Vibrational Structure and Solvent Effects on an Intra-subshell Transition of Osmium (IV) Hexachloro Ions

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The narrow absorption band in the yellow of $OsCl_6{}^{2-}$, caused by an internal transition in the subshell $\gamma_5{}^4$, has an interesting fine structure. The main part is a linear progression (or pseudo-progression) with the characteristic wave-number 170 cm^{-1}, but at a higher wave-number very weak peaks are observed. Their distances from the electronic transition are 1690 cm^{-1} in water, 1450 cm^{-1} in ethanol, and 2980 cm^{-1} in dichloroethane, and may be identified with the O-H bending, C-H bending, and C-H stretching frequencies, respectively.

The narrow lines of lanthanide complexes sometimes have weak satellites caused by co-excitation of vibrations of surrounding molecules. Recently, Young, Gruen, and Satten[1] demonstrated the co-excitation of not only $UCl_6{}^{2-}$ vibrations, but also C-H vibrations of $[N(CH_3)_4]_2[UCl_6]$. The phenomenon is much more difficult to observe in the 3d, 4d, 5d transition groups, since the absorption bands are so much broader. However, Piper and Koertge[2] succeeded in showing, by deuterium substitution in salts of $Ni(H_2O)^{2+}$, that the weak band at 18 700 cm^{-1} of the latter ion is a superposition of the O-H stretching frequency on the narrow band $^3\Gamma_2 \rightarrow {}^1\Gamma_3$ in the red.

As previously mentioned[3], $OsCl_6^{2-}$ has very narrow bands in the near infra-red and in the yellow, representing internal transitions from $^3\Gamma_4$ (the L, S, coupling component with Bethe's double group quantum number Γ_1) to $^1\Gamma_3$ and $^1\Gamma_5$ (at 10 800 and 11 700 cm^{-1}) and to $^1\Gamma_1$ (at 17 240 cm^{-1}), all energy levels belonging to the same subshell configuration γ_4^5. For an explanation of the notation, see Ref. [17]

There are close analogies between these bands and the bands[4] of $ReCl_6^{2-}$ in the red at 14 030 and 15 400 cm^{-1}. As remarked by the present author at several previous occasions[3], and independently by Eisenstein[5], the original assignment[4] of the excited levels $^2\Gamma_3$ and $^2\Gamma_4$ is not correct. These levels are rather the intermediate coupling components Γ_7 and Γ_8 of the highest term, $^2\Gamma_5$ of the lowest subshell configuration γ_3^5.

The former band, representing the transition to Γ_7, has a vibrational structure[4] consisting of seven equi-distant peaks with the mutual distance
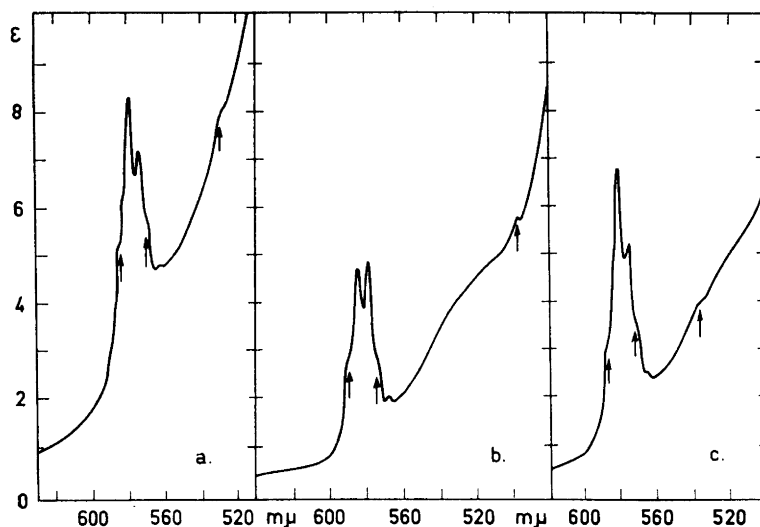
Fig. 1. The absorption spectra of $OsCl_6^{2-}$ in (*a*) 1 M aqueous hydrochloric acid, (*b*) dichloroethane, and (*c*) anhydrous ethanol.

150 to 160 cm^{-1}. The second transition, to Γ_8, produces an irregular band shape[4], and high pressure induces a strong splitting into two parts[6], possibly connected with deviations from the regular octahedral symmetry and removing the degeneracy of the two Kramers doublets in the electronic level Γ_8.

Measurements of $[As(C_6H_5)_4]_2ReCl_6$ in dichloroethane have confirmed the existence[5] of the transition to the nearly degenerate[18] levels Γ_8 and Γ_6 with vibrational structure at 9 110, 9 270, 9 430, 9 570 (maximum, $\varepsilon = 4.5$) and 9 730 cm^{-1}.

The transition in the yellow of $OsCl_6^{2-}$ presents also an equi-distant vibrational structure, as seen in Fig. 1 and in Table 1. The five components observed

Table 1. Wave-number in cm^{-1} of the vibrational components associated with the electronic transition a $\Gamma_1(^3\Gamma_4) \rightarrow {}^1\Gamma_1$ of $\gamma_5{}^4$ in $OsCl_6^{2-}$. Shoulders in parentheses. Three solvents are indicated.

Water	Ethanol	Dichloroethane
(17 090)	(17 000)	(16 960)
17 250	17 170	17 120
17 420	17 330	17 280
(17 540)	(17 500)	(17 430)
17 760	17 680	17 600
(18 940)	(18 620)	20 100

have the characteristic wave-number difference σ_c 170 cm^{-1}, slightly higher than in the case of ReCl$_6^{2-}$.

Though these two hexahalides seem to be exceptional by showing vibrational structure of "ligand field" transitions in solution at room temperature, an even more unusual feature is the very weak peak at relatively much higher wave-number. While the oscillator strength P of the main group of peaks roughly is 1.5×10^{-5}, the additional peak at high wave-number has $P \approx 3 \times 10^{-7}$. The position of this peak is highly dependent on the solvent. Professor Ballhausen was kind enough to indicate that the pure electronic transition $0 \to 0$ without co-excitation of odd vibrations presumably cannot be observed, since the selection rules for electric dipole radiation in O_h are expected to hold as well for OsCl$_6^{2-}$ as for[1] UCl$_6^{2-}$. Consequently, it must be assumed that absorption of (or emission of) one odd vibrational quantum accompanies each of the absorption lines. The lowest such quantum expected is some 160 cm^{-1} (the bending even Γ_5 mode[13] corresponds to 158 cm^{-1} in SnCl$_6^{2-}$ and to 162 cm^{-1} in PtCl$_6^{2-}$. Similar to the proposals by Liehr and Ballhausen[16], it may hence be assumed that a regular progression of the even, totally symmetric stretching mode Γ_1 might be superposed the odd vibration. The wavenumber of Γ_1 is[13] 311 cm^{-1} in SnCl$_6^{2-}$ and 344 cm^{-1} in PtCl$_6^{2-}$, whereas the three odd normal modes of UCl$_6^{2-}$ are situated[1] at 258 cm^{-1} (stretching), 114 and 94 cm^{-1} (bending). Since the force constants are expected to be slightly larger in the platinum group hexachloride anions than in uranium(IV), the wavenumber intervals 150— 170 cm^{-1} would rather be expected to correspond to bending modes. By infrared absorption spectroscopy, Adams[15] found the stretching frequencies of K$_2$OsCl$_6$ at 319 and 340 cm^{-1} and of K$_2$PtCl$_6$ at 345 cm^{-1}.

However, the equi-distant bands may be a pseudo-progression, caused by the accidental phenomenon that the stretching frequency is twice as large as one of the bending frequencies. Thus, Ballhausen suggested that the two first strong peaks (17 250 and 17 420 cm^{-1} in aqueous solution) are caused by co-excitation of the two odd Γ_4 modes, i.e. the mainly bending $\sim$ 160 cm^{-1} and the mainly stretching $\sim$ 330 cm^{-1}.

It seems, from the positions of the "distant peaks" that an odd quantum also might accompany the latter vibrational excitation. If this assumption is correct, the energy above the electronic level of the distant peak is 1690 cm^{-1} in water, 1450 cm^{-1} in ethanol, and 2980 cm^{-1} in dichloroethane.

The possibility that this peak is caused by another electronic level does not look plausible to the present author. The only explanation along this line would involve the Γ_1-component of $^5\Gamma_5$ of $\gamma_5^3\gamma_3$ which might have very low energy (connected with the low interelectronic repulsion energy for the high total spin S), but the necessary effects of intermediate coupling would not be sufficiently efficient to depress the band-width completely from its high value ($\approx$ 1200 cm^{-1}) in a normal $\gamma_5 \to \gamma_3$. The latter transition is probably responsible for the shoulder at 530 mμ observed in the dichloroethane solution (Fig. 1 b).

Comparing with the vibrational levels of the solvent molecules[7], it is remarkable to note the nearly coincidence of the values given above with the O-H bending wave-number of liquid water 1650 cm^{-1} (vapour 1595 cm^{-1}), the C-H bending of ethanol (broad band at 1380—1450 cm^{-1}), and the C-H stretching of dichloroethane (2959, 3002, 3029 cm^{-1}). An alternative interpretation of the
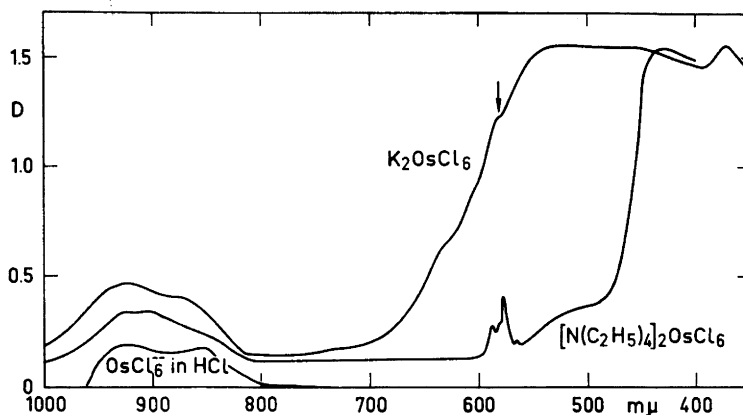
Fig. 2. The reflection spectra of crystalline powders of red $K_2Os_3Cl_6$ and yellow $[N(C_2H_5)_4]_2OsCl_6$. For comparison in the near infra-red, the solution absorption spectrum from Fig. 1 is extended in the region of electronic transitions to $^1\Gamma_3$ and $^1\Gamma_5$ of γ_5^4.

third column of Table 1 would involve the C-H stretching frequencies of the $(n\text{-}C_4H_9)_4N^+$ ion associated with $OsCl_2^-$ in the dichloroethane solution.

In aqueous solution, it is expected that $OsCl_6^{2-}$ polarise surrounding water molecules in such a way that one or both protons are directed towards the anion. Hence, the occurrence of weakly co-excited O-H bending modes is not surprising. It is much more unexpected that C-H bending rather than O-H bending ($1000-1100$ cm^{-1}) is responsible for the very weak peak in ethanol. It suggests that the methyl end rather than the hydroxo group is close to $OsCl_6^{2-}$. How strange this may be, there is some analogous evidence from the measurement[19] of solvent effects on $IrBr_6^{2-}$ and other 5d-group hexahalide complexes. Thus, $[N(C_4H_9)_4]_2[IrBr_6]$ is not particularly soluble in alcohols (*e.g.* *t*-butanol) while it is very soluble in partly chloro-substituted hydrocarbons such as 1,2-dichloroethane and chloroform.

The electronic level has 80 cm^{-1} lower energy in ethanol and 130 cm^{-1} lower energy in dichloroethane than in the aqueous solution. The simplest interpretation of this fact is that the nephelauxetic effect, *i.e.* the decrese of the apparent term values of interelectronic repulsion parameters, compared to the gaseous ion, is slightly larger in the organic solvents. The parameters[3,8] derived from the spectra of $ReCl_6^{2-}$ and $OsCl_6^{2-}$ in aqueous solution are in cm^{-1}:

$$
\begin{array}{llll}
ReCl_6^{2-} & K(4,5) \sim (3\,B + C) = 2800 & \zeta_{5d} = 2300 & \\
OsCl_6^{2-} & = 2500 & \phantom{\zeta_{5d}} = 2800 & \quad (1)
\end{array}
$$

and might conceivably be half a per cent smaller in the organic solvents, though higher-order effects of dispersion forces are not excluded. The internuclear distances between the central metal and halogen seem to be larger in aqueous solution than in the organic solvents. The measurements at high pressure by Balchan and Drickamer[9] of electron transfer spectra of 5d group hexahalides show strong shifts to lower wavenumber. The nephelauxetic effect
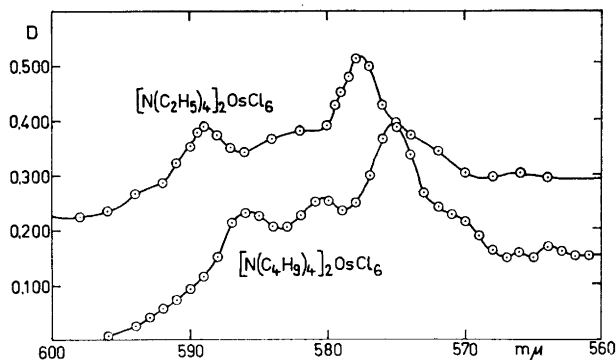
Fig. 3. The reflection spectra of tetra(ethyl)ammonium and tetra(butyl)ammonium osmium(IV) hexachlorides under high dispersion.

seems invariably to become more pronounced by decreased internuclear distance in transition group complexes [10] and in compounds of the trivalent lanthanides [11].

In solid yellow $[N(C_2H_5)_4]_2OsCl_6$, the reflection spectrum shows a complicated structure (Fig. 2) close to 17 310 cm^{-1}, while the dark-red K_2OsCl_6 have stronger electron transfer bands at lower wave-number, and the intra-subshell transition is only seen as a narrow shoulder at 17 120 cm^{-1} on a steep increase (Fig. 2). The yellow crystals of $[N(C_4H_9)_4]_2 OsCl_6$ present a similar structure at slightly larger wave-number, the highest band being at 17 380 cm^{-1}. (Fig. 3 and Table 2). Though the intensities vary in a somewhat irregular manner, the wavenumber intervals are invariant (Table 2). By repetition of the latter measurement on the reflection attachment to the Cary-11 spectrophotometer, the same bands were found as given in Table 2, but at 50 cm^{-1} lower wavenumber and further on, the additional small band at 20 100 cm^{-1} was observed, making the crystals closely comparable to the solution in dichloroethane.

The isoelectronic PtF_6 has the corresponding electronic transition [12] at 15 873 cm^{-1}, but only showing weak vibrational structure, compared to many of the complicated band groups of other intra-subshell transitions in the gaseous 5d-hexafluorides.

Table 2. Wave-numbers in cm^{-1} of the vibrational components in the reflection spectra of two solids (see Fig. 3).

$[N(C_2H_5)_4]_2OsCl_6$	$[N(n\text{-}C_4H_9)_4]_2OsCl_6$
16 980	17 070
(17 150)	17 230
17 310	17 380
(17 460)	(17 530)

EXPERIMENTAL

5 g OsO_4 (H. Drijfhout and Zoon, Amsterdam) was reduced by heating with 7 g ascorbic acid in 100 ml 6 M hydrochloric acid. Prolonged boiling has a tendency to produce brown caramellic materials which must be removed by filtration. When the filtrate is added to the solution of 10 g KCl in 50 ml water, brick-red K_2OsCl_6 precipitates. 0.96 g portions of this salt (2 mmoles) can be dissolved in 20 ml of 1 M HCl and yellow precipitates obtained with an excess of tetra(ethyl)ammonium chloride, or even with 2.5 g tetra(butyl)ammonium bromide (Fluka), dissolved in 10 ml ethanol. It is well known that $OsCl_6^{2-}$, once formed, is very robust against ligand exchange in acid solution [14].

The spectra were measured in 5 cm cells on a registering Cary-11 spectrophotometer. The solution of $[N(n\text{-}C_4H_9)_4]_2[OsCl_6]$ in ethanol, measured in Fig. 1, was supersaturated and crystallised after a while.

Analysis of $N(C_4H_9)_2OsCl_6$: Found: C 43.26; H 8.40; N 3.22; Cl 23.84. Calc. C 43.28; H 8.18; N 3.16; Cl 23.96.

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