

Fig. 1. Thermal ellipsoid drawing of $\text{trans-[Pt(H)\{P(C}_6\text{H}_{11}\}_3\}_2\text{-(NCCH}_3\text{)}]^+$ with the atom-labeling scheme and 30% probability thermal ellipsoids.

this distortion depends on both the size of the ligand X and the Pt— X bond distance.

The phosphorus-bound carbons of the PCy_3 ligands [C(11), C(21), C(31) and C(41), C(51), C(61)] are nearly eclipsed with one another when viewed along the P—P vector. This feature of the structure is common to $\text{trans-(PCy}_3\text{)}_2\text{PtHX}$ compounds containing a planar X ligand that is perpendicular to the PtP_2H plane (Clark & Hampden-Smith, 1987). The Pt—N distance of 2.079 (6) Å is longer than that of

$\text{trans-PtCl}_2(\text{NCC}_6\text{H}_5)_2$, 1.95 (2) Å (Lauher & Ibers, 1975), probably because of the large steric demands of the bulky PCy_3 ligands. The NCCH_3 ligand is essentially linear [Pt—N(1)—C(1) = 174.6 (6)°].

The BPh_4^- anion shows some distortion from regular tetrahedral symmetry, with C—B—C angles ranging from 102.8 (7) to 113.2 (7)°. The CH_2Cl_2 molecule is entirely regular. The cation, anion and solvent of crystallization are all discrete. Considerable thermal motion gives rise to significant apparent distortions in PCy_3 .

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Structure of $[\text{Na}_2(\text{CH}_3\text{OH})_9][\text{Ta}_6\text{Cl}_{12}(\text{OCH}_3)_6] \cdot 3\text{CH}_3\text{OH}$

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Abstract. Tri- μ -methanol-bis(trimethanolsodium) dodeca- μ -chloro-hexamethoxy- $1\kappa\text{O}, 2\kappa\text{O}, 3\kappa\text{O}, 4\kappa\text{O}, 5\kappa\text{O}, 6\kappa\text{O}$ -octahedro-hexatantalate methanol solvate (1/3), $[\text{Na}_2(\text{CH}_3\text{OH})_9][\text{Ta}_6\text{Cl}_{12}(\text{OCH}_3)_6] \cdot 3\text{CH}_3\text{OH}$, $M_r = 2127.82$, hexagonal, $P6_3/m$, $a = 11.696$ (1), $c = 23.110$ (3) Å, $V = 2738$ (1) Å³, $Z = 2$, $D_x = 2.581$ g cm⁻³, $\lambda(\text{Mo K}\alpha) = 0.71073$ Å, $\mu = 124.65$ cm⁻¹, $F(000) = 1964$, $T = 143$ K, final $R = 0.045$, $wR = 0.053$ for 735 observed reflections with $I > 3\sigma(I)$. The crystal structure reveals a dimeric cation, $[\text{Na}_2(\mu\text{-CH}_3\text{OH})_3(\text{CH}_3\text{OH})_6]^{2+}$ with octahedral environment about sodium (Na—O bridging,

2.45 Å; Na—O terminal, 2.37 Å). The octahedral cluster unit, $[\text{Ta}_6\text{Cl}_{12}(\text{OCH}_3)_6]^{2-}$ exhibits Ta—Ta distances of 2.994 (2) and 2.975 (2) Å with Ta—Cl from 2.434 (6) to 2.456 (5) Å (all bridging). Six methoxy groups are in terminal positions with a Ta—O distance of 2.04 (2) Å. The structure is held together by a network of hydrogen bonds between the cations, cluster anions and solvent (methanol) molecules.

Introduction. The research work presented here is part of a project on the investigations of the hexa-

nuclear cluster units M_6 with $M = \text{Nb, Ta, Mo, W}$ (Brničević, Ružić-Toroš & Kojić-Prodić, 1985; Brničević, Mustović & McCarley, 1988). Niobium and tantalum hexanuclear halide clusters $[M_6X_{12}]^{n+}$, $M = \text{Nb, Ta, } X = \text{Cl, Br, I}$, exist in three different oxidation states with $n = 2, 3$ or 4 (McCarley, Hughes, Cotton & Zimmerman, 1965; Spreckelmeyer & Schäfer, 1967). Crystal structures of niobium chloride clusters are known for all n values, and thus, the interatomic distances Nb—Nb and Nb—Cl within the series have been compared (Koknat & McCarley, 1974). However, for the tantalum derivatives data from a limited number of structures are available and bonding parameters as a function of n and X are not so well established. Here we report on the modified preparative procedure used to obtain single crystals of the title cluster (Brničević *et al.*, 1988) and its crystal structure.

Experimental.

Single crystal preparation. A methanolic solution of sodium methoxide was added to a suspension of $[(\text{C}_2\text{H}_5)_4\text{N}]_2[(\text{Ta}_6\text{Cl}_{12})\text{Br}_6]$ (0.250 g), prepared by a published procedure (Hughes, Meyer, Fleming & McCarley, 1970) in methanol in a molar ratio 8:1, respectively. The mixture was stirred until all $[(\text{C}_2\text{H}_5)_4\text{N}]_2[(\text{Ta}_6\text{Cl}_{12})\text{Br}_6]$ was dissolved (~ 10 d). The dark-red solution was filtered off in a dry box and the amount of methanol was reduced on the vacuum line until a volume of 2–3 ml was reached. The clear solution was stored under vacuum and allowed to crystallize. The dark-red, needle-like crystals that appeared after a few days were kept under the mother solution until a crystal was selected and immediately inserted into the cold N₂ stream of the low-temperature device on the diffractometer.

Data were collected at 143 K on an Enraf–Nonius CAD-4 automated diffractometer.

Unit-cell parameters were obtained from a least-squares refinement of 25 reflections in the 2θ range 17 to 34°. Intensities were collected in the $\theta/2\theta$ scanning mode using graphite-monochromated Mo $K\alpha$ radiation. Three standard reflections, 0016, 0110 and 227, measured every 100 reflections, showed no significant loss of intensities. Lorentz and polarization corrections were made and empirical absorption corrections from ψ -scan data for six reflections were also applied. Equivalent reflections were averaged ($R_{\text{int}} = 0.047$ after absorption correction) to give 1660 unique reflections. The structure was solved by direct methods and refined (on F) by a full-matrix least-squares program. The C atoms were refined with isotropic thermal parameters and the positions of the H atoms were not determined. Crystal and refinement data are given in Table 1. Computer programs were supplied by Enraf–Nonius (Sheldrick, 1986; Enraf–Nonius, 1979); atomic scat-

Table 1. Details of data collection and refinement

| | |
|---|--|
| Crystal size (mm) | 0.3 × 0.3 × 0.5 |
| Diffractometer system | Enraf–Nonius CAD-4 |
| Radiation (monochromated in incident beam) | Mo $K\alpha$ ($\lambda = 0.71073 \text{ \AA}$) |
| Temperature (K) | 143 |
| Scan method | θ – 2θ |
| Data collection range, 2θ | 4–50° |
| Range of h, k, l | 0, 11; 0, 11; 0, 26 |
| Total reflections measured | 3374 |
| No. unique data | 1660 |
| No. with $F_o^2 > 3\sigma(F_o^2)$ | 735 |
| No. parameters refined | 70 |
| Empirical abs. corr. | ψ scan (6 reflections) |
| Trans. factors, max., min. | 1.00, 0.6695 |
| R | 0.0445 |
| wR^* | 0.0530 |
| Quality of fit indicator, S | 1.05 |
| Largest shift/e.s.d., final cycle | 0.03 |
| Difference Fourier peaks ($e \text{ \AA}^{-3}$) | +1.43, –1.78 |

* $w = 1/\sigma^2(F_o)$, where $\sigma(F_o)$ is uncertainty derived from counting statistics.

tering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974, Vol. IV). Final atomic coordinates and equivalent isotropic thermal parameters are given in Table 2, while bond distances and angles are listed in Table 3.*

Discussion. The crystal structure of $[\text{Na}_2(\text{CH}_3\text{OH})_9][\text{Ta}_6\text{Cl}_{12}(\text{OCH}_3)_6].3\text{CH}_3\text{OH}$ is based on the presence of a dinuclear cation (Fig. 1), hexanuclear cluster anion (Fig. 2), and solvent molecules.

The Na atoms are located on the threefold axis $[4(f)]$ position of $P6_3/m$ with an octahedral environment of methanol O atoms O(2) [Na—O(2), 2.37 (2) Å, terminal] and O(3) [Na—O(3), 2.45 (2) Å, bridging]. The atom O(3) is positioned on the crystallographic mirror plane $[6(h)]$. Its symmetry-related O atoms generated by the threefold axis form a triple bridge between two Na atoms of a dimeric cation. Thus the two octahedra of the dimeric unit have a common face defined by the O(3) atoms.

The atoms of the octahedral cluster unit, $[\text{Ta}_6\text{Cl}_{12}(\text{OCH}_3)_6]^{2-}$ are located in general positions $[12(i)]$. The threefold axis of the Ta₆ unit is perpendicular to the octahedral faces defined by the shorter Ta—Taⁱⁱ distances of 2.975 (2) Å; the Ta₆ octahedron is slightly elongated in the direction of the threefold axis with Ta—Taⁱ 2.994 (2) Å. Both Ta—Ta distances are slightly longer than the 2.962 (2) Å found in H₂[(Ta₆Cl₁₂)Cl₆].6H₂O (Thaxton & Jacobson, 1971), which also contains the $[\text{Ta}_6\text{Cl}_{12}]^{4+}$ unit.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53402 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Final atomic coordinates and equivalent isotropic thermal parameters

| | x | y | z | B(Å ²) |
|-------|-------------|-------------|-------------|--------------------|
| Ta | 0.02916 (7) | 0.86991 (7) | 0.05305 (4) | 0.89 (1) |
| Cl(1) | 0.2173 (4) | 0.8842 (4) | 0.0008 (3) | 1.1 (1) |
| Cl(2) | 0.0325 (5) | 0.8476 (5) | -0.1208 (2) | 1.2 (1) |
| Na | 0.3330 | 0.6670 | 0.6778 (7) | 1.3 (2) |
| O(1) | 0.0480 (1) | 0.7420 (1) | 0.1068 (6) | 1.7 (3) |
| O(2) | 0.377 (1) | 0.857 (2) | 0.6243 (8) | 2.1 (4) |
| O(3) | 0.286 (2) | 0.495 (2) | 0.750 | 1.4 (4)* |
| O(4) | 0.2690 (3) | 0.9640 (3) | 0.7790 (1) | 2.9 (8)* |
| C(1) | 0.1660 (2) | 0.7300 (2) | 0.1180 (1) | 2.0 (5)* |
| C(2) | 0.481 (3) | 0.896 (3) | 0.581 (1) | 3.7 (7)* |
| C(3) | 0.370 (4) | 0.433 (4) | 0.750 | 3.0 (9)* |
| C(4) | 0.221 (3) | 1.045 (3) | 0.750 | 1.9 (7)* |

* Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Table 3. Interatomic distances (Å) and bond angles (°) with e.s.d.'s in parentheses

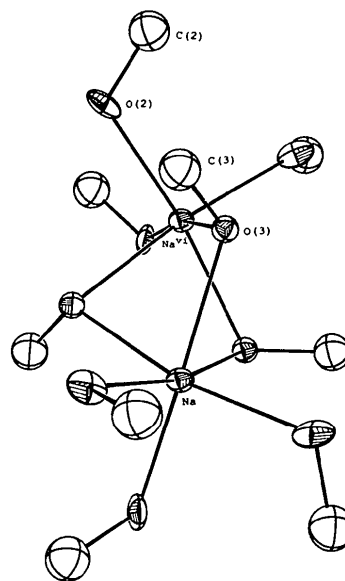
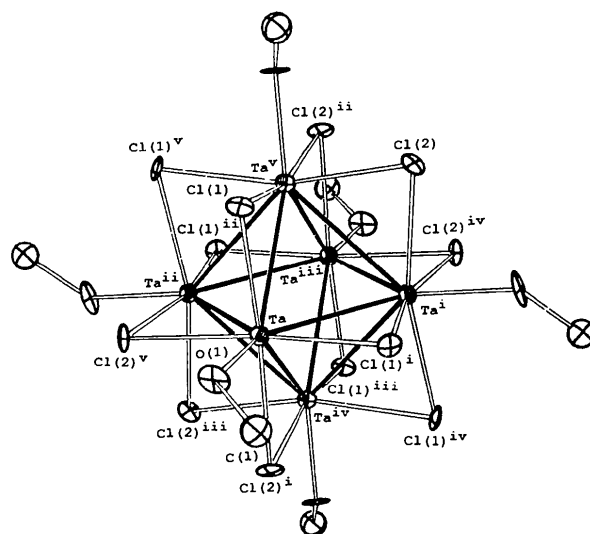
| | | | |
|---|-----------|---|-----------|
| Ta—Ta ⁱ | 2.994 (2) | Na—O(2) | 2.37 (2) |
| Ta—Ta ⁱⁱ | 2.975 (2) | Na—O(3) | 2.45 (2) |
| Ta—Cl(1) | 2.441 (6) | O(1)—C(1) | 1.47 (3) |
| Ta—Cl(1) ⁱ | 2.456 (5) | O(2)—C(2) | 1.45 (4) |
| Ta—Cl(2) ⁱ | 2.452 (6) | O(3)—C(3) | 1.49 (4) |
| Ta—Cl(2) ^v | 2.434 (6) | O(4)—C(4) | 1.48 (5) |
| Ta—O(1) | 2.04 (2) | | |
| Ta ⁱ —Ta—Ta ^{iv} | 60.21 (2) | Cl(1)—Ta—Cl(1) ⁱ | 88.77 (4) |
| Ta ⁱ —Ta—Ta ^v | 59.58 (4) | Cl(1)—Ta—Cl(2) ⁱ | 165.3 (2) |
| Ta ^{iv} —Ta—Ta ^v | 90.00 (0) | Cl(1)—Ta—Cl(2) ^v | 88.2 (2) |
| Ta ⁱ —Ta—Cl(1) | 95.2 (1) | Cl(1) ⁱ —Ta—Cl(2) ⁱ | 88.9 (2) |
| Ta ⁱ —Ta—Cl(1) ⁱ | 52.1 (1) | Cl(1) ⁱ —Ta—Cl(2) ^v | 165.1 (2) |
| Ta ^{iv} —Ta—Cl(1) | 142.5 (1) | Cl(1)—Ta—O(1) | 85.8 (5) |
| Ta ^{iv} —Ta—Cl(1) ⁱ | 95.4 (1) | Cl(1) ⁱ —Ta—O(1) | 82.8 (5) |
| Ta ^v —Ta—Cl(1) | 52.5 (1) | Cl(2) ⁱ —Ta—Cl(2) ^v | 90.3 (3) |
| Ta ^v —Ta—Cl(1) ⁱ | 94.4 (2) | Cl(2) ⁱ —Ta—O(1) | 79.5 (5) |
| Ta ⁱ —Ta—Cl(2) ⁱ | 94.9 (1) | Cl(2) ^v —Ta—O(1) | 82.4 (5) |
| Ta ⁱ —Ta—Cl(2) ^v | 142.8 (1) | Ta—Cl(1)—Ta ^v | 75.4 (1) |
| Ta ^{iv} —Ta—Cl(2) ^v | 52.8 (2) | Ta ⁱ —Cl(2)—Ta ^v | 75.0 (1) |
| Ta ^{iv} —Ta—Cl(2) ⁱ | 52.2 (2) | Ta—O(1)—C(1) | 129. (2) |
| Ta ^v —Ta—Cl(2) ^v | 95.9 (1) | Na—O(2)—C(2) | 114. (2) |
| Ta ^v —Ta—Cl(2) ⁱ | 142.2 (1) | Na—O(3)—Na ⁱⁱ | 85.8 (9) |
| Ta ⁱ —Ta—O(1) | 134.8 (5) | Na—O(3)—C(3) | 118. (1) |
| Ta ^{iv} —Ta—O(1) | 131.7 (5) | | |
| Ta ^v —Ta—O(1) | 138.3 (5) | | |

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

As a consequence of the space-group symmetry, four different Ta—Cl distances in the range 2.434 (6) to 2.456 (5) Å are observed for the $[\text{Ta}_6\text{Cl}_{12}]^{4+}$ cluster unit. However, all Ta—Cl distances in $[\text{Na}_2(\text{CH}_3\text{OH})_9][\text{Ta}_6\text{Cl}_{12}(\text{OCH}_3)_6] \cdot 3\text{CH}_3\text{OH}$ are considerably longer than the 2.414 (5) Å found in $\text{H}_2[(\text{Ta}_6\text{Cl}_{12})\text{Cl}_6] \cdot 6\text{H}_2\text{O}$, but are much closer to the distance of 2.449 (2) Å observed in $\text{NMe}_4[(\text{Ta}_6\text{Cl}_{12})(\text{H}_2\text{O})_6]\text{Br}_4$ (Brničević *et al.*, 1985) with the $[\text{Ta}_6\text{Cl}_{12}]^{3+}$ unit. Evidently, the intracuster distances are not only dependent on the charge $n+$ of the M_6 cluster unit but also on the nature of the ligands in

the terminal positions of the M_6 unit. This structure, with methoxy groups in the terminal positions, $d[\text{Ta}—\text{O}(1)] = 2.04 (2) \text{ \AA}$, is the first to be reported for any alkoxo complex of the $[\text{Ta}_6X_{12}]^{n+}$ units.

The molecular packing of cation and anion moieties in the unit cell is through the hydrogen bonds of the methanol and methoxy groups. Hydrogen bonds between the dimeric cations and the cluster anions are *via* $\text{O}(2)—\text{H}\cdots\text{O}(1)$, 2.775 (4) Å. The C atom of the solvent molecule is located on the mirror

Fig. 1. The cation $[\text{Na}_2(\text{CH}_3\text{OH})_9]^{2+}$ with a crystallographic threefold axis.Fig. 2. The $[\text{Ta}_6\text{Cl}_{12}(\text{OCH}_3)_6]^{2-}$ unit with a crystallographic threefold axis passing through the faces defined by $\text{Ta}^{\text{I}}-\text{Ta}^{\text{III}}-\text{Ta}^{\text{IV}}$ and $\text{Ta}^{\text{I}}-\text{Ta}^{\text{II}}-\text{Ta}^{\text{V}}$.

plane [6(*h*)], but the O atoms O(4) are disordered in position 12(*i*) with 50% occupancy. The intermolecular contacts O(4)—H...O(1), 2.77 (1) Å, between solvent and cluster methoxide groups occur six times per unit cell. The contacts between the dinuclear cation unit [Na₂(CH₃OH)₉]²⁺ and solvent molecules are through O(3)—H...O(4), 2.727 (3) Å.

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Dichloro(*p*-cymene)(*p*-toluidine)ruthenium(II)

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Abstract. [Ru(Cl)₂(C₁₀H₁₄)(C₇H₉N)], *M_r* = 413.33, monoclinic, *P*2₁/*n*, *a* = 8.774 (2), *b* = 12.399 (3), *c* = 15.628 (3) Å, β = 90.97 (2)°, *V* = 1699.91 (2) Å³, *Z* = 4, *D_x* = 1.61 g cm⁻³, Mo *K*α (graphite monochromator), λ = 0.71073 Å, μ = 12.1 cm⁻¹, *F*(000) = 840, *T* = 295 K, *R* = 2.33% for 282 variables and 2682 unique reflections having *I* > 3σ(*I*). The structure confirms that the observed lability of the amine ligand is ascribable to the weak Ru—N bond, reflected in the relatively short Ru—arene bond, 1.637 (2) Å, rather than any steric constraint. Bond alternation, C—C (short) 1.395 (4) Å and C—C (long) 1.414 (4) Å, is present in the cymene ring.

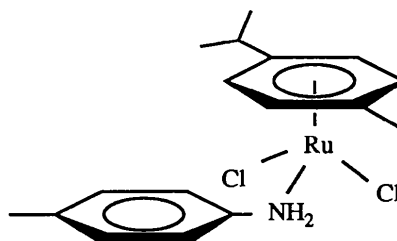
Introduction. The expanding interest in the chemistry of Group 8 arene complexes (Le Bozec, Touchard & Dixneuf, 1989) has led to a need for the structural characterization of a number of simple prototype complexes. Our studies of systems containing the arene ruthenium unit with simple amine ligands (Bates, Begley & Wright, 1990) have provided (*p*-cymene)RuCl₂(*p*-toluidine) as an example. The complex is readily made by simple cleavage of the dimer

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[(*p*-cymene)RuCl₂]₂ in solutions containing an excess of the amine. However, the amine is only weakly bound to the metal and is readily substituted in solution (Bates, Begley & Wright, 1990).



Experimental. The title compound was prepared by a similar method to that used by Bates, Begley & Wright (1990) in preparing the benzene analogue. A red crystal (0.9 × 0.2 × 0.05 mm) was grown from a dichloromethane/hexane solution. Space group *P*2₁/*n* [non-standard setting of *P*2₁/*c* (No. 14)]. Data collected on a Hilger & Watts Y290 diffractometer using ω/2θ scans; 12 reflections having 10 < θ < 12° used to determine lattice parameters; no absorption correction was considered necessary; data with 0 < *h*