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Formation of Ion Pairs between Long-Chain Alkylammonium Ions and Mixed Fluorohaloosmates(IV) in Organic Solvents. Influence of Cations and Solvents

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Different types of ion pairs between long-chain alkylammonium cations and fluorohaloosmates(IV) in organic solvents are studied by spectrophotometric methods. The hydrogen bonding between F of *trans*-$[OsCl_4FI]^{2-}$ and hydrogen-donor alkylammonium cations causes a shift in Os ← I charge-transfer (CT) bands, depending on the nature of solvents, cations, and additional anions. These changes in the spectra lead to the conclusion that tertiary alkylammonium (e.g., trilaurylammonium, $TLAH^+$) salts exist as "intimate" or "contact" ion pairs in nonpolar solvents. "Loosely bonded" ion pairs are formed both by quarternary alkylammonium (e.g., trilaurylethylammonium, $TLAE^+$) salts in polar or nonpolar solvents and by tertiary salts in polar solvents. In protic solvents both of the salts are present as "solvent-separated" ion pairs. The difference in the absorption spectra of tertiary and quaternary salts gives a possibility to calculate the absorption spectrum of the ion triplet *trans*-(TLAH)(TLAEt)$[OsCl_4FI]$ and to estimate the effective ionic radii of anions.

Introduction

The presence of hydrogen bonds in primary, secondary, and tertiary alkylammonium salts has been studied by different methods.[2,3] For the first time the hydrogen bonding between alkylammonium cations and hexahalometalates, e.g., hexahalouranate(IV), was found to exist by using the shift in the absorption spectra.[4] The occurrence of hydrogen bonding in hexahalo complexes of platinum metals is also proved by infrared spectroscopy in solid state as well as in organic solvents.[5] Recently by X-ray studies, evidence was given for Cl···H–C hydrogen bonding in the tetramethylammonium salt $(TMA)_2[PtCl_6]$.[6]

In the last 10 years, a large number of mixed-ligand complexes of platinum metals have been prepared.[7-12] Recently we reported a new method for ligand exchange in nonpolar solvents by the use of phase-transfer catalysis (PTC) and ion-pair reactions.[13-15] By this way it was possible for the first time to prepare complexes containing F^- beside other heavier halides, e.g., *trans*-$[OsCl_4FI]^{2-}$ (F and I are trans to each other).

In these fluorine-containing complexes, a strong hydrogen bonding is expected, because fluorine is the most electronegative element and forms strongest hydrogen bonds with the protons of alkylammonium cations. The interaction with Os–F influences the Os–I bond strength in *trans*-$[OsCl_4FI]^{2-}$ with the trans effect. This is the first example of such an inducing influence of hydrogen bonding on the other ligand–metal bonds.

Experimental Section

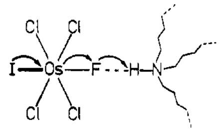
Alkylammonium salts and complexes are prepared as described previously.[2,14] The solvents are dried by standard methods. The spectrophotometric measurements were made with Beckman Acta M 7. The absorption spectra in solution were obtained in a 1-cm quartz cell at room temperature.

Results and Discussion

The charge-transfer (CT) bands in mixed-ligand complexes of Os(IV) are found in the following ranges:[7-9] Os ← I, 500–800 nm; Os ← Br, 400–600 nm; Os ← Cl, 300–450 nm. The electronic spectra of hexahalo- and (mixed-hexahalo)-osmates(IV) show a shift with different cations in organic solvents and also with the same cation in different solvents.

Solvent and Cation Effects. A series of spectra of $(TLAH)_2[OsCl_4FI]$ and $(TLAEt)_2[OsCl_4FI]$ in different solvents is given in Figure 1. In the range of 500–650 nm the two bands 1 and 2 are observed which are characteristic of Os ← I charge transfer. Their position and extinction show a strong dependence on solvent nature.

Due to the trans effect, there is a mutual influence between the Os–I and Os–F bond strength. In tertiary salts the hydrogen bonding is located preferably at F ligand, thus weakening the Os–F bond and simultaneously strengthening the Os–I bond.



This facilitates CT from I to Os, and a red shift is observed. The change in the bond strength is also provided by infrared and Raman spectroscopy.[14]

As the polar character of solvents increases, the ion-pair contact distance also increases which in turn effects the formation of hydrogen bonds between cation and anion. In Figure 1(I) the bands 1 and 2 are shifted toward higher energy as the ion-pair contact distance increases with the polar character of solvents, thus changing the "contact" ion pair to a "loosely bonded" ion pair.

The shift (in nm) shows a good linear dependence of the dielectric constant, DC, of aprotic solvents (Figure 2). The ratio of extinction values of bands 1 and 2 also gives a straight line against DC of solvents. The dipole moment and Gutmann's[16] defined donor and acceptor number do not show linear dependence.

The spectrum of the quaternary salt does not depend very much on the DC of the solvents (Figures 1(II) and 2). Even in nonpolar solvents like benzene, quaternary salts have a similar spectrum as tertiary salts in polar solvents. This concludes that "loosely bonded" ion pairs are formed both by

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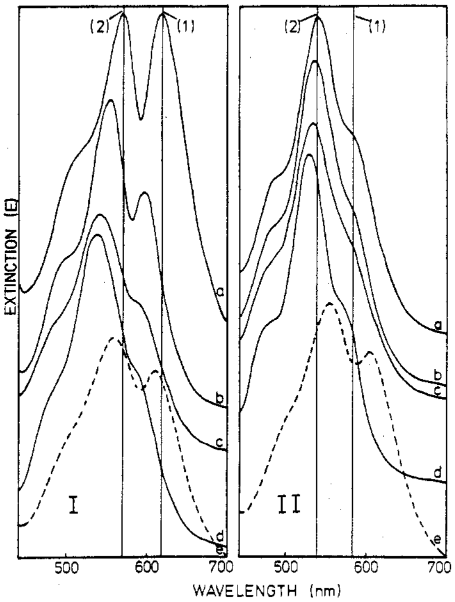

Figure 1. Dependence of CT bands 1 and 2 of $(TLAH)_2[OsCl_4FI]$ (I) and $(TLAEt)_2[OsCl_4FI]$ (II) on solvent: (a) benzene, (b) acetone, (c) nitromethane, (d) acetonitrile, and (e) ethanol (2.10^{-4} mol L^{-1}).

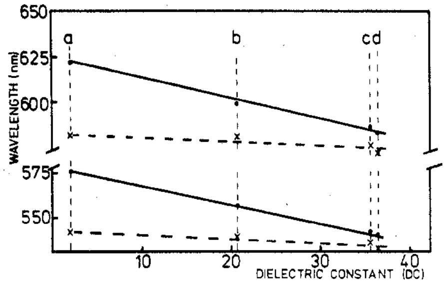

Figure 2. Dependence of position of CT bands 1 and 2 from Figure 1 on the dielectric constant (DC) of the solvents: $(TLAH)_2[OsCl_4FI]$ (–) and $(TLAEt)_2[OsCl_4FI]$ (---).

quaternary salts in polar and nonpolar and by tertiary salts in polar solvents.

In protic solvents like methanol or ethanol, tertiary and quaternary salts show the same spectra (Figure 1e). Both are present as solvent-separated ion pairs. The hydrogen bond between protons of the solvent and F but not a hydrogen-bonding interaction between cation and F ligand is responsible for the change in the spectra. Thus the different cations do not affect the spectra in protic solvents. In aqueous solution and additional red shift results from protonation of the F ligand when pH changes from 7 to 0.

The above discussion gives the following ion pairs in different solvents:

solvents cations	nonpolar	polar	protic
tertiary	contact or intimate	loosely bonded	solvent separated
quaternary	loosely bonded	loosely bonded	solvent separated

Berg[6] described the Cl···H–C hydrogen bonding in $(TMA)_2[PtCl_6]$ in solid state. This type of hydrogen bonding is not found in our investigations in solution. If it exists at all, it must be much weaker than hydrogen bonding discussed above. Otherwise there should be remarkable differences in the Os ← I charge transfer between methylene chloride and carbon tetrachloride, which is not the case here.

The primary, secondary, and tertiary alkylammonium salts of complexes give similar spectra in nonpolar solvents. It does not depend on the number of hydrogen atoms at nitrogen.

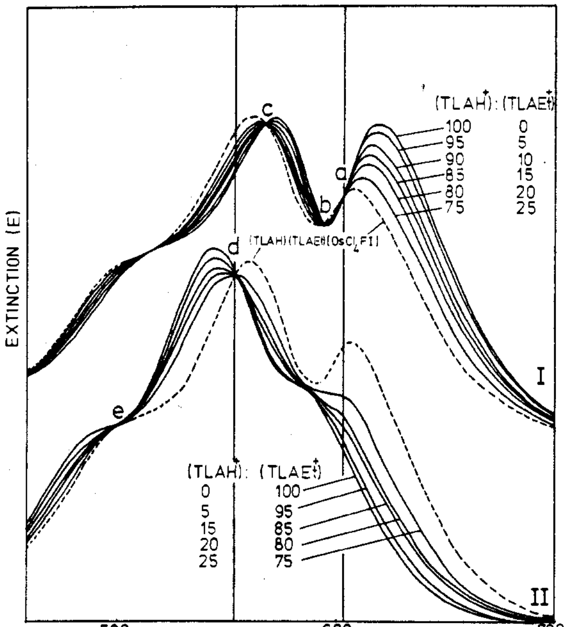

Figure 3. Change of absorption spectrum of $(TLAH)_2[OsCl_4FI]$ (I) and $(TLAEt)_2[OsCl_4FI]$ (II) in toluene on addition of (TLAEt)Br and (TLAH)Br, respectively, and calculated spectrum of $(TLAH)(TLAEt)[OsCl_4FI]$ (---).

Quaternary salts also do not show any significant dependence of the fourth carbon atom chain.

All these discussions support that the change in spectrum depends mainly on the presence and strength of hydrogen bonds. This investigation is restricted not only to mixed-ligand complexes containing fluorine. Tertiary salts of other mixed-ligand complexes, e.g., chlorobromo- and chloroiodo-osmates(IV), show a similar red shift in the Os ← Br or Os ← I charge-transfer region. Because of the lowered tendency of Cl to form hydrogen bonds, the effect is not so strong as with F. The advantage as compared to fluorine-containing complexes is that the Os ← Cl transitions (330–400 nm) can be observed, too. As expected, they are shifted to higher energies in comparison to quaternary salts. This provides a possibility for assignment of CT bands in mixed-ligand complexes.

The hexahalo complexes also show cation and solvent effects, but there is an inversed shift as compared to the above discussed mixed-ligand complexes. The absorption spectra of quaternary salts of hexahaloosmates(IV) are generally shifted about 200–300 cm^{-1} toward lower energy as compared to those of tertiary salts. The hydrogen bonding as interaction between cation and complex anion is not centered to particular ligands. Neither the CT bands nor the vibrational spectra show any splitting, indicating a significant lowering of the octahedral symmetry. Therefore it is supposed that all bonds are weakened to the same extend and the six ligands are obviously equivalent. The increased internuclear distances in tertiary salts make the CT more difficult, which explains the blue shift in the absorption spectra. In acidic aqueous solution more protons are present, and the hydrogen bond interaction with the ligands is strongly increased. Compared to tertiary salts in nonpolar solvents, where only ammonium protons are responsible, a blue shift of 200–300 cm^{-1} is observed.

Calculation of Absorption Spectrum of *trans*-[TLAH][TLAEt][OsCl₄FI]. If a solution of (TLAEt)Br is added gradually to a solution of $(TLAH)_2[OsCl_4FI]$ in toluene, the absorption spectrum changes stepwise. Up to a particular ratio the isosbestic points a, b, and c are observed (Figure 3(I)). If more (TLAEt)Br is added, another group of isosbestic

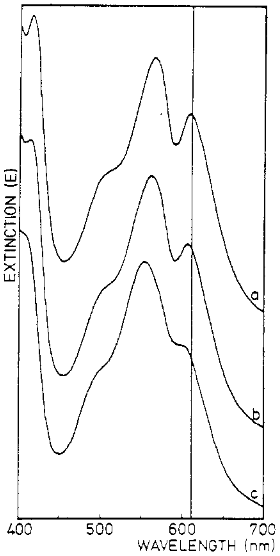

Figure 4. Shift of CT bands of $(TLAEt)_2[OsCl_4FI]$ in toluene on addition of an equimolar amount of (TLAH)X: (a) (TLAH)I, (b) (TLAH)Br, and (c) (TLAH)Cl.

points, d and e, starts (Figure 3(II)). Similar spectra are obtained on addition of (TLAH)Br to a solution of $(TLAEt)_2[OsCl_4FI]$. At first they pass through points d and e and later through a, b, and c. The different isosbestic points in both sets of curves enable the calculation of the absorption spectrum of the triplet $(TLAH)(TLAEt)[OsCl_4FI]$.

As long as the curves run isosbestic, there are only two species in equilibrium. In both sets $(TLAH)(TLAEt)[OsCl_4FI]$ is present, in set I beside $(TLAH)_2[OsCl_4FI]$ and in set II beside $(TLAEt)_2[OsCl_4FI]$. Taking the extinction values of isosbestic points d and of the set I at the same wavelength, we calculated the concentrations of $(TLAH)_2[OsCl_4FI]$ and $(TLAH)(TLAEt)[OsCl_4FI]$ for each curve of set I. The dotted spectrum for 100% of the ion triplet $(TLAH)(TLAEt)[OsCl_4FI]$ is extrapolated. In the same way the concentrations of $(TLAH)(TLAEt)[OsCl_4FI]$ and $(TLAEt)_2[OsCl_4FI]$ are obtained from the extinction values of isosbestic points a and the set of curves II. Extrapolation for $(TLAH)(TLAEt)[OsCl_4FI]$ gives the same spectrum as from set I.

The corresponding cation exchange reactions can be described as

$$(TLAH)_2[OsCl_4FI] \underset{(TLAH)Br}{\overset{(TLAEt)Br}{\rightleftharpoons}} (TLAH)(TLAEt)[OsCl_4FI] \underset{(TLAH)Br}{\overset{(TLAEt)Br}{\rightleftharpoons}} (TLAEt)_2[OsCl_4FI]$$

On adding an excess of (TLAEt)Br to $(TLAEt)_2[OsCl_4FI]$ or (TLAH)Br to $(TLAH)_2[OsCl_4FI]$, we observed no significant change. Thus the change in spectrum is only an effect of cation exchange but not due to added ion pairs which can alter the solvent character.

Anion Effect and Estimation of Effective Ionic Radii. The above equilibrium depends on the nature of the anions that are added: this is due to the different tendencies of the anions to form stable ion pairs. The anions (e.g., Cl^-), forming stronger hydrogen bonding with tertiary cations than with the complex ion, shift the CT bands toward the spectrum of the quaternary salt. The change of the spectrum of $(TLAEt)_2[OsCl_4FI]$ on addition of equimolar amounts of (TLAH)Cl, (TLAH)Br, and (TLAH)I is given in Figure 4. Taking advantage of the rivalry of anions to form stable ion pairs with tertiary cations, it is possible to estimate the effective ionic radii.

Table I. Effective Ionic Radii of Anions

ion	ionic radii, Å	ion	ionic radii, Å
Cl^-	1.81^a	$[OsCl_6]^{2-}$	2.45 ± 0.05
Br^-	1.96^a	ClO_4^-	2.65 ± 0.05
I^-	2.20^a	Cl_3CCOO^-	3.05 ± 0.05
HSO_4^-	2.35 ± 0.05		

^{a} From literature.[17]

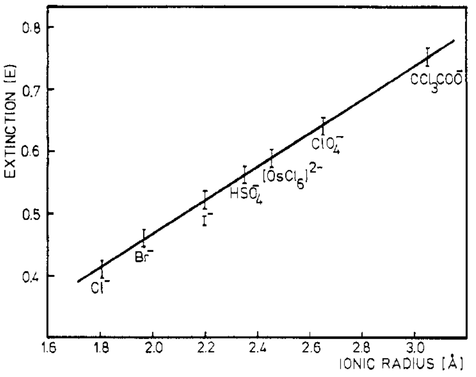

Figure 5. Dependence of the extinction at 610 nm of $(TLAEt)_2[OsCl_4FI]$ in toluene from the ionic radii of different anions X^-, added as an equimolecular solution of (TLAH)X.

On plotting the ionic radii of Cl^-, Br^-, and I^-[17] against their extinctions, measured at 610 nm on equimolecular solutions of $(TLAEt)_2[OsCl_4FI]$ and (TLAH)X in toluene, we obtained a straight line, Figure 5. The extinction values determined in the presence of different anions at the same wavelength and same conditions placed into this standard curve make an estimate of effective ionic radii possible (Figure 5, Table I). The results are in good agreement with the ionic radii obtained by crystallographic or thermochemical measurements.[18,19]

Conclusions

The $(TLAH)_2[OsCl_4FI]$ provides a possibility to demonstrate the formation of all three types of ion pairs, using different organic solvents. The change in the CT bands of mixed-ligand complexes, because of hydrogen bonding, gives a clear picture of the influence of the trans effect on bonding character between ligand and metal ion. This helps to prove the configuration of mixed-ligand complexes and to assign CT bands.

The determination of effective ionic radii gives a possibility of finding agents for back-extraction of anions.[13] They can be stripped from organic solutions with the help of anions of a higher ionic radius, because smaller ions are better hydrated and therefore are preferably transferred to the aqueous phase. For platinum metal complexes the trichloroacetate ion is the most effective stripping agent.

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