The Synthesis of $NR_4[(Ta_6Cl_{12})(H_2O)_6]X_4$ (R = Me or Et, X = Cl or Br) by the Spontaneous Reduction of $[Ta_6Cl_{12}]^{4+}$ to $[Ta_6Cl_{12}]^{3+}$ in Acidic Media: *X*-Ray Structure Analysis of $NMe_4[(Ta_6Cl_{12})(H_2O)_6]Br_4$†

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The treatment of an air-oxidized alkaline methanol–water or aqueous solution of $[Ta_6Cl_{12}]^{4+}$ with concentrated hydrochloric or hydrobromic acid results in spontaneous reduction to $[Ta_6Cl_{12}]^{3+}$; oxidation of some cluster units to hydrated tantalum(V) oxide occurs simultaneously. The isomorphous, paramagnetic series of clusters, $NR_4[(Ta_6Cl_{12})(H_2O)_6]X_4$ (R = Me or Et, X = Cl or Br) has been prepared. Aspects of the reduction of the $[Ta_6Cl_{12}]^{4+}$ unit in acidic media are discussed. The crystal structure of $NMe_4[(Ta_6Cl_{12})(H_2O)_6]Br_4$ has been determined by *X*-ray structure analysis. The compound crystallizes in the cubic space group $Fd\bar{3}m$, with a = 19.926(5) Å and Z = 8. The structure has been determined by Patterson and Fourier methods and refined by full-matrix least squares to R = 0.042. It comprises $[(Ta_6Cl_{12})(H_2O)_6]^{3+}$ octahedra connected by O–H . . . Br hydrogen bonds, NMe_4^+, and Br^- ions. Relevant bond distances are Ta–Ta 2.9059(8), Ta–Cl 2.449(2), and Ta–O 2.22(2) Å, respectively.

According to experimental evidence the cluster $[M_6X_{12}]^{n+}$ (M = Nb or Ta, X = Cl or Br) occurs in three different oxidation states with n = 2, 3, or 4.[1–3] The stable species $[Ta_6Cl_{12}]^{3+}$ was found first in aqueous solution and was prepared by oxidation of $[Ta_6Cl_{12}]^{2+}$ with iron(III) ions[3] in acidic solution. Ions of Co^{III}, Ce^{IV}, Hg^{II}, and Cu^{II} have also been used[4] as oxidants in this reaction, and $KBrO_3$,[5] vanadium(V),[6] or chromium(VI)[7] was employed for the oxidation of $[Ta_6Br_{12}]^{2+}$. The cluster $[Ta_6Br_{12}]^{4+}$ could be reduced by iron(II) ions to $[Ta_6Br_{12}]^{3+}$ and further by Cr^{II} to $[Ta_6Br_{12}]^{2+}$ and was not affected by repeated cycles of oxidation and reduction.[8]

The first solid sample containing the $[M_6X_{12}]^{3+}$ unit, $[Ta_6Cl_{12}]Cl_3{\cdot}6H_2O$,[9] was prepared by oxidation of $[Ta_6Cl_{12}]^{2+}$ in acidic solution by iron(III) ions. Air[10] and aqueous bromine[9b] have been used as oxidants for the preparation of $[Ta_6Cl_{12}]Cl_3{\cdot}7H_2O$ and $[Ta_6Br_{12}]Br_3{\cdot}6H_2O$, respectively. The anhydrous compounds $[Ta_6X_{12}]X_3$ (X = Cl or Br) were prepared by reduction of TaX_5 with tantalum powder.[11] The crystal structures are known for $[Ta_6I_{12}]I_2$,[12] $[(Ta_6Cl_{12})(H_2O)_4]Cl_2{\cdot}3H_2O$,[13] $[Ta_6Cl_{12}]Cl_3$,[14] and also $H_2[(Ta_6Cl_{12})Cl_6]{\cdot}6H_2O$.[15] The structure of $[Ta_6Cl_{12}]Cl_3$ is the only one solved for the $[Ta_6X_{12}]^{3+}$ unit.

In this paper the spontaneous reduction of the cluster $[Ta_6Cl_{12}]^{4+}$ to $[Ta_6Cl_{12}]^{3+}$ in acidic media as a method of preparation of 3+ clusters is discussed, together with the crystal structure of $NMe_4[(Ta_6Cl_{12})(H_2O)_6]Br_4$.

Experimental

Materials.—Aqueous solutions (25%) of NMe_4OH and NEt_4OH were purchased from 'Fluka' and the other chemicals from 'Merck'. The cluster $[Ta_6Cl_{12}]Cl_2{\cdot}8H_2O$ was prepared according to the literature method.[16]

Synthesis of $NR_4[(Ta_6Cl_{12})(H_2O)_6]X_4$ (R = Me *or* Et, X = Cl *or* Br).—The cluster $[Ta_6Cl_{12}]Cl_2{\cdot}8H_2O$ (0.5 g, 0.290 mmol) was dissolved in methanol (20 cm^3) by mixing and warming of the solution at 313 K. After cooling, NMe_4OH (10 cm^3, 0.2 mol dm^{-3}) was slowly added dropwise. During the addition the dark (emerald) green colour of the solution changed to olive-green and finally to dark red. After 2 h the solution was warmed to 313 K over a heating plate and left overnight at room temperature. It was filtered (*ca.* 10 cm^3) in order to remove traces of hydrated tantalum(V) oxide. Concentrated HCl or HBr (4 cm^3) was slowly added dropwise (pH < 1). Upon addition of the first drops a red precipitate of $[Ta_6Cl_{12}][OH]_4{\cdot}10H_2O$[17] appeared which dissolved with further addition of concentrated acid. The resulting clear red acidic solution was left overnight when the colour changed from dark red to olive-green. The solution was filtered again and left to crystallize at ambient temperature. The dark brown crystals that appeared after a few days were washed with concentrated HCl or HBr and air dried; yield 80%.

Physical Measurements.—Tantalum, carbon, hydrogen, and nitrogen analyses were performed as described earlier,[17] and simultaneous determination of chloride and bromide was carried out according to the literature method.[18] Analytical data are summarized in Table 1. Infrared spectra (4 000—200 cm^{-1}) were recorded on a Perkin-Elmer model 580B spectrophotometer (Table 2). Magnetic measurements were performed at 295 K according to the Gouy method. Thermogravimetric measurements were carried out on a Chan RG electromicroanalytical balance with a heating rate of 2 °C min^{-1} in air.

Crystallography.—*Crystal data.* $NMe_4[(Ta_6Cl_{12})(H_2O)_6]Br_4$, M = 2 013.0, cubic, space group $Fd\bar{3}m$ (no. 227), a = 19.926(5), U = 7 911.53 Å^3, Z = 8, D_c = 3.39 Mg m^{-3}, μ(Mo-K_α) = 212.45 cm^{-1}, λ(Mo-K_α) = 0.7107 Å, F(000) = 7 080.

Intensity measurements. The preliminary cell dimensions and space group were determined from oscillation and Weissenberg photographs recorded with Cu-K_α radiation; final cell dimensions were refined from diffractometer measurements using 20 reflections. The intensities were collected for an octahedral crystal of dimensions 0.26 × 0.26 × 0.26 mm, on a Philips PW 1100 computer-controlled four-circle diffractometer in the ω scan mode [scan width 1.60°(θ), scan speed 0.04°(θ) s^{-1}] with graphite-monochromated Mo-K_α radiation. During the data collection differences in the intensities of symmetry-

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† Tetramethylammonium hexa-aquadodeca-μ-chloro-*octahedro*-hexatantalum tetrabromide.

Supplementary data available (No. SUP 56110, 3 pp.): thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Table 1. Analytical, magnetic, and physical data for the complexes (all dark brown)

Complex	Analysis (%)[a]						Decomp. pt.[b] (K)	$\mu_{eff.}$[c]/ B.M.
	Br	C	Cl	H	N	Ta		
(1) $NMe_4[(Ta_6Cl_{12})(H_2O)_6]Cl_4$		2.50	30.75	1.40	0.70	58.90	339	1.57
		(2.6)	(30.9)	(1.30)	(0.75)	(59.15)		
(2) $NEt_4[(Ta_6Cl_{12})(H_2O)_6]Cl_4$		5.10	29.9	1.80	0.80	57.15	374	1.62
		(5.10)	(30.0)	(1.70)	(0.75)	(57.40)		
(3) $NMe_4[(Ta_6Cl_{12})(H_2O)_6]Br_4$	15.7	2.30	21.0	1.20	0.75	53.7	336	1.58
	(15.9)	(2.40)	(21.15)	(1.20)	(0.70)	(53.95)		
(4) $NEt_4[(Ta_6Cl_{12})(H_2O)_6]Br_4$	15.3	4.70	20.4	1.40	0.75	52.15	338	1.65
	(15.45)	(4.65)	(20.5)	(1.55)	(0.70)	(52.45)		

[a] Calculated values are given in parentheses. [b] From thermogravimetric decomposition curves. [c] At 295 K, B.M. ≈ 9.27×10^{-24} A m^2.

Table 2. I.r. absorption bands (1 000—200 cm^{-1}) for complexes (1)—(5)

(1)	(2)	(3)	(4)	(5)*	Assignment
977s	978s	977s	976s		ν(C–N)
946s		946s			
	798w		798w		
600m,br	550m,br	570m,br	530m,br		OH_2 wagging
412m	412m	412m	412m		ν(Ta–O)
326vs	326vs	326vs	326vs	341vs	ν(Ta–Cl_b)
				250s	ν(Ta–Cl_t)

* $H_2[(Ta_6Cl_{12})Cl_6]\cdot6H_2O$; data from ref. 15.

Table 3. Final atom parameters of $NMe_4[(Ta_6Cl_{12})(H_2O)_6]Br_4$ with estimated standard deviations in parentheses

Atom	Position	X/a	Y/b	Z/c
Ta	48 f	0.021 88(4)	0.125	0.125
Cl	96 g	0.125 9(3)	Z/c	0.246 5(1)
O	48 f	0.339 4(8)	0.125	0.125
Br	96 h	0	0.174 4(2)	−0.1744
N	8 b	0.375	0.375	0.375
C	32 e	0.332(3)	X/a	X/a

related reflections were noticed. Therefore the intensities on half of the reciprocal lattice (1 470) were measured in the range $3 < \theta < 30°$. A final set of 375 independent reflections with averaged intensities $[I \geqslant 2\sigma(I)]$ were used in the crystal structure determination. The data were corrected for background, Lorentz and polarization effects and absorption.

Structure solution and refinement. The position of the tantalum atom was determined from a Patterson map. A Fourier synthesis based on the position of this atom revealed chlorine, oxygen, and bromine atoms. The bromine atom exhibited disorder as a consequence of a partly occupied site. A difference synthesis was used to locate the nitrogen and carbon atoms. The final Fourier synthesis indicated no significant residuals for hydrogen atoms. The structure was refined by full-matrix least-squares methods minimizing $\Sigma w(|F_o| - |F_c|)^2$ and with unit weights. Anisotropic refinement resulted in $R = 0.042$. The anisotropic thermal parameter for the carbon atom is rather high $U_{11} = 0.29(6)$ Å^2 but the difference synthesis clearly located its position. Scattering factors from Cromer and Mann[19] were used. An anomalous-dispersion correction for tantalum, chlorine, and bromine atoms was applied according to Cromer and Liberman.[20] Calculations were carried out on a UNIVAC 1110 computer at the University Computing Centre in Zagreb with the *X*-RAY system.[21] Final atomic co-ordinates are listed in Table 3.

Results and Discussion

The reaction of air-oxidized alkaline methanol–water or aqueous solutions[17] of $[Ta_6Cl_{12}]^{4+}$ with concentrated hydrochloric or hydrobromic acid results in spontaneous reduction to $[Ta_6Cl_{12}]^{3+}$ together with oxidation of some cluster units to hydrated tantalum(V) oxide (*ca.* 10%). The presence of the latter can be detected in the crystallization of $[Ta_6Cl_{12}]^{3+}$ clusters. A similar disproportionation reaction of $[Ta_6Cl_{12}]^{4+}$ in acidic solution was observed earlier[3] in the absence of oxidant.

These reactions include several steps. (*i*) Before addition of acid the starting alkaline methanol–water solution of $[Ta_6Cl_{12}]^{2+}$ is completely oxidized by air to $[Ta_6Cl_{12}]^{4+}$ and methanol mostly evaporates. The presence of methanol results in the precipitation of $[Ta_6Cl_{12}]^{4+}$ and $[Ta_6Cl_{12}]^{3+}$ simultaneously. For this reason the solutions were evaporated at 313 K for 2 h and, without addition of acid, left for a further 20 h in the air at room temperature. (*ii*) The amount of acid added must be controlled. With larger amounts (>6 or >10 cm^3 for HCl or HBr respectively) the simultaneous crystallization of $[Ta_6Cl_{12}]^{4+}$ and $[Ta_6Cl_{12}]^{3+}$ occurs rapidly. (*iii*) The reduction reaction is time dependent and the reduction of $[Ta_6Cl_{12}]^{4+}$ to $[Ta_6Cl_{12}]^{3+}$ is complete after leaving the solution with added acid for several hours (usually overnight) at ambient temperature. The crystals of $[Ta_6Cl_{12}]^{3+}$ were obtained after a few days.

The dark brown halide clusters listed in Table 1 are crystalline and according to their *X*-ray powder diffraction patterns, isomorphous solids. They are soluble in methanol, ethanol, and dimethyl sulphoxide. Their magnetic moments (Table 1) indicate the presence of one unpaired electron as expected for the $[Ta_6Cl_{12}]^{3+}$ cluster.[22] Some significant absorption bands in the i.r. spectra are given in Table 2. For comparison, data for the isomorphous compound $H_2[(Ta_6Cl_{12})Cl_6]\cdot6H_2O$,[15] containing the $[Ta_6Cl_{12}]^{4+}$ unit, are also given. Band assignments were made according to the literature.[23–25] The absorption bands in the region 500—600 cm^{-1} orginating from Ta–O (Ta–OH_2) stretching (Table 2) are missing from the spectrum of $H_2[(Ta_6Cl_{12})Cl_6]\cdot6H_2O$, where co-ordinated water molecules are not present. The very strong absorption band found at 326 cm^{-1} for complexes (1)—(4), corresponding to the Ta–Cl_b (b = bridging) vibrations, is observed at 341 cm^{-1} in the spectrum of $H_2[(Ta_6Cl_{12})Cl_6]\cdot6H_2O$ (5) indicating stronger bonding in the latter compound as confirmed by the shorter bond distance from the *X*-ray structure analysis (Table 4). The absorption band corresponding to Ta–Cl_t (t = terminal) is found at 250 cm^{-1} for compound (5), and as expected[25] is absent for the other complexes discussed.

The crystal structure of $NMe_4[(Ta_6Cl_{12})(H_2O)_6]Br_4$ has been established. It consists of NMe_4^+ cations and $[(Ta_6Cl_{12})(H_2O)_6]^{3+}$ octahedra joined in a three-dimensional framework by hydrogen bonds to the Br^- ions (Figure 1). The compounds $NMe_4[(Ta_6Cl_{12})(H_2O)_6]Br_4$ and $H_2[(Ta_6Cl_{12})Cl_6]\cdot6H_2O$[15] are isostructural. The terminal chlorine atoms

Table 4. Interatomic distances (Å) in compounds with $[Ta_6Cl_{12}]^{n+}$ units

	$[Ta_6Cl_{12}]Cl_2\cdot7H_2O$ [13]	$[Ta_6Cl_{12}]Cl_3$ [14]	$NMe_4[(Ta_6Cl_{12})(H_2O)_6]Br_4$	$H_2[(Ta_6Cl_{12})Cl_6]\cdot6H_2O$ [15]
Space group	$P\bar{3}1m$	$Ia3d$	$Fd3m$	$Fd3m$
Cluster unit	$[Ta_6Cl_{12}]^{2+}$	$[Ta_6Cl_{12}]^{3+}$	$[Ta_6Cl_{12}]^{3+}$	$[Ta_6Cl_{12}]^{4+}$
d(Ta–Ta)	2.63(1)—3.27(3)	2.925(4)	2.905 9(8)	2.962(2)
d($Ta-Cl_b$)	2.28(3)—2.86(9)	2.413(12)—2.462(12)	2.449(2)	2.414(5)
d($Ta-Cl_t$)	2.35(14)	2.564(25)		2.507(9)
d(Ta–O)*	2.25(10)		2.22(2)	
d(Cl_b-Cl_b)	2.91(16)—3.95(17)	3.27(5)—3.49(5)	3.450(6), 3.398(6)	3.384(17)
d(Cl_b-Cl_t)	3.29(12)—3.43(12)	3.16(3)—3.39(3)		3.250(8)
d(Cl_b-O)*	2.94(9)—3.16(8)		3.05(1)	

* Oxygen from co-ordinated water molecules.

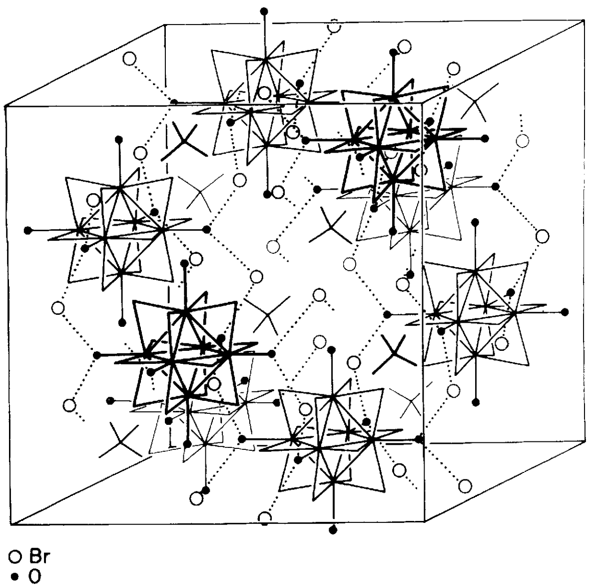

Figure 1. The packing of NMe_4^+, $[(Ta_6Cl_{12})(H_2O)_6]^{3+}$, and Br^-; NMe_4^+ is represented by a tetrahedral stick model. Hydrogen bonds are indicated by dotted lines. For the sake of simplicity, only oxygen and bromine atoms are illustrated and only one of three possible locations for the Br atoms is shown

from the $[(Ta_6Cl_{12})Cl_6]^{2-}$ unit are replaced by oxygen atoms from water molecules. Both structures reveal the same structural patterns. The regular $[(Ta_6Cl_{12})(H_2O)_6]^{3+}$ octahedra (Figure 2) are centred at ($\frac{1}{8}$, $\frac{1}{8}$, $\frac{1}{8}$) and symmetry-related positions; the NMe_4^+ cations are situated in holes (diameter *ca.* 9 Å) with the nitrogen atoms at ($\frac{3}{8}$, $\frac{3}{8}$, $\frac{3}{8}$). In the present structure the bromine atoms occupy one third of the available positions (96 h) in a disordered way. It can be assumed on the basis of the present structure determination that the water molecules in $H_2[(Ta_6Cl_{12})Cl_6]\cdot6H_2O$ occupy the same positions as the bromine atoms but with an occupancy factor of 0.5.

In the title compound the water molecules from the cluster units are involved in hydrogen bonding with Br^- ions, O–H ··· Br [3.168(9) Å] (Figure 1). Interatomic distances are listed in Table 4 and compared with values in other $[Ta_6Cl_{12}]^{n+}$ clusters. The Ta–Ta [2.905 9(8) Å] and Ta–O [2.22(2) Å] bond distances are in accord with the observed lengthening of metal–metal, and shortening of metal–terminal atom, bonds upon oxidation of the cluster unit.[26] The Cl–Cl [3.398(6) and 3.450(6) Å] and Cl–O [3.05(1) Å] distances are in the range characteristic of these cluster species. In the tetramethylammonium ion the C–N distance [1.48(3) Å] is normal for a single carbon–nitrogen bond.

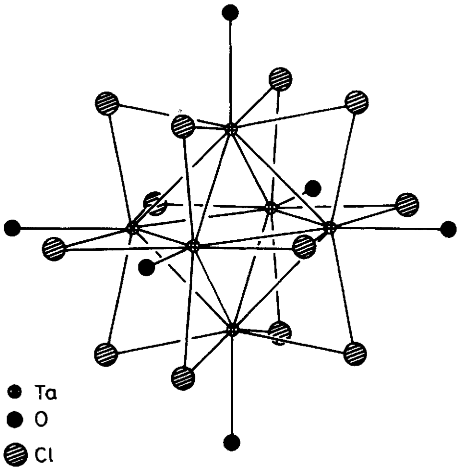

Figure 2. The $[(Ta_6Cl_{12})(H_2O)_6]^{3+}$ cluster unit

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