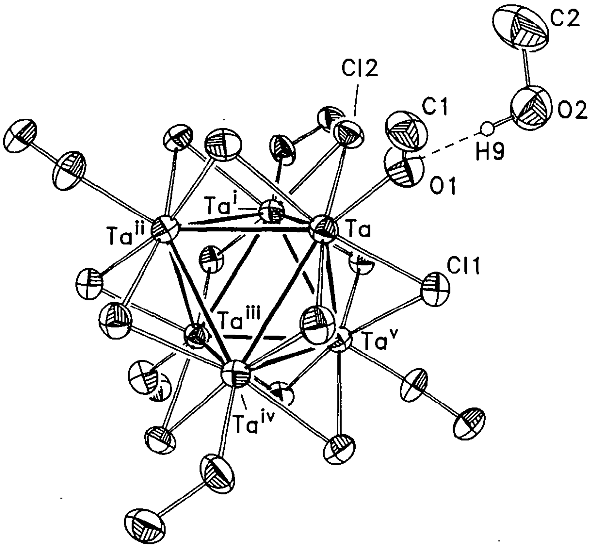


Fig. 1. The $[Ta_6Cl_{12}(OCH_3/OH)_6]^{2-}$ anion drawn at a probability level of 50%. Most H atoms and some labels have been omitted for clarity. One of the hydrogen-bonded methanol molecules is shown. Roman superscripts refer to the symmetry codes given in Table 2.

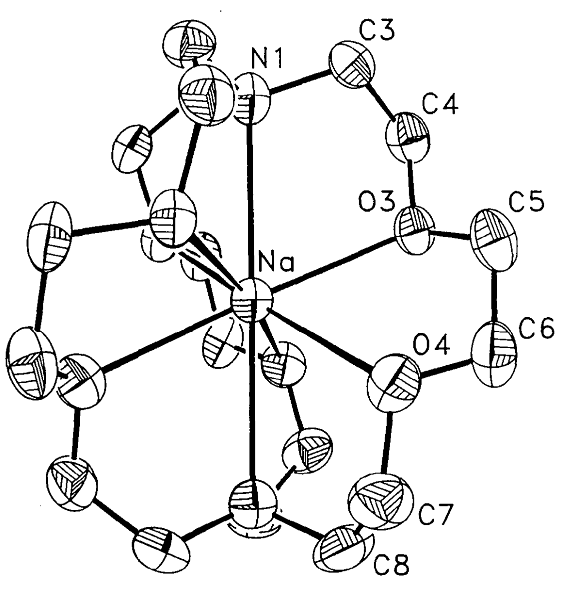


Fig. 2. The $(C_{18}H_{36}N_2O_6Na)^+$ cation drawn at a probability level of 50%.

Experimental

1.68 g (0.8 mmol) $Na_2Ta_6Cl_{12}(OCH_3)_6.12CH_3OH$, prepared according to Brničević, Muštović & McCarley (1988), was dissolved in 15 ml of dry methanol and mixed with 0.604 g (1.6 mmol) $C_{18}H_{36}N_2O_6$ (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane; Merck, Germany) in 25 ml methanol. The volume of the mixture was reduced to 15 ml *in vacuo* and after three days in contact with the vapour of diethyl ether, 1.55 g of the title compound was isolated (73% yield).

Crystal data

$[Na(C_{18}H_{36}N_2O_6)]_2[Ta_6Cl_{12}(CH_3O)_{5.4}(OH)_{0.6}].6CH_3OH$
$M_r = 2679.5$
Rhombohedral
$R\overline{3}$ (hexagonal obverse setting)
$a = 15.068$ (2) Å
$c = 32.303$ (6) Å
$V = 6352$ (2) Å^3
$Z = 3$
$D_x = 2.101$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 50 reflections
$\theta = 13-17.5°$
$\mu = 8.087$ mm^{-1}
$T = 173$ K
Hexagonal platelet
0.45 × 0.4 × 0.4 mm
Brown

Data collection

Syntex $P2_1$ four-circle diffractometer
ω-2θ scans
Absorption correction: empirical, ψ-scans
$T_{\min} = 0.622$, $T_{\max} = 0.797$
2504 measured reflections
2230 independent reflections
1846 observed reflections $[F_o > 3\sigma(F_o)]$
$R_{\rm int} = 0.0354$
$\theta_{\max} = 24°$
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 14$
$l = -36 \rightarrow 36$
3 standard reflections monitored every 60 reflections intensity variation: 1.0013 to 0.9531, smoothed

Refinement

Refinement on F
$R = 0.0424$
$wR = 0.0427$
$S = 1.2085$
1846 reflections
157 parameters
$w = 1/\{[\sigma^2(F) + 0.0001F^2] \times [1-\exp\{-4(\sin\theta/\lambda)^2\}]\}$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 1.58$ e Å^{-3}
$\Delta\rho_{\min} = -1.58$ e Å^{-3}
Atomic scattering factors from *SHELXTL-Plus* (Sheldrick, 1991)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Ta	0.37090 (3)	0.57609 (3)	0.20447 (1)	0.0275 (2)
Cl(1)	0.5236 (2)	0.6049 (2)	0.16649 (9)	0.0339 (12)
Cl(2)	0.4825 (2)	0.7105 (2)	0.25316 (8)	0.0348 (12)
O(1)	0.4130 (6)	0.4911 (6)	0.2403 (3)	0.041 (4)
C(1)†	0.3549 (11)	0.3960 (10)	0.2592 (4)	0.041 (6)
O(2)	0.6054 (9)	0.5600 (8)	0.2668 (3)	0.061 (5)
C(2)	0.6078 (16)	0.5810 (17)	0.3087 (6)	0.091 (11)
Na	2/3	1/3	0.1337 (2)	0.037 (2)
N(1)	2/3	1/3	0.2183 (6)	0.040 (5)
N(2)	2/3	1/3	0.0484 (6)	0.046 (6)

O(3)	0.4894 (6)	0.2592 (6)	0.1629 (3)	0.040 (4)
O(4)	0.5634 (7)	0.4094 (7)	0.1025 (3)	0.051 (4)
C(3)	0.5621 (9)	0.3049 (10)	0.2321 (4)	0.042 (5)
C(4)	0.4821 (10)	0.2252 (10)	0.2052 (4)	0.046 (6)
C(5)	0.4446 (11)	0.3220 (10)	0.1563 (5)	0.050 (7)
C(6)	0.4577 (10)	0.3509 (11)	0.1121 (5)	0.052 (6)
C(7)	0.5842 (13)	0.4374 (12)	0.0603 (4)	0.058 (7)
C(8)	0.5899 (13)	0.3577 (14)	0.0345 (4)	0.061 (8)

† Atom C(1) was refined at 90% occupancy.

Table 2. *Selected geometric parameters* (Å, °)

Ta—Ta^{i}	2.978 (1)	O(1)—C(1)	1.39 (2)
Ta—Ta^{iv}	2.987 (1)	O(2)—C(2)	1.39 (2)
Ta—Cl(1)	2.447 (3)	O(1)—O(2)	2.68 (2)
Ta—Cl(1^{iv})	2.449 (3)	Na—N(1)	2.73 (2)
Ta—Cl(2)	2.449 (3)	Na—N(2)	2.76 (2)
Ta—Cl(2^{ii})	2.447 (3)	Na—O(3)	2.508 (9)
Ta—O(1)	2.049 (10)	Na—O(4)	2.557 (12)
Cl(1)—Ta—Cl(2^{ii})	165.0 (1)	O(3)—Na—O(4)	66.2 (3)
Ta—Cl(1)—Ta^{v}	75.2 (1)	O(3)—Na—O(3^{vi})	106.8 (3)
Ta—O(1)—C(1)	131.3 (9)	O(4)—Na—O(3^{vi})	170.3 (2)
N(1)—Na—O(3)	67.9 (2)	O(4)—Na—O(3^{vii})	82.1 (2)
N(1)—Na—O(4)	113.2 (3)	O(4)—Na—O(4^{vi})	105.4 (3)

Symmetry codes: (i) $1 - y, 1 - y + x, z$; (ii) $-x + y, 1 - x, z$; (iii) $\frac{2}{3} - x, \frac{4}{3} - y, \frac{1}{3} - z$; (iv) $y - \frac{1}{3}, \frac{1}{3} - x + y, \frac{1}{3} - z$; (v) $\frac{2}{3} + x - y, \frac{1}{3} + x, \frac{1}{3} - z$; (vi) $1 - y, -y + x, z$; (vii) $1 + y - x, 1 - x, z$.

The brown crystals are sensitive to moisture and air and so crystals were selected under dry petroleum, fixed with grease and sealed in glass capillaries (0.5 mm diameter) under an atmosphere of argon saturated with methanol. Despite these precautions, the crystals decomposed at room temperature within one day. Another crystal was sealed and immediately transferred to a four-circle diffractometer and cooled to 173 K at a rate of 15 K h^{-1}. Rhombohedral lattice type and Laue class $\bar{3}$ followed from a rapid data collection. The positions of the Ta and Cl atoms were determined by the Patterson method, all other non-H atoms being located in difference Fourier syntheses. The H atoms were located easily after refinement with anisotropic temperature coefficients. All methyl and methylene H atoms were refined with the C—H distance set to 0.96 Å while the isotropic displacement parameter was kept at a common value within the methyl and methylene groups. The acidic H(9) atom of the methanol molecule was refined with an isotropic displacement parameter. Final calculations were performed with the H atoms riding on their associated C atoms.

Because of the high water content of the starting material and oxidation in an oxygen atmosphere, we suspected partial substitution of OCH_3^- by OH^-. Indeed, the refined site occupancy of the C(1) atom was only 0.90 (5). To check the significance of the deviation from unity we refined the occupancy of atoms O(1) and C(3). The values of 1.00 (3) and 1.01 (6) for O(1) and C(3), respectively, support our result for C(1). Therefore, C(1) and the connected H atoms were refined at 90% occupancy in the final least-squares cycles. All calculations were performed on a VAX 3200 computer using the *SHELXTL-Plus* program package (Sheldrick, 1990).

The Ta—Ta distances and their e.s.d.'s did not change when the refinement was performed with 2174 $F_o > 1\sigma(F_o)$ data or with all 2230 $(F_o)^2$ data. Nevertheless, the significance of the slight difference needs to be checked carefully with more precise and extensive data.

We wish to thank the unknown referee for valuable suggestions.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71635 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SH1052]

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Acta Cryst. (1994). C**50**, 697–700

Di-μ-chlorobis[hydrogen bis(diphenylphosphinito)(1 −)-*P*,*P*′]dipalladium, $[Pd_2Cl_2\{(C_6H_5)_2PO\cdots H\cdots OP(C_6H_5)_2\}_2]$

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Abstract

The title compound consists of dinuclear chloro-bridged palladium units with two coordinated diphenylphosphinito groups per Pd atom, linked by a hydrogen bridge. The average O···O distance in the O···H···O bridges of the two independent molecules is 2.406 (4) Å, which is comparable to values in similar phosphinato groups.

Comment

As part of a study on the reactions of secondary phosphines with palladium complexes, we reacted an orthometallated azobenzenepalladium chloride dimer (Bruce, Liddell & Pain, 1989) with diphenylphosphine in toluene. The initial product was orange in colour; recrystallization in air using dichloromethane/methanol gave a small quantity of pale yellow material. A second recrystallization from nitromethane gave pale yellow needles, which surprisingly contained no nitrogen. In order to establish the structure, an X-ray diffraction study was performed and this revealed the complex to be the title