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Cluster Hydroxides of the Composition $M_2[Ta_6Cl_{12}](OH)_6 \cdot nH_2O$, With M=Na, K, Rb, $(CH_3)_4N^+$ and $(C_2H_5)_4N^+$; Air Oxidation of the Cluster Unit $[Ta_6Cl_{12}]^{2+}$ in Alkaline Medium*

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Air oxidized methanol or methanol-water alkaline (pH > 10) solutions of $[Ta_6Cl_{12}]Cl_2 \cdot 8H_2O$ were used for the preparation of cluster hydroxides of the composition, $M_2[Ta_6Cl_{12}](OH)_6 \cdot nH_2O$ with M = Na, K, Rb, $(CH_3)_4N^+$ and $(C_2H_5)_4N^+$. These crystalline, water-soluble compounds exhibit magnetic and spectral properties confirming the +4 cluster unit.

Aspects of air oxidation of the cluster unit in alkaline medium are discussed. The insoluble cluster hydroxide, $[Ta_6Cl_{12}](OH)_4 \cdot 10H_2O$ and soluble halide clusters, $[Ta_6Cl_{12}]X_4 \cdot nH_2O$ and $[Ta_6Cl_{12}]X_6^{2-}$, X = Cl, Br, are the products of reactions with acids. There is no evidence for entry of the OH^- ions into the inside coordination sphere of the cluster unit.

INTRODUCTION

According to the literature[1-5] the cluster cation $[M_6X_{12}]^{n+}$, M = Nb, Ta; X = Cl, Br, may occur in three different oxidation states with n = 2, 3 and 4. The oxidation potentials for oxidation of these cluster units are known[3,6,7]. It is also known that the $[M_6X_{12}]^{n+}$ cluster framework is not affected by repeated cycles of oxidation and reduction[3]. Experimental evidence from the literature[4] indicates easier oxidation of acidic than of neutral or alkaline solutions of these clusters. In this respect the most sensitive is $[Ta_6Cl_{12}]^{2+}$, whose acidic solutions are slowly oxidized by air oxygen.

The oxidation of these clusters in an alkaline medium has been reported only recently[8]. Investigation of the influence of OH^- ions on these cluster units gave evidence of fast air oxygen oxidation of these clusters, especially $[Ta_6Cl_{12}]^{2+}$, in alkaline medium. This fact was explored for the preparation of a series of +4 cluster hydroxides as described here.

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* Dedicated to Professor D. Grdenić on occasion of his 65th birthday.

RESULTS AND DISCUSSION

The reactions of cluster compounds, $[M_6X_{12}]X_2 \cdot 8H_2O$, M = Nb, Ta, X = Cl, Br, in methanol or methanol-water mixtures with alkali metal, tetramethyl- or tetraethylammonium hydroxides in air or oxygen atmosphere, led to the oxidation of the cluster units in alkaline medium (the exception was $[Nb_6Cl_{12}]Cl_{12} \cdot 8H_2O$). The same reactions in oxygen-free atmosphere were discussed earlier[8]. The oxidation was found to be very fast (within a few hours, Experimental section) especially in methanol only. It was faster than the oxidation of methanol solutions before titration with hydroxides. The methanol solutions of these clusters are acidic ($pH < 3$) as a consequence of reaction with methanol molecules[9] and the oxidation occurs within a few days. It follows that air oxidation of alkaline methanol or methanol-water solutions of these clusters is much faster than air oxidation of acidic solutions of the same clusters. The oxidized alkaline solutions of these clusters were rather unstable. Fast decomposition of the cluster units to hydrated tantalum(V) oxide took place. In this respect the most stable solution was that of $[Ta_6Cl_{12}]^{2+}$ and this fact made possible the isolation of the +4 cluster hydroxides listed in Table I. The decomposition of the cluster units to hydrated tantalum(V) oxide is a function of the temperature of the titrated alcohol or alcohol-water solutions and the hydroxide employed, and is proportionally higher with increasing temperature. It is also higher for alkali metal hydroxides than for tetramethyl- and tetraethylammonium hydroxides. The isolated cluster hydroxides are dark red, crystalline and, as expected for +4 clusters, diamagnetic (Table I) materials. They are soluble in water, dimethyl sulphoxide and *N'N'*-dimethylphormamide. Recrystallisation from water leads to hydrolysis and decomposition of the compounds. The compounds are rather stable at room temperature, losing water molecules slowly over several weeks, and with them their crystallinity and solubility. According to X-ray diffraction patterns, the dehydrated substances are amorphous. It seems that the presence of water molecules and a system of hydrogen bonds are surely responsible for the high crystalline nature of these compounds. The thermogravimetric curves indicate the start of dehydration at about 300K (Table I). The water molecules could be easily removed by drying the substances over KOH, or in an evacuated tube overnight. During these processes the reduction of the cluster unit to 2+ (confirmed spectrophotometrically) together with the formation of traces of hydrated tantalum(V) oxide was observed. The X-ray diffraction patterns indicate isomorphism between sodium and rubidium, but not among the other salts in this series. Especially nice crystals were obtained for tetramethyl- and tetraethylammonium salts, but the crystals were twins and crystal structure determination was not possible.

Reactions with acids. — If aqueous solutions ($5 \cdot 10^{-3}$ mol dm^{-3}) of any of these freshly prepared cluster hydroxides were titrated with diluted (0.1 mol dm^{-3}) HCl or HBr the same titration curves were obtained. A typical one is represented in Figure 1. On addition of the first drops of acid a red precipitate appears and the precipitation is complete on addition of 2 mol of acid/cluster according to the following equation:

$$M_2[Ta_6Cl_{12}](OH)_6 + 2HA \rightarrow [Ta_6Cl_{12}](OH)_4 + 2MA + 2H_2O$$

With further addition of acid the cluster hydroxide, $[Ta_6Cl_{12}](OH)_4 \cdot nH_2O$, dissolves forming a soluble complex species of the probable composition

TABLE I

Analytical, Magnetic and Physical Data for the Complexes

Complex	Colour	Analysis (%)[a]					Dec. p.[b] (K)	$X_g \cdot 10^6$ [c] ($cm^3 g^{-1}$)
		C	Cl	H	Na, K Rb or N	Ta		
$Na_2[Ta_6Cl_{12}](OH)_6 \cdot 16H_2O$	dark red		21.91 (21.85)		2.22 (2.36)	55.52 (55.75)	304	—0.11
$K_2[Ta_6Cl_{12}](OH)_6 \cdot 16H_2O$	dark red		21.46 (21.49)		3.90 (3.95)	54.63 (54.84)	303	—0.08
$Rb_2[Ta_6Cl_{12}](OH)_6 \cdot 16H_2O$	dark red		20.62 (20.53)		7.90 (8.25)	52.02 (52.39)	307	—0.16
$[(CH_3)_4N]_2[Ta_6Cl_{12}](OH)_6 \cdot 20H_2O$	dark red	4.70 (4.53)	20.02 (20.05)	3.36 (3.33)	1.61 (1.32)	50.96 (51.17)	301	—0.22
$[(C_2H_5)_4N]_2[Ta_6Cl_{12}](OH)_6 \cdot 12H_2O$	dark red	8.94 (9.19)	20.57 (20.35)	3.09 (3.38)	1.68 (1.34)	52.31 (51.95)	301	—0.16
$[Ta_6Cl_{12}](OH)_4 \cdot 10H_2O$	dark red		24.06 (24.18)			61.48 (61.71)	301	—0.17

[a] Calculated values are given in parentheses. [b] Obtained from thermogravimetric decomposition curves. [c] Measured at 295 K.

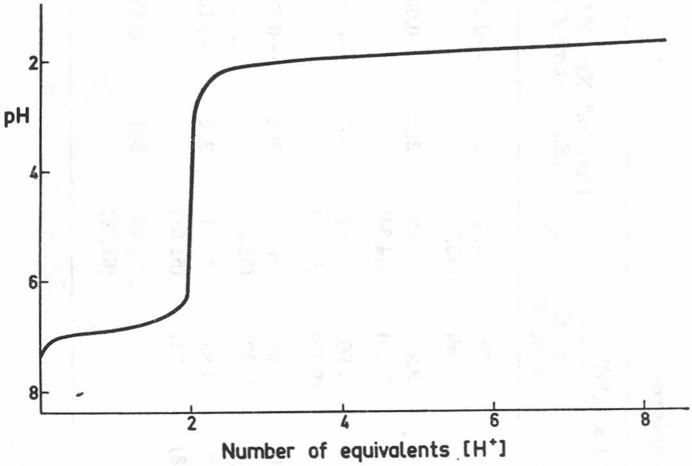

Figure 1. Neutralisation curve of $[Ta_6Cl_{12}](OH)_6^{2-}$

$[Ta_6Cl_{12}]X_4$ (X = Cl, Br) and further $[Ta_6Cl_{12}]X_6^{2-}$. Since the dissolution of $[Ta_6Cl_{12}](OH)_4 \cdot nH_2O$ is very slow and is observed to be complete at $8H^+$/cluster (at a rate of addition of 0.1 mol dm^{-3} HCl 0.10 cm^3/min.), the above mentioned steps are not recognized on the titration curve (Figure 1).

It is interesting that these results are very comparable to those obtained for $[Mo_6Cl_8](OH)_6^{2-}$ titration with acid[10] where the analogous $[Mo_6Cl_8](OH)_4 \cdot 14H_2O$ was isolated.

The isolated cluster hydroxide, $[Ta_6Cl_{12}](OH)_4 \cdot 10H_2O$, (Table I) is a crystalline substance, insoluble in water and common organic solvents, but soluble in diluted and concentrated acids. Its thermal stability, magnetic and spectral (infrared) properties are similar to those found for other cluster hydroxides described here.

If solids of $M_2[Ta_6Cl_{12}](OH)_6 \cdot nH_2O$, M = Na, K, Rb, were heated at 333K for 6 hours, or refluxed with conc. HBr, in order to obtain information on the entry of OH^--groups from the outside into the inside coordination sphere of a cluster unit and their subsequent substitution by bromide ions. In all experiments the mixed halide cluster, $[Ta_6Cl_{12}]Br_4 \cdot nH_2O$ was isolated and no evidence for OH^--groups coming into the inside coordination sphere of a cluster unit was obtained.

Spectral properties. — Infrared spectra of these compounds are similar to the spectra of +2 cluster hydroxides[11,12]. The spectra show the presence of OH stretching (3600—3650 cm^{-1}) originating from hydroxyl groups, stretching (3400—3200 cm^{-1}) and wagging vibrations of water molecules and, for the tetramethyl- and tetraethylammonium salts in the region 1500—1300 and 1200—900 cm^{-1}, CH and CN vibrations respectively, originating from the presence of cations.

Medium intensity bands at 460, 468 and 470 cm^{-1} for alkali metal, tetramethyl- and tetraethylammonium salts respectively could correspond to Ta—O(OH) stretching. In the spectrum of $[Ta_6Cl_{12}](OH)_4 \cdot 10H_2O$ this band is observed at 471 cm^{-1}. A band of the same intensity was earlier observed at 409 cm^{-1} in the spectrum of $[Nb_6Cl_{12}](OH)_2 \cdot 8H_2O$[11,12] and assigned to Nb—O(OH) vibrations. The same band was not observed in the spectrum of analogous $[Ta_6Cl_{12}](OH)_2 \cdot 8H_2O$[12], but is observed at 460 cm^{-1} in the spectrum of $[Ta_6Cl_{12}](OH)_2 \cdot 6H_2O \cdot 2CH_3OH$[13].

The position of sharp absorption bands at 321, 327 and 323 cm^{-1} for alkali metal, tetramethyl- and tetraethylammonium salts respectively, assigned earlier[14] to the $(Me—X^i)_2$ (i, inside), is relevant to the position (322—332 cm^{-1}) of this band in the $[Ta_6Cl_{12}]^{n+}$ cluster unit.

In these cluster hydroxides all outside halide atoms are substituted by OH^- ions. Comparing the infrared spectra of these cluster compounds in the region below 300 cm^{-1} with a series of compound $[Ta_6Cl_{12}]Cl_6^{2-}$, it is possible to assign the absorption band corresponding to Ta—Cl^a (a, outside) stretching in the latter compounds. In the spectra of the +4 cluster hydroxides there are no absorption bands in the region 200—300 cm^{-1} and the earlier assignment of bands in this region in the spectra of $[Ta_6Cl_{12}]Cl_6^{2-}$ to Ta—Cl^a seems to be correct[15].

The absorption spectra were recorded for methanol solutions of $M_2[Ta_6Cl_{12}](OH)_6 \cdot nH_2O$, M = $(CH_3)_4N^+$ and $(C_2H_5)_4N^+$, and the position of the absorption bands (Table II) is similar to that found earlier for +4 clusters of tantalum[16].

TABLE II

Absorption Spectra for $[Ta_6Cl_{12}](OH)_6^{2-}$ in CH_3OH

Compound	Absorption bands (kK)							
	a	b	c	d	e	f	g	h
$[(CH_3)_4N]_2[Ta_6Cl_{12}](OH)_6 \cdot 20H_2O$	6.9s	10.0m	17.5s	20.8s	27.6m	34.6s	41.7s	47.2m
$[(C_2H_5)_4N]_2[Ta_6Cl_{12}](OH)_6 \cdot 12H_2O$	6.9s	10.1m	17.4s	20.8s	27.7m	34.5s	43.5s	47.6m

kK = 1000 cm^{-1}; m, minimum; s, shoulder

EXPERIMENTAL SECTION

All chemicals were analytical grade, purchased from »Fluka« and »Merck«. The cluster $[Ta_6Cl_{12}]Cl_2 \cdot 8H_2O$ was prepared according to the literature[17].

Preparation of the compounds. — $M_2[Ta_6Cl_{12}](OH)_6 \cdot nH_2O$, M = Na, K, Rb

0.6 g (0.348 mmol) of $[Ta_6Cl_{12}]Cl_2 \cdot 8H_2O$ was dissolved in 40 cm^3 CH_3OH by mixing and warming of the solution at 313K. The clear, dark green solution was filtered off (G-4 fritte) in order to remove any traces of hydrated tantalum(V) oxide that might be present. To this solution, 10 cm^3 of 0.2 mol dm^{-3} of sodium, potassium, or rubidium hydroxide was added dropwise. A black precipitate of $[Ta_6Cl_{12}](OH)_2 \cdot nH_2O \cdot nCH_3OH$[13] appeared and was dissolved by addition of a further 10 cm^3 0.2 mol dm^{-3} of the appropriate alkali metal hydroxide, with mixing and warming of the suspensions at 313K. During addition of alkali metal hydroxides the dark green color of the solution changes to olive green and finally to dark red (pH = 10.5). The solution was evaporated at a temperature of 308 K until a volume of 10 cm^3 was reached. After cooling the solution was filtered off and left to crystallise for several days. The obtained dark-red crystals were washed with water once and air dried overnight; yield 60%.

$M_2[Ta_6Cl_{12}](OH)_6 \cdot nH_2O$, $M = (CH_3)_4N^+$, $(C_2H_5)_4N^+$. — For the preparation of these clusters the same amount of methanol solution of $[Ta_6Cl_{12}]Cl_2 \cdot 8H_2O$ was used as above, but only 10 cm³ of 0.2 mol dm⁻³ $(CH_3)_4NOH$ or $(C_2H_5)_4NOH$ was slowly dropped into the solution. The change of colour from dark green to dark red was faster than in the case of alkali metal salts preparation, the decomposition of the cluster to hydrated tantalum(V) oxide was less and, consequently, the yield (80%) was higher.

$[Ta_6Cl_{12}](OH)_4 \cdot 10H_2O$. — 0.4 g of any of the above prepared substances was dissolved in 20 cm³ of water and titrated with 0.1 mol dm⁻³ HCl or 0.1 mol dm⁻³ HBr until 2 moles of acid per mol of cluster were added. The red insoluble substance formed was left to settle, filtered off, washed twice with water and dried over KOH; yield 96%.

Analysis. — Tantalum was determined as the pentoxide after decomposition of compounds according to the following procedure. To 50 mg of the complex in a Kjeldahl flask, 1 cm³ of conc. H_2SO_4 was added and the mixture carefuly heated over a small flame until the complex was completely dissolved. With 10 cm³ of 0.2 mol dm⁻³ $H_2C_2O_4 \cdot 2H_2O$ the clear solution was transferred to a beaker and tantalum precipitated either in the form of tannic acid complex at pH 5.5, or as hydrated tantalum(V) oxide by addition of conc. ammonia at pH 8—9. The »H-tube« method[18] was used for determination of tantalum in $[Ta_6Cl_{12}](OH)_4 \cdot 10H_2O$. Alkali metals were determined as sulphates and by flame photometry in the filtrate after determination of tantalum. Chlorides were determined by potentiometric titration with standard silver nitrate solution after decomposition of the compounds with potassium hydroxide and H_2O_2.

Carbon, hydrogen and nitrogen quantitative analyses were performed in the Microanalytical Laboratory of the »Ruđer Bošković« Institute, Zagreb.

Physical Measurements. — Infrared spectra (4000—200 cm⁻¹) were recorded on a Perkin-Elmer Model 580B infrared spectrophotometer as nujol mulls and KBr presslings. The region 400—40 cm⁻¹ of the spectra was recorded on a Fourier Transform spectrophotometer FS-720 between polyethylene plates in nujol. Electronic spectra were determined with a Cary Model 17 recording spectrophotometer using 0.1 cm quartz cells. Magnetic measurements were performed according to Gouy at 295K for the starting substance and all complexes. Thermogravimetric measurements were carried out on a Cahn RG electromicroanalytical balance with a heating rate of 2° C/min. in air. X-ray difraction patterns were recorded on a Philips X-ray diffractometer with a proportional counter using graphite monochromatized CuK_α radiation. Potentiometric titrations were performed with a Metrohm potentiograph Model E 436 at 25 °C. The concentrations were 5×10^{-3} and 0.1 mol dm⁻³ for the complexes and hydrochloric acid respectively.

CONCLUSIONS

1. The air oxidation of methanol or methanol-water alkaline solutions of $[M_6X_{12}]^{2+}$ M = Nb, Ta; X = Cl, Br, is faster than the air oxidation of acidic solutions of the same clusters. The most stable oxidized alkaline methanol or methanol-water solution was that of $[Ta_6Cl_{12}]^{4+}$. The same alkaline solutions of other clusters undergo hydrolysis.

2. The presence of $(CH_3)_4N^+$ and $(C_2H_5)_4N^+$, often used in the chemistry of $[M_6X_{12}]^{n+}$ clusters[5], stabilizes the methanol-water alkaline solutions of $[Ta_6Cl_{12}]^{4+}$ resulting in a high yield isolation of the +4 cluster hydroxides.

3. Although partial decomposition of the clusters, $M_2[Ta_6Cl_{12}](OH)_6 \cdot nH_2O$ to hydrated tantalum(V) oxide took place during the process of dehydration, reactions with concentrated acids gave no evidence of entry of OH^- ions into the inside coordination sphere of the cluster unit.

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SAŽETAK

Klasterski hidroksidi sastava $M_2[Ta_6Cl_{12}](OH)_6 \cdot nH_2O$, M = Na, K, Rb, $(CH_3)_4N^+$ i $(C_2H_5)_4N^+$; Oksidacija klasterske jedinice $[Ta_6Cl_{12}]^{2+}$ kisikom iz zraka u lužnatom mediju

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Metanolne ili metanol-vodene alkalne otopine (pH > 10) $[Ta_6Cl_{12}]Cl_2 \cdot 8H_2O$ lako se oksidiraju kisikom iz zraka. Oksidirane otopine su upotrijebljene za pripravu klasterskih hidroksida sastava: $M_2[Ta_6Cl_{12}](OH)_6 \cdot nH_2O$, M = Na, K, Rb, $(CH_3)_4N^+$ i $(C_2H_5)_4N^+$. Kristalni u vodi topljivi spojevi posjeduju magnetska i spektroskopska svojstva koja potvrđuju klastersku jedinicu +4. Raspravlja se o uvjetima oksidacije klasterske jedinice u alkalnom mediju.

Netopljivi klasterski hidroksid, $[Ta_6Cl_{12}](OH)_4 \cdot 10H_2O$ i topljivi halidni klasteri $[Ta_6Cl_{12}]X_4 \cdot nH_2O$ i $[Ta_6Cl_{12}]X_6^{2-}$, X = Cl, Br, produkti su reakcije s kiselinama. Nisu dobivene informacije o ulasku OH^- iona u unutrašnju sferu klasterske jedinice.