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Electron Transfer Spectra of Osmium(IV) Mixed Chloro-Iodo and Bromo-Iodo Complexes

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The eight possible mixed chloro-iodo and bromo-iodo complexes (including each three pairs of geometrical isomers) of osmium(IV) were separated by electrophoresis, and the detailed absorption spectra measured of acidic aqueous solutions. The bands in the near infra-red are due to intra-sub-shell transitions and the rest are electron transfer bands. The detailed assignment of symmetry types of the excited levels should be possible if both the differences of optical electronegativity, the effects of ligand-ligand repulsion, and the strong relativistic effects in bromide and iodide are taken into account. It is only possible to make definite identifications in a smaller part at present. However, the results contribute to a better understanding of the hexa-iodo complex too.

Introduction

The electron transfer spectra of hexahalide complexes MX_6^{+z-6} have been the subject for many studies[1-3] and the assignments of the transitions based on M.O. theory in the point-group O_h seem safe[4] after a recent modification of the orbital energies suggested by measurements of the Faraday effect of circular dichroism induced by a strong magnetic field[5,6] indicating a more pronounced effect of ligand-ligand repulsion[7,8] than previously expected. As a matter of fact, the energy difference between $(\pi)t_{1g}$ (producing the first, Laporte-forbidden, electron transfer band) and $(\pi)t_{2u}$ (producing the second among the Laporte-allowed transitions) is almost invariantly 10 kK in hexafluorides and 7 kK in hexachlorides (1 kilokayser = 1000 cm^{-1} = 0.124 eV). This particular energy difference is not influenced by bonding with central atom orbitals. Previously, we investigated[9] the mixed chloro-bromo complexes $MCl_xBr_{6-x}^{2-}$ of M = osmium(IV) and iridium(IV). This choice of the central atom was partly determined by the relative simplicity[1,4] of the behaviour of the $(5d)t_{2g}$ sub-shell of the central atom changing from 4 to 5 electrons in the case of Os^{IV} and from 5 to 6 (completely filled) by the electron transfer to Ir^{IV}; and partly by the possibility of separating all ten complexes (including the geometrical isomers for x = 2, 3, and 4) by electrophoresis[10] and exploiting the slow and stereospecific kinetics of halide exchange.[11] The most interesting conclusions[9] from the study of the mixed chloro-bromo complexes were that effects of ligand-ligand repulsion are comparable to the difference between the optical electro-negativity[2,12] $\chi_{opt} = 3.0$ for Cl^- and 2.8 for Br^- corresponding to an intrinsic difference of 6 kK between excitation energy for an electron transfer transition to a definite central atom orbital; and, most surprisingly, that the concept of holohedrized symmetry[8] could be applied to fac-$MCl_3Br_3^{2-}$ showing the electron transfer spectrum expected for the M^{IV} complex of the hypothetical ligand $(Cl^- + Br^-)/2$ having $X_{opt} = 2.9$. On the other hand, mer-$MCl_3Br_3^{2-}$ had a more structured spectrum clearly exhibiting the lower symmetry.

Recently, the mixed chloro-iodo complexes $OsCl_xI_{6-x}^{2-}$ were reported.[13] Further on, we have prepared all the isomers of the mixed bromo-iodo complexes[14] $OsBr_xI_{6-x}^{2-}$. Similar iodo complexes of iridium(IV) are difficult to prepare because of the strongly oxidizing character of the central atom. One expects a better distinction between electron transfer from the two types of ligands, because $\chi_{opt} = 3.0$ for Cl^- and 2.5 for I^- correspond to a difference of 15 kK between the excitation energies. Further on, it is well recognized[1,9] that the relativistic effects (spin-orbit coupling) are far more pronounced in iodide ligands having the Landé parameter ζ_{5p} close to 5 kK. Actually, the electron transfer bands of hexa-iodo complexes are remarkably narrow (half-widths δ between 0.5 and 0.8 kK, less than a-third of the δ values for the inter-sub-shell transitions treated in «ligand field» theory) and it is possible to detect fine-structure which could not be observed in hexachloro complexes at room temperature. Thus, the three Laporte-allowed transitions correspond to two bands each, separated by 0.4 to 0.8 kK. The

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most acceptable explanation is the Jahn-Teller effect[6,8] separating the two Kramers doublets forming the excited levels of symmetry type Γ_{8u} (we use here Bethe's double-group quantum numbers Γ_6, Γ_7, and Γ_8 and not Griffith's nomenclature E′, E″, and U′) which are known[9] to be the excited levels of the first and the third Laporte-allowed transitions. This explanation cannot be used for the second Laporte-allowed transition where the excited level Γ_{7u} consists of only one Kramers doublet. However, it is conceivable that the shoulder observed[15] in OsI_6^{3-} is due to an adjacent symmetry-forbidden transition. As a matter of fact most of the iodine-containing complexes of osmium(IV) have a background between the narrow absorption bands, the molar extinction coefficient ε being between 500 and 1000, possibly representing broad, weak bands.

The species $OsCl_5I^{2-}$ has a rather complicated history.[13,15] It is now firmly established that it has three sharp bands at 15.25 kK($\varepsilon = 2200$), 16.65 kK ($\varepsilon = 1800$), and 22.7 kK ($\varepsilon = 1900$) having so low a wavenumber that they must be due, almost exclusively, to iodide excitation. The first strong shoulder ($\varepsilon = 3100$) at 26.0 kK has a wave-number similar to the Laporte-allowed transitions at 27.0 and 30.1 kK of$OsCl_6^{2-}$ and is the inevitable consequence of the presence of the five chloride ligands. The absorption spectrum of $OsCl_5I^{2-}$ presents two other features which are not readily incorporated in a M.O. description of electron transfer: a shoulder ($\varepsilon = 90$) at 10.5 kK adjacent to a sharp maximum ($\varepsilon = 210$) at 11.25 kK. We find similar features in the 9 to 11 kK region in all our other iodine-containing complexes and we tend to ascribe them to the intra-sub-shell transitions from Γ_{1g} to the adjacent excited levels Γ_{5g} and Γ_{3g} which are observed[16,17] at 10.8 and 11.7 kK in $OsCl_6^{2-}$. These transition energies are mainly determined by parameters of interelectronic repulsion, and these are known to be decreased by the nephelauxetic effect[18] in TcX_6^{2-} and ReX_6^{2-} going from X=F over Cl and Br to I. These intra-sub-shell transitions are not only Laporte-forbidden in the symmetry O_h but also spin-forbidden in the limit of RussellSaunders coupling. However, it is known[19] from $Co(NH_3)_5I^{2+}$ and related complexes that spin-forbidden transitions can be intensified to a remarkable extent by the presence of iodide as a ligand. The soulder at 19.0 kK is unexplained.

Returning to the three transitions of $OsCl_5I^{2-}$ at 15.25, 16.65 and 22.7 kK, M.O. theory offers only one plausible possibility of ($\omega = 3/2$) and two ($\omega = 1/2$) components of the 5p shell of iodide as the main constituents of the orbitals from where the transferred electron comes. It cannot be argued that the splitting between 15.25 and 16.65 kK is due to deviations from the linear symmetry of the osmium-iodine system because each of the three ω-components consists of only one Kramers doublet. It might, of course, be argued that the excited state of the central atom, reduced to osmium(III), is Γ_{7g} and correspondingly, more than one energy level corresponds to the simultaneous presence of two partly filled sets of M.O. However, this solution is not satisfactory in view of the general absence[1,4] of such a coupling in osmium(IV) complexes. The ($\omega = 3/2$) component is a pure π orbital of iodide, having the energy $E_\pi + (\zeta_{5p}/2)$ whereas the energy of the two ($\omega = 1/2$) components are the eigenvalues E of

$$\begin{vmatrix} (2E_\sigma + E_\pi)/3 + (\zeta_{5p}/2) - E & \sqrt{2}(E_\pi - E_\sigma)/3 \\ \sqrt{2}(E_\pi - E_\sigma)/3 & (E_\sigma + 2E_\pi)/3 - \zeta_{5p} - E \end{vmatrix}$$

$$\begin{vmatrix} E_\pi - (\zeta_{5p}/2) - E & (\zeta_{5p}/\sqrt{2}) \\ (\zeta_{5p}/\sqrt{2}) & E_\sigma - E \end{vmatrix} = 0 \qquad (1)$$

where the first secular determinant is a «weak field» determinant[20] having diagonal elements corresponding to J=3/2) and 1/2 of the iodine atom, whereas the equivalent, second «strong field» determinant has the diagonal elements corresponding to a large energetic separation ($E_\pi - E_\sigma$).

The distance 7.45 kK between the first and the third strong transition of $OsCl_5I^{2-}$ agrees with the separation ($3\zeta_{5p}/2$)=7.60 kK in the free iodine atom (as found in certain iodide complexes[2] and first pointed out by Katzin[21]) suggesting a small value of ($E_\pi - E_\sigma$). As a matter of fact, the adaptation of the two experimental energy differences to eq. (1) gives $\zeta_{5p} = 4.8$ kK and ($E_\pi - E_\sigma$)=2.4 kK. $OsBr_5I^{2-}$ has the narrow intra-sub-shell transition at 11.0 kK and the three first electron transfer bands at 14.0, 15.65, and 17.65 kK. Of these, the two first suggest also ($E_\pi - E_\sigma$) close to 3 kK whereas the third transition is too close to the first band (at 17.7 kK) of $OsBr_6^{2-}$ to allow identification as predominantly iodide excitation.

The value ($E_\pi - E_\sigma$)=2.4 kK might seem unexpectedly low, because it is usually argued that the difference between $(\pi + \sigma)t_{1u}$ and $(\sigma + \pi)t_{1u}$ in hexahalides is 12 to 15 kK. However, this argument neglects the repulsion[9] between orbitals belonging to different ligands, producing the mixing of (about 75 and 25 percent) π and σ character in the two sets of M.O. Hence, the energy difference between the diagonal elements E_π and E_σ may be smaller, and of the order of magnitude 6 kK. It is well-known that effects of charge separation[3,12] decrease the difference between excitation energies of π and σ orbitals in electron transfer spectra relative to the differences between ionization energies measured by photo-electron spectroscopy.[8,22,23] Actually, Linhard and Weigel[24] found the electron transfer bands of $Co(NH_3)_5I^{2+}$ at 26.1 and 34.9 kK, and Yamatera[25] interpreted these transitions as excitation of the two ($\omega = 1/2$) components of eq. (1) producing a difference ($E_\pi - E_\sigma$)=8 kK if $\zeta_{5p} = 4.8$ kK. However, this interpretation implies an excitation of ($\omega = 3/2$) at 22.8 kK, admittedly producing a much weaker absorption band, hidden in the region between the spin-allowed inter-sub-shell trans-

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ition of $Co(NH_3)_5I^{2+}$ at 17.25 kK, and 26.1 kK. The alternative that the band at 26.1 kK is due to the excitation of ($\omega=3/2$) would be compatible with (E_π–E_σ) $=3.6$ kK and $\zeta_{5p}=4.8$ kK. The truth may be somewhere between these two alternatives, because the somewhat asymmetric band observed at 26.1 kK may be a superposition of ($\omega=3/2$) and the first ($\omega=1/2$) component.

If the assignment in $OsCl_5I^{2-}$ is correct, one expects *trans*-$OsCl_4I_2^{2-}$ to have the three transitions at roughly the same energy as the mono-iodo complex, corresponding to the odd linear combination of iodide eigenfunctions, whereas the even linear combinations should produce almost coinciding, weak (Laporte-forbidden) transitions. Actually, *trans*-$OsCl_4I_2^{2-}$ shows a sharp band at 16.55 kK ($\varepsilon=4050$) surrounded by three shoulders at 13.8 kK ($\varepsilon=1100$), 15.9 kK ($\varepsilon=3600$) and 18.5 kK ($\varepsilon=1400$) agreeing well with this prediction, as well as the third component remaining as a maximum at 23.0 kK ($\varepsilon=1200$). On the other hand, *cis*-$OsCl_4I_2^{2-}$ have four strong electron transfer bands in the visible at 13.55, 16.9, 20.5, and 23.1 kK (and two weak bands at 15.15 and 18.2 kK) since Laporte's rule does not prevent transitions from the six Kramers doublets formed by electron transfer from two iodides, and it is important for the M.O. energies whether a node-plane occurs or not between the two iodide ligands.

The ligands in *fac*-$OsCl_3I_3^{2-}$ are too different to allow the application of the principle of holohedrized symmetry[8,9] in which case the spectrum would have been similar to that of $OsBr_6^{2-}$. The shoulder at 9.9 kK ($\varepsilon=510$) and band at 10.7 kK ($\varepsilon=1100$) are extraordinarily intense for being intra-sub-shell transitions and may be due to electron transfer from a linear combination of iodide orbitals having many node-planes between the ligands.[9] Otherwise the strongest bands occur at 13.2 kK ($\varepsilon=3450$), 15.7 kK ($\varepsilon=1700$), 20.2 kK ($\varepsilon=3100$) and 22.4 kK ($\varepsilon=2700$) at almost the same positions as in *cis*-$OsCl_4I_2^{2-}$. On the other hand, *mer*-$OsCl_3I_3^{2-}$ has five or six strong bands in the same region. It is interesting to note that *fac*-$OsCl_3I_3^{2-}$ has nearly as low wave-numbers of its prominent electron transfer bands as OsI_6^{2-} ($a\ \Gamma_{8u}$ at 11.7 and 12.4 kK; Γ_{7u} at 15.2 kK; and $b\ \Gamma_{8u}$ at 18.3 and 18.6 kK) clearly showing that the difference between intrinsically reducing character of iodide and chloride has become more important than the ligand-ligand repulsion effects. Incidentally, the smaller difference between Γ_{7u} and $b\ \Gamma_{8u}$ (which is[15] 2.7 kK in OsI_6^{3-}) than between $a\ \Gamma_{8u}$ and Γ_{7u} (22.6-18.8=3.8 kK in OsI_6^{3-}) is compatible with a lower value of (E_π–E_σ) than previously assumed.

Actually, it is possible to describe a hexa-iodo complex with small (E_π–E_σ) as having three sets of six Kramers doublets as the states of the collectively oxidized[7] ligands I_6^{5-} having lost an electron. The set most difficult to excite consists of the linear combinations of one ($J=1/2$) and five closed-shell situations. Each state with $J=1/2$ corresponds a spherically symmetric electron density, and the double-group quantum numbers γ_{8g}, γ_{8u}, γ_{6u}, and γ_{6g} (having 2, 1, 1, and 0 node-plane, respectively) are the same as for pure σ orbitals (whereas $J=1/2$ corresponds to two-thirds π and a- third σ character). The next set of six Kramers doublets are the ($\omega=1/2$) components of ($J=3/2$). The squared amplitude of two-thirds σ and a-third π character corresponds to a prolate electronic density concentrated, like a cigar, close to the Os–I axis. Hence, one expects only mild ligand-ligand respulsion effects. The most easily excited (ω = $3/2$) is a pure π orbital, and one expects strong ligand - ligand repulsion for these six Kramers doublets. The double - group quantum numbers are γ_{8g}, γ_{7g}, γ_{8u}, and γ_{7u}. Of these, γ_{7g} is exactly $(\pi)t_{2g}$ and has two node-planes whereas γ_{7u} is exactly $(\pi)t_{2u}$ and has three node-planes. A major difference is that $(\pi)t_{1g}$ and $(\pi)t_{2u}$ are essentially non-bonding seen from the point of view of the central atom, whereas $(\pi)t_{2g}$ binds with the central atom 5d lower sub-shell. The two levels γ_{8g} and γ_{8u} have an additional node-plane because of their orthogonalization on the ($\omega=1/2$) components of ($J=3/2$).

At present, it is only possible in hexa-iodides to identify the series of parentage states of the excited levels $a\Gamma_{8g}<a\Gamma_{8u}<\Gamma_{7u}<b\Gamma_{8u}$ among the electron transfer bands to the lower sub-shell, and it would be valuable if the four other levels belonging to ($J=3/2$) excitation could be identified among the much weaker absorption bands. The three transitions to the higher sub-shell $(5d)e_g$ (occurring at 26.8, 30.0, and 35.6 kK in OsI_6^{2-} and at 20.25, 22.75, and 29.15 kK in PtI_6^{2-}) can be ascribed[3,9] to the excited levels $a\Gamma_{8u}<\Gamma_{6u}<b\Gamma_{8u}$ obtaining some σ-character. Of course, the transitions from $c\Gamma_{8u}$ (at 44.6 kK in OsI_6^{2-} and 39.8 kK in PtI_6^{2-}) are even stronger.

The transitions from the 18 π and σ orbitals of the six halide ligands to the upper sub-shell $(5d)e_g$ are much broader than to the lower sub-shell $(5d)t_{2g}$ because of the σ-anti-bonding character of the two $(5d)e_g$ orbitals. The oscillator strength is much larger since both the maximum molar extinction coefficient ε and the half-widths are several times greater. However, the intensity is concentrated on a few transitions according to the amount of σ character in the lower orbital[1] and as a matter of fact, hexachlorides show only two such transitions (from $(\pi+\sigma)t_{1u}$ and $(\sigma+\pi)t_{1u}$), hexabromides three (from the three Γ_{8u}) and hexa-iodides four, as mentioned above. $OsCl_6^{2-}$ has the first of the two intense transitions[26] at 47.9 kK, and actually, our complexes all show a strong band above 45 kK when they contain many chloride ligands. By the same token, $OsBr_6^{2-}$ has the strong transitions at 36.0 and 41.2 kK (and the third[26] at 51.9 kK beyond the region studied here) and comparable transitions are found in mixed chloro-bromo complexes[11] and bromo-iodo complexes containing three, four or five bromide ligands. In Table I, we indicate ($\rightarrow e_g$) when the transition goes to the upper sub-shell, but no arrow when it goes to $(5d)t_{2g}$, and we use three sets of quantum numbers: ($\omega=3/2$) and ($\omega=1/2$) in the case of a single iodide ligand (in MX_5I having the symmetry C_{4v} the appropriate double-group quantum numbers are γ_{t7} and γ_{t6}) and in the case of two iodide ligands in *trans*-position (MX_4I_2 having the symmetry D_{4h} has γ_{t7u} and $_{t6u}$ for the combinations possessing odd parity); Γ_{8g}, Γ_{8u}, Γ_{7u}, *etc.* which are the double-group quantum numbers in oc-

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Table I. The absorption maxima (shoulders in parentheses) with wave-numbers ν in kK (1000 cm^{-1}), wave-lengths λ in mμ (nm) and molar extinction coefficients ε. The assignments are: « i.s.s. » = intra-sub-shell transition; transitions to the lower (t_{2g}) sub-shell are marked by the symmetry type (ω or Mulliken symbol) of the filled M.O. loosing the electron; transitions to the higher sub-shell are marked$\rightarrow e_g$.

	ν	λ	ε	
$OsCl_5I^{2-}$	(10.5)	(953)	(90)	i.s.s.
	11.25	888.5	210	i.s.s.
	15.25	656	2200	$(\omega=3/2)$
	16.65	600.5	1800	$a(\omega=1/2)$
	(19.0)	(525)	(650)	
	22.7	441	1900	$b(\omega=1/2)$
	(26.0)	(385)	(3100)	$(\pi+\sigma)t_{1u}$
	(28.5)	(351)	(5450)	
	29.9	334	6100	$(\pi)t_{2u}$ and $a(\omega=1/2)\rightarrow e_g$
	(33.2)	(301)	(2400)	
	(35.2)	(284)	(2400)	
	(39.8)	(251)	(10700)	$b(\omega=1/2)\rightarrow e_g$
	(45.9)	(218)	(19.200)	
	46.8	213.5	20800	$(\pi+\sigma)t_{1u}\rightarrow e_g$
trans-$OsCl_4I_2^{2-}$	(10.4)	(960)	(60)	i.s.s.
	11.0	911.5	70	i.s.s.
	(13.8)	(726)	(1100)	
	(15.9)	(629)	(3600)	
	16.55	604	4050	
	(18.5)	(541)	(1400)	
	(21.2)	(472)	(690)	
	23.0	434.5	1200	$b(\omega=\tfrac{1}{2})$
	(27.7)	(361)	(6000)	
	30.1	332	12700	sharp, $a(\omega=\tfrac{1}{2})\rightarrow e_g$
	(34.2)	(292)	(6600)	
	37.6	266	20700	sharp, $b(\omega=\tfrac{1}{2})\rightarrow e_g$
	(42.4)	(236)	(9000)	
cis-$OsCl_4I_2^{2-}$	(10.3)	(967)	(430)	i.s.s.
	10.95	914	510	i.s.s.
	13.55	738	2150	
	15.15	659	1250	
	16.95	590	2000	
	(18.2)	(550)	(1800)	
	20.5	488	1900	
	23.1	432	1800	
	(25.7)	(389)	(3500)	
	27.3	366	4000	
	28.7	349	3950	
	(36.0)	(278)	(5500)	
	44.6	224	23100	
fac-$OsCl_3I_3^{2-}$	(9.95)	(1005)	(510)	i.s.s.
	10.75	931	1100	i.s.s. ?
	13.2	758	3450	
	15.7	636.5	1700	
	20.2	495.5	3100	
	22.4	446.5	2700	
	(24.5)	(408)	(1900)	
	25.75	388	2800	
	27.6	362	3500	
	29.05	344	3700	
	30.4	329	3750	
	31.0	322.5	3750	
	(35.0)	(286)	(6500)	
	41.1	243	21600	
	(44.4)	(225)	21100	
mer-$OsCl_3I_3^{2-}$	(9.97)	(1003)	(530)	i.s.s.
	10.6	942.5	620	i.s.s.
	(13.1)	(764)	(1600)	
	16.0	626	3500	
	(18.15)	(551)	(1950)	
	20.2	495	1600	
	22.55	443.5	1700	
	(24.1)	(415)	(1800)	
	(25.2)	(397)	(2600)	
	26.1	383	4100	
	(27.7)	(361)	(5500)	
	30.15	331.5	6650	
	(36.7)	(272)	(12000)	
	(42.0)	(238)	(18300)	
	(47.0)	(213)	(25700)	

Table I. (Continued)

	ν	λ	ε	
trans-$OsCl_2I_4^{2}$	9.5	1053	285	i.s.s.
	11.1	(900)	(650)	
	12.4	807	2000	
	(14.8)	(676)	(4800)	
	15.7	638	6300	
	(16.7)	(598)	(4300)	
	(17.9)	(559)	(2300)	
	21.6	463.5	1800	
	22.8	439	2200	
	25.55	391.5	7600	sharp
	(27.5)	(364)	(7700)	
	29.4	340	11400	
	(30.1)	(332)	(9900)	
	(35.2)	(284)	(11500)	
	39.0	256.5	25400	sharp
	44.6	224	24700	
cis-$OsCl_2I_4^{2-}$	(9.6)	(1043)	(670)	
	10.3	970	1200	
	(11.7)	(856)	(1400)	
	12.75	785	2650	
	(14.2)	(706)	(2700)	
	15.5	644.5	4200	
	16.85	593	3200	
	20.75	482	2550	
	22.1	452.5	2050	
	(23.7)	(423)	(2700)	
	25.65	390	4200	
	(27.0)	(371)	(7100)	
	30.0	333	9300	
	(38.0)	(263)	(13700)	
	(41.0)	(244)	(14900)	
$OsClI_5^{2-}$	(9.17)	(1090)	(490)	
	10.0	1000	1200	
	(11.7)	(855)	(1900)	
	12.8	781	3500	
	14.0	715.5	3500	
	16.0	624	5300	
	(16.5)	(607)	(5100)	
	20.05	498.5	1500	
	21.65	462	2300	
	23.15	432	3500	
	(25.65)	(390)	(4200)	
	30.3	330	7500	
	(31.8)	(314)	(8000)	
	37.0	270	15600	sharp
OsI_6^{2-}	9.4	1065	580	Γ_{8g}
	(11.7)	(852)	(3300)	$a\Gamma_{8u}$
	12.4	805.5	4850	
	(14.7)	(679)	(4600)	even
	15.25	656	8200	Γ_{7u}
	17.0	586	1100	even
	18.35	545	5800	$b\Gamma_{8u}$
	18.6	537	5850	
	(20.9)	478	(1400)	even
	26.8	373.5	12.300	$a\Gamma_{8u} \rightarrow e_g$
	30.3	330	9650	$\Gamma_{6u} \rightarrow e_g$
$OsBr_6^{2-}$	17.75	563	1120	Γ_{8g}
	(19.2)	(520)	(2860)	Γ_{6g} ?
	20.6	486	6350	$a\Gamma_{8u}$
	22.6	442	8890	Γ_{7u}
	24.05	416	5270	$b\Gamma_{8u}$
	25.3	395	5490	
	36.0	278	9850	$a\Gamma_{8u} \rightarrow e_g$
	41.2	243	19620	$b\Gamma_{8u} \rightarrow e_g$
$OsBr_5I^{2-}$	11.0	910	390	i.s.s. ?
	14.0	715	1730	$(\omega = 3/2)$
	15.65	640	1260	$a(\omega = 1/2)$
	17.65	566	2020	
	(19.1)	(523)	(3350)	
	19.8	505	4050	$a\Gamma_{8u}$
	21.85	458	5750	Γ_{7u}
	24.65	406	5180	$b\Gamma_{8u}$
	(28.5)	(351)	(1880)	

Table I. (Continued)

	ε	λ	ν	
	(35.5)	(282)	(7150)	$a\Gamma_{8u}\rightarrow e_g$
	40.0	250	13850	$b\Gamma_{8u}\rightarrow e_g$
trans-$\mathrm{OsBr_4I_2}^{2-}$	8.8	1135	30	i.s.s.
	10.6	945	150	i.s.s.
	(12.9)	(777)	(680)	
	(14.0)	(715)	(1400)	
	15.45	647	2660	
	(16.0)	(625)	(2520)	
	(18.7)	(536)	(850)	
	21.6	463	2690	
	24.3	411	3750	
	29.4	340	6000	$a(\omega=\frac{1}{2})\rightarrow e_g$
	(36.4)	(275)	(9450)	$b(\omega=\frac{1}{2})\rightarrow e_g$
	39.7	252	12750	$b\Gamma_{8u}\rightarrow e_g$
cis-$\mathrm{OsBr_4I_2}^{2-}$	8.7	1150	80	i.s.s.
	(10.1)	(990)	(400)	
	10.6	941	550	
	12.85	778	1260	
	14.4	694	1470	
	15.65	640	1900	
	17.75	563	2050	
	18.8	532	2720	
	20.8	481	3350	
	(22.5)	(444)	(2900)	
	24.1	415	3530	
	(29.1)	(344)	4700	
	(34.0)	(294)	(9450)	
	39.0	256	18400	
fac-$\mathrm{OsBr_3I_3}^{2-}$	(8.7)	(1150)	(130)	i.s.s.
	(9.9)	(1010)	(610)	
	10.5	952	800	
	12.9	776	1640	
	14.7	681	1850	
	(15.5)	(645)	(1800)	
	(16.8)	(596)	(1840)	
	17.8	562	2040	
	19.7	507	2680	
	21.75	460	2350	
	23.25	430	2420	
	(29.1)	(344)	(4700)	
	32.15	311	6450	
	38.0	263	12700	
mer-$\mathrm{OsBr_3I_3}^{2-}$	(9.9)	(1010)	(240)	i.s.s.
	10.6	945	350	i.s.s.
	(12.2)	(820)	(650)	
	(13.1)	(763)	(1000)	
	(14.5)	(690)	(1750)	
	15.55	643	2560	
	(16.8)	(595)	(1750)	
	(19.8)	(505)	(1430)	
	21.4	467	2170	
	22.65	441	2130	
	24.15	414	2760	
	29.6	338	5900	
	(32.4)	(309)	6500	
	38.75	258	13450	
trans-$\mathrm{OsBr_2I_4}^{2-}$	(8.7)	(1150)	(50)	i.s.s.
	(9.8)	(1020)	(250)	
	(10.5)	(952)	(320)	
	11.3	886	580	
	12.15	823	1230	
	(13.8)	(724)	(1700)	
	14.65	682	3000	
	16.1	621	2980	
	(16.7)	(599)	(2370)	
	20.3	493	1360	
	21.8	458	1900	
	23.1	432	2480	
	28.8	347	5950	
	(31.4)	(318)	(5250)	
	37.0	270	11950	

Table I. (Continued)

	ε	λ	ν	
cis-$OsBr_2I_4^{2-}$	8.62	1160	80	i.s.s.
	(9.7)	(1030)	(470)	
	10.1	990	610	
	12.4	808	1320	
	13.4	746	1670	
	14.6	686	2220	
	16.2	617	2170	
	18.4	543	1670	
	(19.0)	(526)	(1380)	
	(20.8)	(481)	(1800)	
	21.55	464	1910	
	(22.1)	(452)	(1780)	
	29.7	337	6850	
	(36.2)	(276)	(11000)	
	37.3	268	11920	
$OsBrI_5^{2-}$	(8.85)	(1130)	(250)	
	9.95	1005	520	
	(11.7)	(855)	(870)	
	12.45	803	1200	
	13.5	741	1590	
	(15.7)	(637)	(1690)	
	16.4	610	1950	
	18.25	548	900	
	19.3	518	1060	
	20.6	485	1400	
	21.8	459	1140	
	28.8	347	5130	$a\Gamma_{8u}\rightarrow e_g$
	(30.8)	(325)	(4980)	$\Gamma_{6u}\rightarrow e_g$
	36.6	273	7700	$b\Gamma_{8u}\rightarrow e_g$
$Os(H_2O)I_5^-$	(9.1)	(1100)	360	
	10.1	990	1200	
	11.95	837.5	1600	
	13.1	762.5	4450	
	14.6	684	3500	
	16.6	601.5	6000	
	(19.05)	(525)	(1550)	
	(23.8)	(420)	(2350)	
	(26.8)	(373.5)	(6200)	$a\Gamma_{8u}\rightarrow e_g$
	30.3	330	9800	$\Gamma_{6u}\rightarrow e_g$

tahedral symmetry O_h of the parentage state of 35 electrons in the 18π and σ orbitals when six (or slightly fewer) bromide and iodide ligands are present; and $(\pi)t_{1g}$, $(\pi+\sigma)t_{1u}$ and $(\pi)t_{2u}$ in the corresponding case of six or five chloride ligands showing much weaker relativistic effects than bromide and iodide.

Obviously, it is easier to detect transitions from iodide occurring among less reducing ligands. Interestingly enough, these absorption bands not only have lower wave-numbers but also conspicuously half-widths corresponding to the good approximation of localized transitions from the heavy[20] iodide ligands. Because of the requirement of σ-character of the lower orbital, only the two eigenvalues of eq. (1), $a(\omega=1/2)$ at lower and $b(\omega=1/2)$ at higher wave-numbers, are readily detected. The phenomenon is not as evident in $OsCl_5I^{2-}$ where the transition $a(\omega=1/2)\rightarrow e_g$ of the iodide ligand at 29.9 kK coincides with $(\pi t_{2u}\rightarrow t_{2g}$ of the five chloride ligands, and where $b(\omega=1/2)\rightarrow e_g$ is only seen as a shoulder at 39.8 kK on the strong band due to $(\pi+\sigma)t_{1u}\rightarrow e_g$ of the chloride ligands. But the two sharp bands of *trans*-$OsCl_4I_2^{2-}$ at 30 1 and 37.6 kK clearly are due to excitations of the odd linear combinations of two $(\omega=1/2)$ orbitals. The three sharp bands of $OsBr_5I^{2-}$ at 19.8, 21.8, and 24.6 kK are probably closely simi-

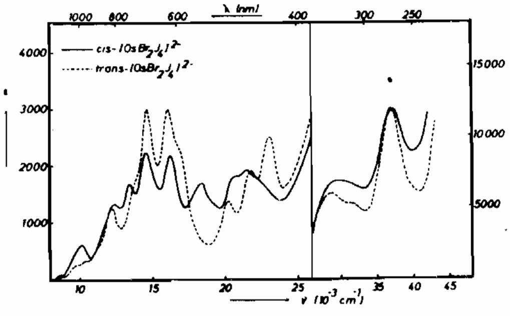

Figure 1. Absorption spectra of *cis*- and *trans*- $OsBr_2I_4^{2-}$ in 1 *M* H_2SO_4 at 0°C.

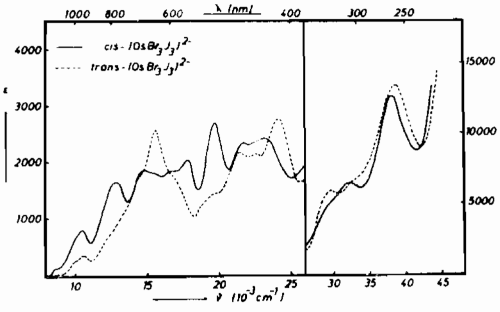

Figure 2. Absorption spectra of *cis*- and *trans*- $OsBr_3I_3^{2-}$ in 1 *M* H_2SO_4 at 0°C.

lar to the transitions to (5d)t_{2g} of $OsBr_6^{2-}$ at 20.6, 22.6 and 25.3 kK, and the absence of strong transitions from iodide between 25 and 35 kK in $OsBr_5I^{2-}$ is somewhat perplexing. One solution of this problem would be that the iodide-iodide interaction in *trans*-$OsCl_4I_2^{2-}$ is sufficiently strong to decrease the excitation energy of the odd combinations of ($\omega = 1/2$) to the extent of some 10 kK, $OsCl_5I^{2-}$ perhaps having these transitions at 39.8 and 45.9 kK. However, this suggestion seems too radical *Trans*-$OsBr_4I_2^{2-}$ has bands at 29.4 and 36.4 kK most readily ascribed to the two transitions from odd combinations of ($\omega = 1/2$) iodine orbitals though their intensities are lower than in *trans*-$OsCl_4I_2^{2-}$. Extremely sharp bands are seen in *trans*-$OsCl_2I_4^{2-}$ at 25.55 and 39.0 kK; they are undoubtedly transitions in the coplanar OsI_4 group. In quadratic MX_4, the excitation energies of the odd orbitals are expected[2] to increase $(\pi+\sigma)\gamma_{t5u} < (\pi)\gamma_{t4u} < (\pi)\gamma_{t2u} < (\sigma+\pi)\gamma_{t5u}$ and the two strong absorption bands[20] of low-spin d^8 (palladium(II) and gold(III)) tetra-chloro and tetra-bromo complexes are due to the transitions from the orbitals showing mixed σ and π character to the empty orbital consisting mainly of central atom (x^2–y^2). When strong relativistic effects are present, these orbitals correspond[9] to three γ_{t6u} and three γ_{t7u}. Correspondingly, PdI_4^{2-} has bands[27] at 18.5 and 22.3 kK and PtI_4^{2-} at 25.9 and 30.3 kK[28] separated by slightly less than 5 kK. An important difference from our complexes and low-spin octahedral d^6 and quadratic d^8 complexes is that the intensity in the two latter cases is almost exclusively concentrated in transitions from orbitals having, at least some, σ-bonding character.

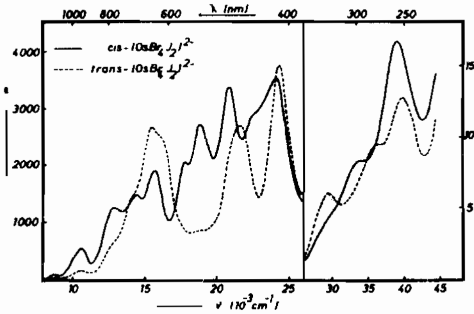

Figure 3. Absorption spectra of *cis*- and *trans*- $OsBr_4I_2^{2-}$ in 1 *M* H_2SO_4 at 0°C.

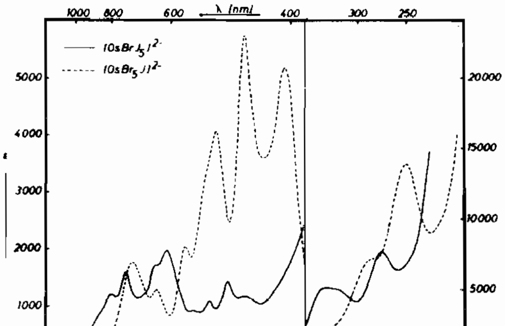

Figure 4. Absorption spectra of $OsBrI_5^{-2}$ and $OsBr_5I^{2-}$ in 1 *M* H_2SO_4 at 0°C.

The more than 200 electron transfer bands given in Table I of 19 complexes have only been assigned definite group-theoretical quantum numbers in about 40 cases. However, we find it worthwhile to publish the results, if for no other reason, in order to attract the theorists' interest for this class of highly complicated and detailed spectra. It is conceivable that calculations taking into account effects of comparable order of magnitude of difference in optical electronegativity, ligand-ligand repulsion and, in the case of bromide and iodide, «spin-orbit coupling» would be able to describe all 200 excited states. On the other hand there is no evidence at all that it is necessary to consider the coupling between the parentage state Γ_J of the collectively oxidized[7] set of six halide ligands lacking one electron in their eighteen π and σ orbitals, and the two possible levels Γ_{7g} and Γ_{8g} of the excited state containing five electrons in the lower sub-shell (5d)t_{2g}. However, an additional complication comes from the splitting to the extent of about 1 kK of Γ_{8u} states in the unsubstituted hexahalides due to the Jahn-Teller effect.[4,6] Said in other words, it cannot be argued that the instantaneous symmetry[7,8] is sufficiently close to the point-group characterizing the static picture (of the seven nuclei of the complex possessing the highest symmetry) to allow predictions better than 1 to 2 kK. This is a serious limitation in the case of complexes having some ten electron transfer bands between 15 and 30 kK. Some conclusions may become accessible from measurements of the Faraday effect of our complexes started by Dr. Schatz.

Unfortunately, it is not possible to apply a simple perturbation treatment extrapolating from OsI_6^{2-} to $OsXI_5^{2-}$ or to *trans*-$OsX_2I_4^{2-}$. The reason is that the distribution over more than 10 kK of the excitation energies of OsI_6^{-2} itself is determined by a complicated co-operation of relativistic and ligand-ligand effects, and that replacing one iodide ligand changes the energy levels to a considerable extent. Thus, $OsClI_5^{2-}$ has a spectrum rather similar to the blue species $Os(H_2O)I_5^-$ formed[13] by aquation of OsI_6^{-2} at 0°C in 1 molar sulphuric acid which is complete after six hours (it is highly improbable that sulphate complexes are formed) and which reacts very rapidly with Cl^- to form $OsClI_5^{-2}$. In both cases, the band positions are quite modified relative to OsI_6^{-2} without obvious regularities.

Experimental Section

The techniques of electrophoresis for separating complex anions were previously described[10,11] as well as the preparation of the chloro-iodo[13] and chloro-bromo[14] complexes discussed here.

The absorption spectra were measured of 10^{-4} *M* solutions of the caesium salts in 1 *M* aqueous sulphuric acid kept at 0°C on a Beckman DK-2A spectrophotometer. The kinetics of the aquation of OsI_6^{2-}, $OsBrI_5^{2-}$, and $OsClI_5^{2-}$ to $Os(H_2O)I_5^-$ was followed at 3°C. The aquation proceeds with a half-life of 36 minutes for OsI_6^{2-}, 41 minutes for $OsBrI_5^{2-}$, and 53 minutes for $OsClI_5^{2-}$.

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[27] P. Day, M.J. Smith, and R.J.P. Williams, *J. Chem. Soc.* (*A*), 668 (1968).

[28] B. Corain and A.J. Poë, *J. Chem. Soc.* (*A*), 1318 (1967).