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Reactions of $[(M_6X_{12})(H_2O)_4X_2]\cdot 4H_2O$ (M = Nb, Ta; X = Cl, Br) in Methanol. Substitution of Coordinated Water and Halogen by Methanol As Determined by ^1H NMR Spectra and Conductance Data

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Introduction

The hydrated niobium and tantalum halide cluster compounds $[(M_6X_{12})(H_2O)_4X_2]\cdot 4H_2O$[1] are most readily soluble in methanol and ethanol. While aqueous solutions of the bromides, $[(M_6Br_{12})(H_2O)_4Br_2]\cdot 4H_2O$, can be readily prepared, the chlorides, $[(M_6Cl_{12})(H_2O)_4Cl_2]\cdot 4H_2O$, are only slightly soluble in water, and solutions generally are prepared in alcohol–water mixtures. Studies of electronic spectra show that solutions of these cluster compounds in methanol and ethanol exhibit absorption bands at essentially equal wavenumbers, whereas the absorption bands are shifted to significantly higher wavenumbers in aqueous solutions.[2] Potentiometric titrations of these compounds with alkali metal hydroxides also showed significant differences in methanol, methanol–water, and water solutions only.[3] In an early attempt to potentiometrically titrate terminal halide atoms in $[(Ta_6Cl_{12})(H_2O)_4Cl_2]\cdot 4H_2O$ in ethanol with an ethanolic solution of $AgNO_3$ only 0.35 Cl^- per cluster was precipitated.[4] In another experiment an aqueous solution of $[(Ta_6Cl_{12})(H_2O)_4Cl_2]\cdot 4H_2O$ was first refluxed, and then using the same titrimetric procedure 1.86 Cl^- per cluster was found to precipitate.[4] From an aqueous solution of $[(Ta_6Br_{12})(H_2O)_4Br_2]\cdot 4H_2O$ at room temperature 2.0 Br^- per cluster were easily precipitated with $AgNO_3$ solution.[5] The same result was obtained by the titration of acidic (H_2SO_4) aqueous or water–methanol solutions of $[(M_6Br_{12})(H_2O)_4Br_2]\cdot 4H_2O$ and $[(M_6Br_{12})(H_2O)_4Cl_2]\cdot 4H_2O$ (M = Nb, Ta) with CH_3COOAg, whereas the results for $[(M_6Cl_{12})(H_2O)_4Cl_2]\cdot 4H_2O$ were approximately 25% lower than expected.[6] Most of these differences can be explained by slower ionization of terminal chloride[7] and slower replacement of ligand water with methanol molecules from the solvent. This idea is supported by the results described here of the study of ^1H NMR spectra of methanolic solutions, of specific conductance measurements, and finally of free chloride and bromide using ^{35}Cl and ^{81}Br NMR spectroscopy.

Experimental Section

Materials. Reagent grade methanol (Mallinckrodt or Kemika, water content 0.02 or 0.05%, respectively) and CD_3OD (Mallinckrodt) were used as received. Triply distilled water was used for obtaining the conductance data. The starting materials $[(M_6X_{12})(H_2O)_4X_2]\cdot 4H_2O$ (M = Nb, Ta; X = Cl, Br) were prepared by the literature method.[8]

Physical Measurements. ^1H NMR spectra were recorded at 499.5 MHz using a Varian Unity 500 spectrometer. The 0.1 mol dm^{-3} solutions of $[(M_6X_{12})(H_2O)_4X_2]\cdot 4H_2O$ were prepared in CH_3OH–CD_3OD (1:5) mixtures. The following conditions were used: rf pulse length 2 μs (=20°), 16 transients, spectral width 4000 Hz, temperature 21 ± 1 °C. A control spectrum of the solvent-calibrated chemical shifts was obtained by assigning 3.35 ppm to the signal of CH_3 groups in free CH_3OH. All subsequent spectra were recorded under identical conditions, and the positions of the latter peak remained within ±0.002 ppm of the stated value. The ^{35}Cl and ^{81}Br NMR spectra were recorded at 200 MHz with a Bruker NMR spectrometer for 0.05 mol dm^{-3} solutions of $[(M_6X_{12})(H_2O)_4X_2]\cdot 4H_2O$ in methanol (X = Cl, Br) or water (X = Br). Solutions of the chlorotantalum cluster were allowed to stand for 3 days before measurement. Because of the strong quadrupole coupling for the bound Cl or Br (either bridging or terminal), NMR resonances were observed only for the free ions. Specific conductance data were obtained for 0.001 mol dm^{-3} methanol–water solutions. The exact amount of the cluster compound was added to 25 mL of methanol or water thermostated at 25 ± 0.01 °C, and the electrical conductance was followed by using a Tacussel Eléctronique conductance bridge (cell constant 1.19 cm^{-1}). The specific conductance values of 1.03×10^{-6} and 2.79×10^{-6} S cm^{-1} for methanol and water, respectively, were subtracted from the conductance data of a particular cluster compound.

Results and Discussion

Conductance and Halogen NMR Studies. Clear evidence for reactions of $[(M_6X_{12})(H_2O)_4X_2]\cdot 4H_2O$ with methanol molecules has been obtained from specific conductance (λ_{sp}) measurements. These data demonstrate a distinct difference between the chloride and bromide derivatives in alcohol solutions. For a 10^{-3} mol dm^{-3} solution of $[(Ta_6Cl_{12})(H_2O)_4Cl_2]\cdot 4H_2O$ in methanol at 25 ± 0.01 °C (Table I, Figure 1) λ_{sp} reaches the value of 41.1×10^{-6} S cm^{-1} after 10 min and changes continuously over times greater than 30 min; equilibrium is not reached even after a period of several weeks. The values of λ_{sp} = 110.4 and 107.5×10^{-6} S cm^{-1}, obtained for $[(Ta_6Br_{12})(H_2O)_4Br_2]\cdot 4H_2O$ and $[(Nb_6Br_{12})(H_2O)_4Br_2]\cdot 4H_2O$, respectively, in the same solvent after 10 min, are considerably higher than those of the chloro clusters and change only slightly with time. These data are surely related to the complete dissociation of the two terminal bromide ions in bromo clusters in comparison to the incomplete and slow dissociation of the two chloride ions in $[(M_6Cl_{12})(H_2O)_4Cl_2]\cdot 4H_2O$. The λ_{sp} values for niobium and tantalum bromo clusters in water (Table I, Figure 1) indicate complete dissociation of the two terminal bromide ligands (2:1 electrolyte type).

These data are in close agreement with the amount of the free bromide and chloride in methanolic solutions determined by ^{35}Cl and ^{81}Br NMR spectroscopic measurements. The observed value of 2.02 mol of free bromide/mol of $[(Ta_6Br_{12})(H_2O)_4Br_2]\cdot 4H_2O$ in methanolic solution indicates complete dissociation of the two terminal bromide ligands. In contrast, the amount of dissociated chloride per mole of cluster, 0.92 and 0.80, obtained on solutions that had stood for 3 days for $[(Nb_6Cl_{12})(H_2O)_4Cl_2]\cdot 4H_2O$ and $[(Ta_6Cl_{12})(H_2O)_4Cl_2]\cdot 4H_2O$, respectively, indicates that less than one Cl^- is dissociated in methanolic solution and the remainder is coordinated to the cluster units. The terminal sites vacated upon dissociation of the bromide and chloride ligands are then occupied by either coordinated water or methanol molecules.

The following observations have been made that show the differences in relative rates of substitution of terminal ligands between the chloro and bromo clusters.

Starting with the hydrated compounds, it is possible to prepare the insoluble clusters $[(M_6X_{12})(CH_3OH)_6]X_2$ (M = Nb, Ta) from methanol solutions; only slight reduction of the volume on the vacuum line is needed for conversion of the bromide

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† Rudjer Bošković Institute.
‡ Iowa State University.

(1) See the following and references therein: (a) Hughes, B. G.; Meyer, J. L.; Fleming, P. B.; McCarley, R. E. *Inorg. Chem.* **1970**, *9*, 1343. (b) Schäfer, H.; Plautz, B.; Plautz, H. *Z. Anorg. Allg. Chem.* **1972**, *392*, 10.

(2) Spreckelmeyer, B. *Z. Anorg. Allg. Chem.* **1969**, *365*, 225.

(3) Brničević, N.; Schäfer, H. *Z. Anorg. Allg. Chem.* **1978**, *441*, 219. Brničević, N. *Z. Anorg. Allg. Chem.* **1978**, *441*, 230.

(4) Lindner, K.; Feit, H. *Z. Anorg. Allg. Chem.* **1924**, *137*, 66.

(5) Harned, H. S. *J. Am. Chem. Soc.* **1913**, *35*, 1078.

(6) Schäfer, H.; Plautz, H.; Baumann, H. *Z. Anorg. Allg. Chem.* **1973**, *401*, 63.

(7) The structure reported for $[(Ta_6Cl_{12})Cl_2]\cdot 8H_2O$ shows that the two outer chlorine atoms are indeed coordinated to the cluster unit as indicated by the formula $[(Ta_6Cl_{12})(H_2O)_4Cl_2]\cdot 4H_2O$: Burbank, R. D. *Inorg. Chem.* **1966**, *5*, 1491.

(8) Koknat, F. W.; Parsons, S. A.; Vongvusharintra, A. *Inorg. Chem.* **1974**, *13*, 1699.

0020-1669/93/1332-3786$04.00/0

Table I. Specific Conductance (S cm^{-1} × 10^{-6}) at 25 ● 0.01 °C[a]

time (min)	$Nb_6Cl_{14}\cdot 8H_2O$	$Ta_6Cl_{14}\cdot 8H_2O$	$Nb_6Br_{14}\cdot 8H_2O$		$Ta_6Br_{14}\cdot 8H_2O$	
	CH_3OH	CH_3OH	CH_3OH	H_2O	CH_3OH	H_2O
1	28.4	34.0	106.5	206.7	104.9	210.8
2	30.7	35.3	107.3	210.3	108.5	211.5
3	31.6	36.3	107.5	211.5	109.1	212.7
4	33.5	37.1	107.5	211.5	109.7	213.8
5	34.7	37.9	107.5	211.5	109.7	215.0
6	36.2	38.7	107.5	212.7	110.0	215.3
7	36.8	39.4	107.5	212.7	110.1	215.5
8	37.8	39.9	107.5	212.7	110.2	215.8
9	38.5	40.5	107.5	212.7	110.3	216.0
10	39.0	41.1	107.5	212.7	110.4	216.2
12	40.1	42.2	107.5	212.7	110.9	216.2
14	41.1	43.0	107.8	212.7	110.9	217.0
16	42.2	43.6	107.9	212.7	110.9	217.2
18	47.8	44.3	108.0	213.9	111.0	217.4
20	43.3	45.2	108.0	213.9	111.0	217.4
22	44.2	45.6	108.1	213.9	111.0	217.4
24	44.8	46.0	108.2	215.0	111.1	217.4
26	45.4	46.5	108.2	215.0	111.3	217.4
28	46.1	47.1	108.2	215.0	111.6	217.4
30	46.8	47.7	108.5	215.0	111.8	217.4
60	52.2	51.8	108.5	216.2	112.3	218.6
90	55.9	54.8	108.5	217.4	113.2	219.8
120	58.5	56.7	108.5	218.6	114.0	219.0
150	60.6	57.9	108.5	218.6	114.2	219.8
180	62.1	58.5	108.7	218.6	114.4	219.8

[a] Data for 1 × 10^{-3} mol dm^{-3} solutions in all cases.

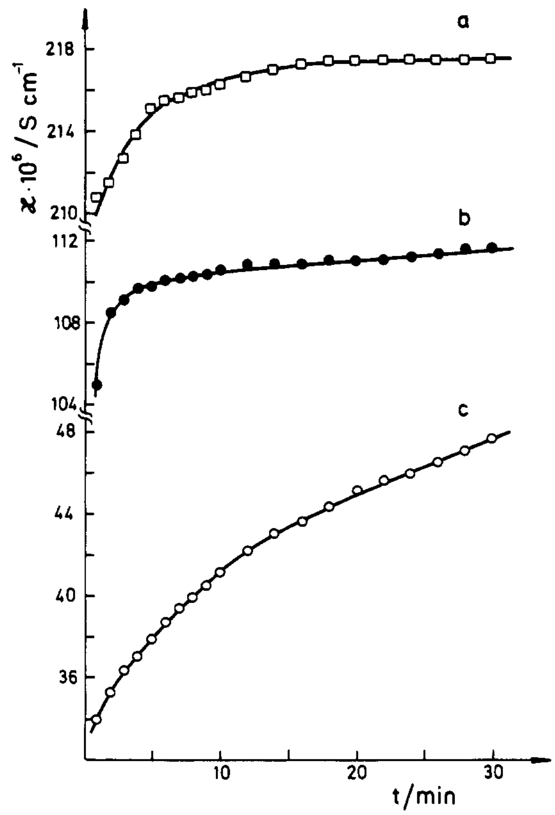

Figure 1. Specific conductance as a function of time for (a) $[(Ta_6Br_{12})(H_2O)_4Br_2]\cdot 4H_2O$ in water, (b) the same compound in methanol, and (c) $[(Ta_6Cl_{12})(H_2O)_4Cl_2]\cdot 4H_2O$ in methanol.

compounds, but three evaporations to dryness on the vacuum line with fresh methanol are required for the corresponding chlorides.[9] Also, from concentrated methanolic solutions (≥5 × 10^{-2} mol dm^{-3}) the $[(M_6Br_{12})(CH_3OH)_6]Br_2$ compounds crystallize out over a period of only a few hours.[9] This is not observed for the niobium and tantalum chloro clusters. Evidently, the strong coordination of chloride ligands in the terminal positions is responsible for the very low solubility observed for the niobium and tantalum chloro cluster octahydrates in water.

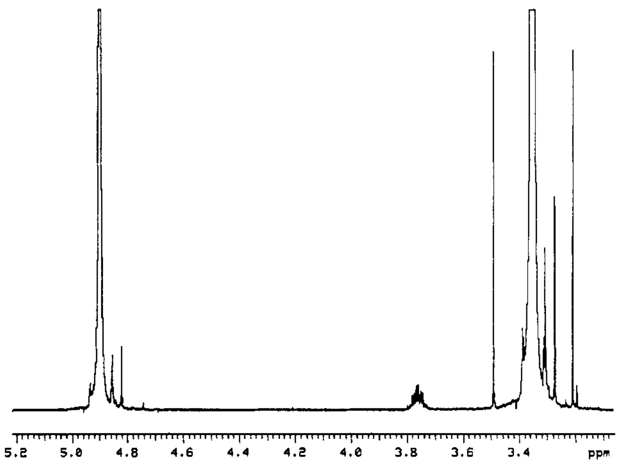

Figure 2. ^1H NMR spectrum of $[(Ta_6Br_{12})(H_2O)_4Br_2]\cdot 4H_2O$ dissolved in a mixture of $CH_3OH–CD_3OD$ (1:5). The vertical scale has been expanded so that smaller peaks are observable.

Proton NMR Studies. Methanolysis and formation of methoxide ligands can be eliminated as important reactions in these cases because infrared spectra of the solutions show an absence of the band near 400 cm^{-1} where M–O stretching from methoxide ligands is expected.[10] The present study of the ^1H NMR spectra of methanol solutions was undertaken in order to examine these surprising effects in more detail, and the results confirm pronounced differences in the chloride and bromide cases, with remarkably slow substitution rates for the chloride cluster species. The NMR spectra also show that 10 or more separate species may simultaneously populate these solutions at equilibrium, depending upon the relative concentrations of water and methanol.

Samples were prepared by dissolving the hydrated compounds[7] in a solvent mixture consisting of *ca.* 1 part of CH_3OH and 5 parts of CD_3OD. Figure 2 shows a typical spectrum over the range 3.0–5.0 ppm. The large peaks at 3.2–3.5 ppm arise from free methanol in the solvent, and the large peak at 4.9 ppm arises from the averaged OH protons of CH_3OH and H_2O which undergo rapid proton exchange. The distinctive group of resonances at 3.7–3.8 ppm arise from the methyl hydrogens of coordinated CH_3OH and confirm that substitution of H_2O or halogen by CH_3OH in the terminal sites of the cluster can be followed by ^1H NMR.

The expanded spectra for several different solutions in the 3.7–3.8 ppm region are presented in Figure 3. Analysis of these spectra permits identification of each species in the substitution series, even including all possible isomers. The resulting distribution of chemical shifts may lead to a deceptively regular pattern as shown for $[(Ta_6Br_{12})(H_2O)_{6-x}(CH_3OH)_x]^{2+}$ in Figure 3a. In this case the relative concentrations of methanol and water in the sample solution were fortuitously adjusted in such a way that both kinds of molecules were competing for the coordination sites with equal probability. The six terminal coordination sites of the cluster ions are disposed at the apices of the M_6 octahedron, and the exact chemical shift of a coordinated methanol molecule will depend not only on bonding to the metal atom but also on the substituents at the other apex positions. The pattern and intensities of the 10 resonances shown in Figure 3a, which result from the nine distinct substitutional and isomeric species containing from one to six coordinated methanol molecules ($1 \leq x \leq 6$), can be explained quantitatively on a statistical basis as follows. There is only one combination which puts six methanol molecules into the structure. The six equivalent CH_3 groups give rise to a single resonance at 3.797 ppm and relative intensity of

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[9] Kashta, A.; Brničević, N.; McCarley, R. E. *Polyhedron* **1991**, *10*, 2031.

[10] Brničević, N.; Muštović, F.; McCarley, R. E. *Inorg. Chem.* **1988**, *27*, 4532.

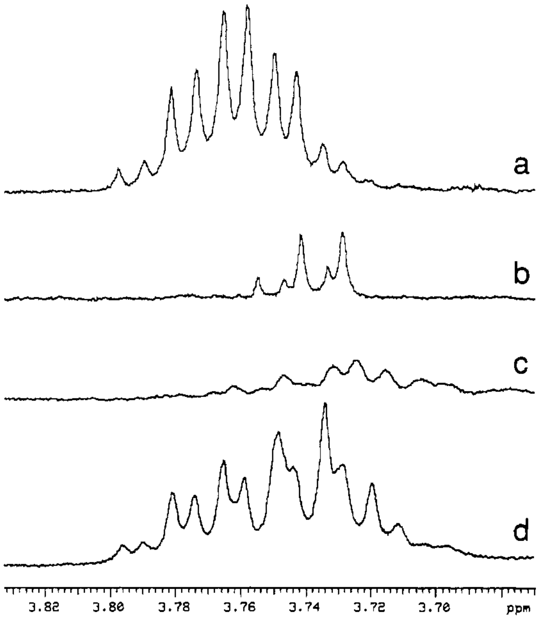

Figure 3. ^{1}H NMR spectra of coordinated CH_3OH in the region 3.68–3.82 ppm for (a) $[(Ta_6Br_{12})(H_2O)_4Br_2]\cdot 4H_2O$ in methanol 3 h after preparation, (b) solution a after addition of a small amount of water, (c) $[(Ta_6Cl_{12})(H_2O)_4Cl_2]\cdot 4H_2O$ in methanol 1.5 h after preparation, and (d) solution c after 3 days.

18 units (for 18 magnetically equivalent protons). The member with 1 H_2O + 5 CH_3OH will give rise to two different resonances: one CH_3OH *trans* to H_2O (intensity of 6 × 1 × 3 = 18) and four CH_3OH *cis* to H_2O (intensity of 6 × 4 × 3 = 72). With respect to the foregoing species, we find that the chemical shift of CH_3OH *trans* to H_2O is –0.007 ppm and that *cis* to H_2O is –0.015 ppm. Further combinations are given by replacement of two to five methanol molecules, which give rise to the additional CH_3 resonances. Chemical shifts of the latter are calculated by subtracting 0.015 ppm for each H_2O molecule in a neighboring (*cis*) apex site and 0.007 ppm for a H_2O molecule in a *trans* apex site. In this fashion, the model predicts 10 resonances with relative intensities of 18, 18, 72, 72, 108, 108, 72, 72, 18, and 18 units, each resonance separated from the next by 0.007 ppm, in close agreement with experimental results. A small addition of water to the solution giving the spectrum shown in Figure 3a shifts the equilibrium so that the concentrations of species with $x \geq 4$ become very low and those of species with more water are increased, as shown in Figure 3b. From this change we also verify assignment of the final signal at 3.728 ppm (Figure 3a) to the cluster with 1 CH_3OH + 5 H_2O in the coordination sites.

The solution giving the spectrum in Figure 3a reached this equilibrium state after only 3 h. In contrast, a solution of $[(Ta_6Cl_{12})(H_2O)_4Cl_2]\cdot 4H_2O$ attained equilibrium much more slowly. As shown in Figure 3c the process was very incomplete after 1.5 h and attained the equilibrium spectrum shown in Figure 3d after *ca.* 3 days. The latter spectrum is even more complicated than that of $[(Ta_6Br_{12})(H_2O)_{6-x}(CH_3OH)_x]^{2+}$ because of participation by Cl^-, along with H_2O and CH_3OH, in the substitution process. These results indicate that the $(Ta_6Cl_{12})^{2+}$ cluster species with four to six coordinated methanol molecules, $[(Ta_6Cl_{12})(H_2O)_{6-x}(CH_3OH)_x]^{2+}$ with $4 \leq x \leq 6$, are not affected by the presence of coordinated Cl^- ions. However, species containing higher numbers of coordinated water molecules ($0 \leq x \leq 2$) show a higher probability of containing a coordinated Cl^- ion, e.g., $[(Ta_6Cl_{12})(H_2O)_4(CH_3OH)Cl]^+$. Attempts were made to reduce the number of species by addition of water and then measuring the substitution rate of a particular methanol/water cluster species. These efforts failed because of the fast substitution rate of methanol for coordinated water or Br^- ligands in the bromo clusters, but also because of simultaneous formation of several mixed methanol/water coordinated cluster species. Decreasing the temperature to –20 °C (the minimum possible before freezing of the solution began) was also without success. Less rapid were the substitution reactions of chloro clusters, especially at low temperature. However, in all experiments, including those at –20 °C, several signals were observed in the ^{1}H NMR spectra, and consequently several different species were formed in the solution simultaneously.

Conclusions

All of the above experimental observations on $[(M_6X_{12})(H_2O)_4X_2]\cdot 4H_2O$ in water–methanol solutions indicate a lower degree of dissociation for chloride outer ligands than for bromide. This is the same as the stability order for halo complexes usually observed for most pre-, early-, and middle-transition metal ions.[11] The $M_6X_{12}^{2+}$ clusters also exhibit the stability order H_2O > CH_3OH ~ Cl > Br for the coordinated outer ligands. Very likely this is the order of decreasing $M–L^a$ bond energies although solvation effects also must be considered. It seems quite likely that $M–Cl^a$ bonds are much stronger than $M–Br^a$ bonds in the $M_6X_{12}^{2+}$ complexes. However, to support this, there are no structural data yet available for direct bond distance comparisons between corresponding $[(M_6X_{12})L_{6-n}Y_n]^{(2-n)+}$ species, with X = Cl or Br, Y = Cl or Br, and L = a neutral donor ligand.

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(11) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; John Wiley & Sons: New York, 1988; p 556.