Raman Spectroscopic Investigations of the Molten CsCl–TaOCl$_3$–TaCl$_5$ System

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Rosenkilde, C., Voyiatzis, G. A. and Østvold, T., 1995. Raman Spectroscopic Investigations of the Molten CsCl–TaOCl$_3$–TaCl$_5$ System. – Acta Chem. Scand. 49: 405–410 © Acta Chemica Scandinavica 1995.

Raman spectroscopy has been used to study the liquid system CsCl–TaCl$_5$–TaOCl$_3$ at temperatures between 500 and 750°C. In the binary CsCl–TaOCl$_3$ the equilibrium $TaOCl_4^- + Cl^- = TaOCl_5^{2-}$ is established. As the TaOCl$_3$ concentration increases, formation of oligomeric ions with bridging oxygen bonds also becomes significant. In the central part of the ternary system considerable oligomerisation occurs, and some melts in this region form glasses when cooled rapidly.

Lately we have investigated the chemistry and electrochemistry of niobium and tantalum chlorides and oxochlorides in molten alkali chloride melts.[1-6] As a part of these investigations, Raman spectroscopic and *ab initio* quantum-mechanical calculations of molecules and complex ions in the molten system CsCl–NbOCl$_3$–NbCl$_5$ have been presented.[7] Motivated by the lack of spectroscopic data available for tantalum oxochlorides and the interesting results obtained by the Raman studies of the niobium system, we have performed a Raman study of the analogue tantalum system.

Only a few studies concerned with the vibrational spectra of Ta(V) chlorides have been found in the literature.[5,8-11] Spectroscopic evidence for the existence of the octahedral tantalum chloride ion $TaCl_6^-$ in molten alkali chlorides has been reported several times.[5,8,9] No spectroscopic studies of Ta(V) oxochlorides have been found. However, infrared reflection spectroscopy of hydrolysed Ta(V) ions dissolved in alkali fluoride melts showed that $TaOF_5^{2-}$ was present.[10] This ion shows a Ta = O stretching band at 900 cm^{-1}. Moreover, the ion $Ta_2OF_{10}^{2-}$ was studied by infrared and Raman spectroscopy[11] in alcoholic solutions of $[Et_4N]_2Ta_2OF_{10}$. Both Raman and infrared spectra show a band at 880 cm^{-1} which was attributed to a Ta–O–Ta bond.

Studies of the CsCl–NbOCl$_3$–NbCl$_5$ system[7] showed that an equilibrium between $NbOCl_4^-$ and $NbOCl_5^{2-}$ was established in the subsystem CsCl–NbOCl$_3$. In melts relatively dilute in Nb(V) and with $0 < n_O/n_{Nb} < 1$ the ions $NbCl_6^-$ and $NbOCl_5^{2-}$ coexisted. However, when the CsCl concentration was lower than 33 mol% and the

molar ratio $n_O/n_{Nb} \geq 0.5$, oligomeric ions with bridging oxygen bonds formed. Moreover, at these concentrations, the melts formed glasses when cooled rapidly.

Morozov and Morozov[12] measured the phase diagram CsTaOCl$_4$–CsCl and found that it was of the simple eutectic kind, with a eutectic point at 530°C and 59.5 mol% CsCl (i.e. 71.2/28.8 CsCl/TaOCl$_3$). They also found that CsTaOCl$_4$ melts at 700°C and that it is stable at temperatures up to 978°C.

Experimental

All samples (typically 300 mg) were prepared by mixing TaCl$_5$ (Alfa 99.999, twice resublimed), Ta$_2$O$_5$ (Alfa, 99.9%, dried at 200°C at 10^{-3} mbar) and CsCl (Merck, 99.9%, melt bubbled with dry HCl and recrystallised) in a quartz cell ($\phi 4 \times 2$ mm). All handling of the salts was performed in a dry-box with water and oxygen levels below 1 ppm. The filled cell was sealed off on a vacuum line ($< 10^{-2}$ mbar). Salts were melted and mixed and kept in the molten state until all Ta$_2$O$_5$(s) was dissolved. The melting and mixing procedure was done carefully owing to the high vapour pressures of TaCl$_5$ (b.p. 242°C); for the same reasons, the volume above the molten mixtures was kept below 20% of the total volume. To record the spectra, the cell was introduced into a specially designed furnace allowing transmission of laser light and collection of scattered light at an angle of 90° to the laser beam.[13] The compositions of the samples are given in Table 1 and Fig. 1.

The excitation source was an argon laser emitting green light at 514.5 nm with an effect of typically 100 mW. The

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Table 1. Nominal compositions of the mixtures studied in this work. Concentrations in mol%.

Sample	CsCl	TaOCl$_3$	TaCl$_5$	Description	Spectra in Figure
I	50	0	50	CsTaCl$_6$	
II	50	50	0	CsTaOCl$_4$	3
III	66.6	33.3	0	CsTaOCl$_4$+CsCl	3
IV	84	16	0	4CsTaOCl$_4$+17CsCl	3
V	95[a]	5	0	(Cs,Na)TaOCl$_4$+18(Cs,Na)Cl	2
VI	33.3	33.3	33.3	CsTaOCl$_4$+TaCl$_5$	4
VII	55	28	17	CsCl/TaOCl$_3$/TaCl$_5$ (55/28/17)	4
VIII	42	42	16	CsTaOCl$_4$/TaCl$_5$ (72/28)	4
IX	40	30	30	CsCl/TaOCl$_3$/TaCl$_5$ (40/30/30)	4

[a] 95 mol% of the CsCl–NaCl eutectic melt.

scattered light was analysed by a Spex 1403, 0.85 m double monochromator, equipped with an RCA photomultiplier cooled to $-20°$C, an EG&G/ORTEC photon counter and a rate meter connected to a PC. Spectra with both horizontal and vertical polarised laser beams were recorded. The slits of the monochromator were adjusted to give a resolution of 3 cm^{-1}.

Results

Bands at 376, ca. 275 and 175 cm^{-1} were observed in the Raman spectra of CsTaCl$_6$ (sample I in Fig. 1). No bands belonging to the oxochlorides were present in the spectra, indicating salts practically free from oxides and insignificant corrosion of the fused silica cells. Figure 2 shows spectra of a NaCl–CsCl eutectic melt with 5 mol% TaOCl$_3$ at 958 K (sample V in Fig. 1). The melt was almost colourless. Figure 3 shows spectra of melts in the system CsCl–TaOCl$_3$ with various TaOCl$_3$ concentrations at different temperatures. As the TaOCl$_3$ concentration increased, the colour of the melt changed from yellow (16 mol% TaOCl$_3$, sample IV) to green (33 mol%

TaOCl$_3$, sample III) and blue (50 mol% TaOCl$_3$, sample II).

Within the ternary region, the melts were green. Spectra of melts with the compositions CsTaOCl$_4$–TaCl$_5$ (VI), CsCl/TaOCl$_3$/TaCl$_5$ (55/28/17 mol%, VII), CsTaOCl$_4$/TaCl$_5$ (72/28 mol%, VIII) and CsCl/TaOCl$_3$/TaCl$_5$ (40/30/30 mol%, IX) were recorded at 923 K. Spectra of these melts are given in Fig. 4. The melts of samples VI, VIII and IX formed deep yellow glasses when the quartz cells were quenched in cold water. Included in the figure
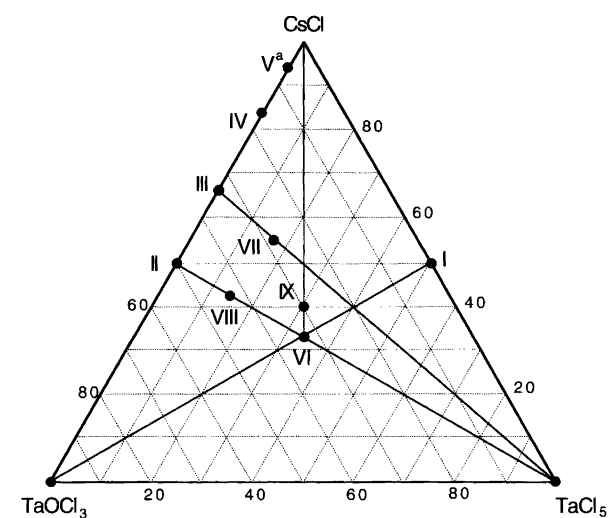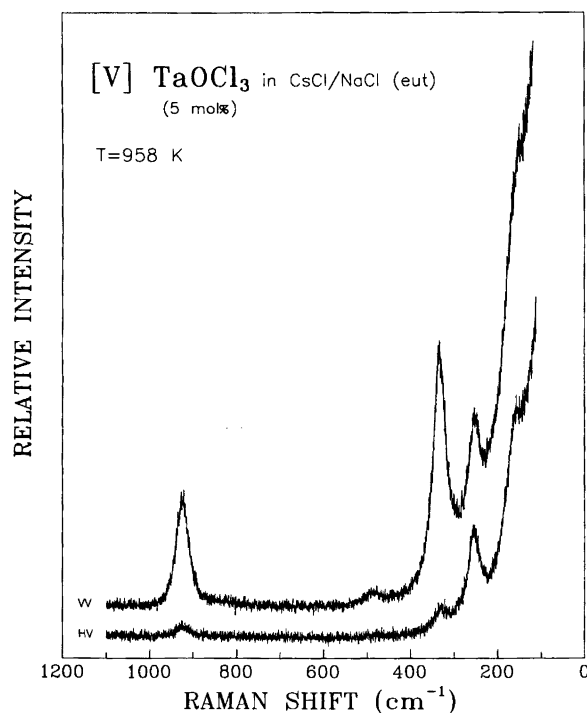

Fig. 2. Raman spectra of 5 mol% TaOCl$_3$ in the eutectic CsCl–NaCl (Sample V) at 958 K. Roman numbers in brackets refer to the sample numbers in Fig. 1 and Table 1. The weak band at 480 cm^{-1} is probably due to the quartz cell. VV and HV refers to the direction of polarization of the laser light entering and exciting the sample. VV indicates that incident and scattered radiation is polarised perpendicular to the scattering plane. HV indicates that incident radiation is polarised in the scattering plane and the scattered radiation analysed perpendicular to the scattering plane.

Fig. 1. Compositions of the different samples studied, plotted in a CsCl–TaOCl$_3$–TaCl$_5$ ternary diagram. [a]Sample V is 5 mol% TaOCl$_3$ in the CsCl–NaCl eutectic melt.
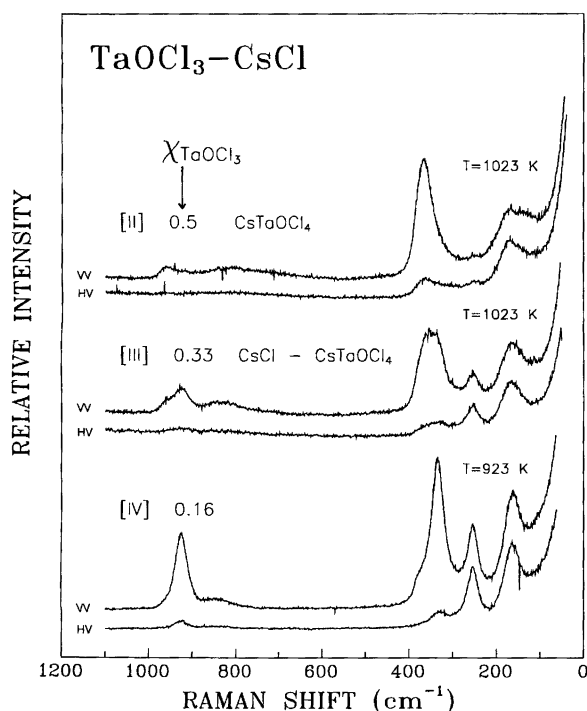
Fig. 3. Raman spectra of three melts with different compositions in the system CsCl–TaOCl₃. From the bottom and up, the compositions and temperatures in the melts were: 16 mol% TaOCl₃ in CsCl (sample IV) at 923 K; 33.3 mol% TaOCl₃ in CsCl (sample III) at 1023 K; 50 mol% TaOCl₃ in CsCl (sample II) at 1023 K. Roman numbers in brackets refer to the sample numbers in Fig. 1 and Table 1.
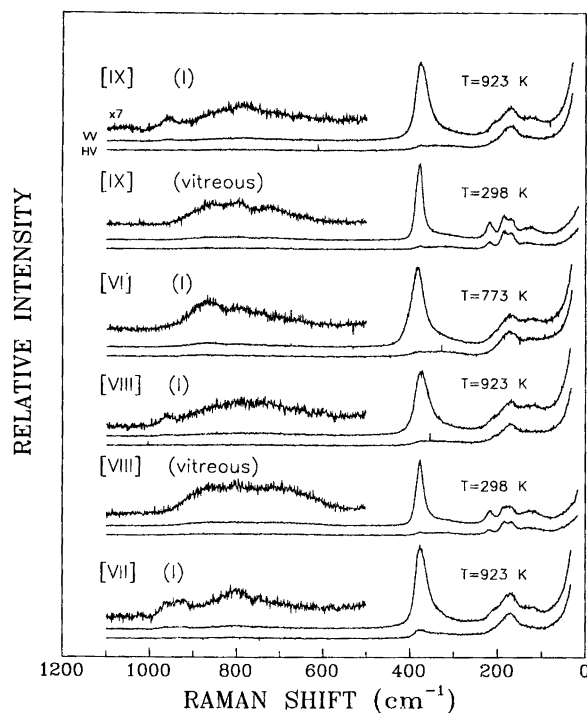

Fig. 4. Raman spectra of four samples with different compositions in the system CsCl–TaOCl₃–TaCl₅. For two of the samples, Raman spectra of both molten and vitreous samples are given. From the bottom and up, the compositions and temperatures for the samples were: molten CsCl/TaOCl₃/TaCl₅ (55/28/17 mol%, sample VII) at 923 K; vitreous CsCl/TaOCl₃/TaCl₅ (55/28/17 mol%, sample VII) at 298 K; molten CsTaOCl₄/TaCl₅ (72/28 mol%, sample VIII) at 923 K; molten CsTaOCl₄+TaCl₅ (sample VI) at 923 K; vitreous CsCl/TaOCl₃/TaCl₅ (40/30/30 mol%, sample IX) at 298 K; molten CsCl/TaOCl₃/TaCl₅ (40/30/30 mol%, sample IX) at 923 K. Roman numbers in brackets refer to the sample numbers in Fig. 1 and Table 1.

are also spectra recorded at 298 K of the glasses formed from melts of samples IX and VIII. The glass formed from the $CsTaOCl_4$–$TaCl_5$ (VI) melt cracked, and Raman spectra of acceptable quality were not obtained.

A survey of the frequencies of the bands observed is given in Table 2.

Discussion

As will be shown below, several complexes coexist in most of the melts studied. Consequently, it is difficult to attribute specific bands to specific complexes. For the same reason, we have not tried to resolve the complete structure and symmetries of the complexes present. The discussion is therefore focused on major structural features and comparison with the corresponding Nb(V) melts.

$CsTaCl_6$. The frequencies observed in the spectra of $CsTaCl_6$ (I) agree with previous work.[8] Assignments of the bands observed for molten $CsTaCl_6$ based on the assignment of $NbCl_6^-$ are given in Table 3.

The binary $CsCl$–$TaOCl_3$. The spectra of 5 mol% $TaOCl_3$ dissolved in a CsCl–NaCl eutectic melt at 958 K

(sample V) (Fig. 2) are almost identical to those of 5 mol% $NbOCl_3$ dissolved in CsCl at 923 K,[7] except for minor shifts in the vibrational frequencies. Increasing the $TaOCl_3$ concentration (Fig. 3) has a similar effect on the spectra as that observed in the CsCl–$NbOCl_3$ system. The intensities of the polarised band at 925 cm⁻¹ decrease, while a new polarised band appears at 960 cm⁻¹. In the niobium system, this change was ascribed to an equilibrium between $NbOCl_5^{2-}$ and $NbOCl_4^-$. Thus, in analogy with the niobium system, the band at 925 cm⁻¹ is ascribed to the stretching of the terminal oxygen $TaOCl_5^{2-}$, and the band at 960 cm⁻¹ to the same mode in $TaOCl_4^-$. The band at 334 cm⁻¹ in the spectra in Fig. 2 and the lower one in Fig. 3 is, as for the corresponding band of $NbOCl_5^{2-}$, ascribed to symmetrical stretching of equatorial chlorides. Based on the spectra in Figs. 2 and 3, it is reasonable to assume that an equilibrium similar to the one observed in the niobium system is established in the tantalum system.

$$Cs_2TaOCl_5 = CsTaOCl_4 + CsCl$$

Table 2. Wavenumbers and characteristics of bands observed in the spectra of the different samples. [a]

Sample description:	CsTaCl$_6$	CsCl+ 50% TaOCl$_3$	CsCl+ 33% TaOCl$_3$	CsCl+ 16% TaOCl$_3$	(Cs,Na)Cl+ 5% TaOCl$_3$	CsTaOCl$_4$+ TaCl$_5$	CsCl/TaOCl$_3$/ TaCl$_5$ 55/28/17	CsCl/TaOCl$_3$/ TaCl$_5$ 42/42/16	CsCl/TaOCl$_3$/ TaCl$_5$ 40/30/30
Sample number:	I	II	III	IV	V [b]	VI	VII	VIII	IX
Temperature/K:	806	1023	1023	923	958	773	923	923	923
Bands/cm^{-1}									
		960w,p	960w,p				962w,p	962w,p	960w,p
		918vw,p	923m,p	926s,p	925s,p		922w,p		
		(700-850)br	845m,br			(873-793-653)br	805br	(872-794-722-653)br	(873-796-702)br
	376s,p	365s,p	364s,p	382sh		383s,p	377vs,p	375vs,p	376vs,p
		(327)	336s,p	334s,p	335s,p	329vw,dp	(325)	(333)	326vw
								~315br	
	~275vw,dp					(285)			(285)
		253vw,dp	254m,dp	254m,dp	254m,dp				
						210m,p	211vw	209w	209w
	175m,dp	169m,dp	167m,dp	162m,dp	156w,dp	170m,dp	173m,dp	169m,dp	171m,dp
		149vw,dp							
						(129)dp			
		123vw,p				(119)p	119w,p	117w,p	117w,p

[a] Abbreviations: s: strong; m: medium; w: weak; v: very; sh: shoulder; br: broad; p: polarised; dp: depolarised.
[b] In a CsCl–NaCl eutectic melt.

Table 3. Assignment of bands observed for $TaOCl_5^{2- a}$ and $TaCl_6^-$.

$TaCl_6^-$, O_h		$TaOCl_5^{2-}$, C_{4v}	
Assignment	Frequency/cm^{-1}	Assignment	Frequency/cm^{-1}
A_{1g}	375	$A_1, \nu_{Ta=O}$	925
e_g	~275	A_1, ν_{TaCl_4}	335
T_{2g}	175	B_1, ν_{TaCl_4}	254
		E	156

[a] Assignments for $TaOCl_5^{2-}$ are based on assignments for $NbOCl_5^{2-}$.[7]

The close resemblance of the spectra of $TaOCl_5^{2-}$ and $NbOCl_5^{2-}$ indicates that $TaOCl_5^{2-}$ belongs to the same symmetry group as $NbOCl_5^{2-}$, C_{4v}. An assignment of the bands observed for $TaOCl_5^{2-}$ based on the assignment of $NbOCl_5^{2-}$ is given in Table 3.

There are, however, differences between the spectra of the two systems. Spectra of the CsCl–$TaOCl_3$ system show bands at wavenumbers between 700 and 850 cm^{-1} which are not present in the niobium system. Bridging oxygen bonds typically show vibrational bands in this wavenumber region.[7,11,14,15] It therefore seems reasonable to ascribe the bands in the region 700–850 cm^{-1} in the tantalum system to Ta–O–Ta bonds. With this interpretation, Fig. 3 shows that there is considerable tendency to form bridging oxygen bonds between tantalum atoms, even at tantalum concentrations as low as 10–20 mol%. Thus, in contrast to the niobium system, the situation in the CsCl–$TaOCl_3$ system cannot be described simply by the equilibrium between $TaOCl_5^{2-}$ and $TaOCl_4^-$. Further equilibria involving formation of oligomeric ions with bridging oxygen must be responsible for the bands observed at 700–850 cm^{-1}.

The intensities of the band at 960 cm^{-1} and the bands at 700–850 cm^{-1} in the spectra of $CsTaOCl_4$ (II) and $CsTaOCl_4$–CsCl (III) (Fig. 3) indicate that the concentrations of $TaOCl_4^-$ and the oligomeric Ta-containing ions are comparable. The band at 365 cm^{-1} is therefore probably due to symmetrical stretching of chlorides both in $TaOCl_4^-$ and oligomeric ions.

The ternary CsCl–$TaOCl_3$–$TaCl_5$. The spectra in Fig. 4 show broad bands around 800 cm^{-1}, typical of a bridging oxygen.[7,11,14,15] The spectra of the CsCl/$TaOCl_3$/$TaCl_5$ (55/28/17 mol%, VII) melt are particularly interesting. These spectra clearly show that complexes with both bridging and terminal oxygen atoms are present in the melt, while spectra of a similar niobium melt (CsCl/NbOCl$_3$/NbCl$_5$ 50/25/25 mol%) showed only bands belonging to $NbCl_6^-$ and $NbOCl_4^-$. Moreover, the spectra of the $CsTaOCl_4$–$TaCl_5$ (VI) melt show no bands belonging to terminal oxygen atoms, while such bands are present in the spectra of the corresponding niobium melt. This indicates that the ratio between oligomeric and monomeric ions is higher in Ta(V) oxochloride-containing melts than in the corresponding Nb(V) melts. Thus,

Ta(V) has a stronger ability to form oligomers with bridging oxygen bonds in caesium oxochloride melts than Nb(V).

As for the niobium melts, bands due to bridging oxygens are broad, indicating many related structural configurations of bridging oxygen, or bridges with very short lifetimes. Consequently, the melts contain many different oligomeric complexes in equilibrium, and no simple interpretation of the spectra can be given. Nevertheless, some suggestions about the origins of the various vibrational bands can be made. Most of the spectra in Fig. 4 show strong polarised bands at 375–377 cm^{-1} and depolarised bands of medium intensity at 169–173 cm^{-1}, close to the A_{1g} and T_{2g} modes of $TaCl_6^-$, respectively. It is therefore reasonable to assume that $TaCl_6^-$ is present in these melts. However, since bands due to Ta = O are weak and $n_O/n_{Nb} \geq 0.5$, the concentrations of oligomeric complexes with bridging oxygen are significant. In analogy with the niobium system, symmetrical stretching of Ta–Cl bonds in the oligomeric complexes should show bands near the frequency of symmetrical stretching of Ta–Cl in $TaCl_6^-$. These bands probably partly overlap with the $TaCl_6^-$ band at 377 cm^{-1}. In the spectra of $CsTaOCl_4$–$TaCl_5$ (VI), the strong polarised band due to Ta–Cl is at 383 cm^{-1}, a slightly higher frequency than the other strong polarised bands at 375–377 cm^{-1}. In the niobium system, polarised bands at slightly higher frequencies than the Nb–Cl symmetrical stretch for $NbCl_6^-$ were observed in melts with oligomeric ions. Thus, it is possible that the band at 383 cm^{-1} is mainly due to symmetrical stretching of Ta–Cl in the oligomeric complexes.

In the spectra of the CsCl/$TaOCl_3$/$TaCl_5$ (55/28/17 mol%, VII) melt, bands at 960, 922 and 805 cm^{-1} show that considerable amounts of $TaOCl_5^{2-}$ and $TaOCl_4^-$ in addition to complexes with Ta–O–Ta bonds are present. Hence, the band at 377 cm^{-1} in these spectra is probably due to $TaCl_6^-$, oligomeric species and $TaOCl_4^-$. A shoulder at 325 cm^{-1} belonging to $TaOCl_5^{2-}$ is also present in the spectra.

Spectra showing bands due to bridging oxygens at around 800 cm^{-1} also show a weak polarised band at 117–119 cm^{-1}. This band is not present in spectra of monomeric species (Figs. 2 and 3). Since this band is polarised, it is caused by symmetrical vibrations, and its low frequency indicates that the vibrations are due to either a weak bond or vibrations of heavy atoms or atom groups. Possible origins of the band are breathing vibrations of tantalum complexes where tantalum atoms are bonded through bridging oxygens.

Comparing the spectra of the glasses with spectra of the corresponding melts, similar spectral features are observed. Not surprisingly, the bands in the glasses are sharper than the bands in the melt, indicating that the complexes are less distorted at lower temperatures. Lower distortion of the geometry of a complex results in more narrow Raman bands. Moreover, bands due to Ta = O are weaker in spectra of the glasses, indicating

that terminal oxygen atoms in the melt form bonds to other tantalum atoms when the melt is quenched. These oligomeric tantalum oxochlorides are most probably enthalpy-stabilised and entropy-destabilised. A lower temperature will therefore favour their formation, as indicated by the spectra. Other interesting aspects of the glass spectra are also noteworthy. Firstly, the numerous bands in the region of the bridging oxygen bonds indicate that the variety of oligomeric complexes in the melt is preserved during quenching. Secondly, the relatively sharp bands due to symmetrical Ta–Cl stretching suggest rather similar structures of the oligomeric units (e.g. $TaOCl_x^{(3-x)-}$). The numbers of chlorides and oxygen atoms are therefore probably the same for each unit.

Conclusions

Raman spectra of melts in the system $CsCl-TaOCl_3-TaCl_5$ are quite similar to those of melts in the $CsCl-NbOCl_3-NbCl_5$ system. In the subsystem $CsCl-TaOCl_3$, the equilibrium

$$Cs_2TaOCl_5 = CsTaOCl_4 + CsCl$$

is established, similar to that found in the corresponding niobium system. In the tantalum system, however, equilibria involving formation of oligomeric tantalum complexes with bridging oxygen bonds are also established.

Raman spectra of melts in the central regions of the ternary also show that Ta(V) has a higher ability to form complexes with bridging oxygen than Nb(V).

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