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

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The previous M.O. treatment of unsubstituted hexahalides has been modified, taking the results on FARADAY effect obtained at the University of Virginia into account. The absorption spectra previously measured of the complexes (M=Os, Ir) *trans*-$\text{MCl}_4\text{Br}_2^{--}$ and *trans*-$\text{MCl}_2\text{Br}_4^{--}$ are interpreted by a M.O. treatment for the symmetry D_{4h} as electron transfer transitions, including a first-order relativistic (spin-orbit coupling) correction. The concept of holohedrized symmetry is sufficiently valid to allow a description of $\text{MCl}_5\text{Br}^{--}$ and MClBr_5^{--} as if they were tetragonal with centre of inversion and *fac*-(or *cis*-)$\text{MCl}_3\text{Br}_3^{--}$ as if they were cubic. It is shown that the ligand-ligand antibonding effects have the same order of magnitude as the moderate difference in optical electronegativity between Cl^- and Br^-.

The absorption spectra of mixed halide complexes are theoretically very interesting. Such spectra are for instance known for chlorobromo complexes of bismuth (III)[1], uranium (IV) in nitromethane solution[2], palladium (II)[3] and gold (III)[4]. The equilibria are almost instantaneous in these cases, and the individual spectra have been calculated from formation constants and the solution spectra by the technique first applied by BJERRUM[5]. In the 5d group the complexes are frequently robust and can be separated by electrophoresis or chromatography at room temperature. Such a separation is much easier in the case of mixed complexes of a neutral ligand (water, ammonia) and an anion, because the charge of the complex molecule then varies with the composition. However, it has been possible for MÜLLER[6] to separate the seven rhenium (IV) complexes $\text{ReCl}_x\text{Br}_{6-x}^{--}$ all having the same charge. Unfortunately the electron transfer bands are not easy to study because they are superposed to a great extent, as is also true[7] for ReCl_6^{--} and ReBr_6^{--}. The complexes $\text{OsCl}_x\text{Br}_{6-x}^{--}$ and $\text{IrCl}_x\text{Br}_{6-x}^{--}$ were separated by BLASIUS and PREETZ[8] and recently, even the geometrical isomers *cis*- and *trans*- (in the case of MCl_3Br_3 also called *fac*- and *mer*-) have been characterized[9] using kinetic control of the reaction path.

The absorption spectra[8, 9] contain many narrow bands due to electron transfer from the eighteen filled orbitals mainly delocalized on the six halide ligands to the partly filled shell, the preponderant electron configuration being $5d^4$ for osmium (IV) and $5d^5$ for iridium (IV). The spectra of Ir (IV) lacking one electron in the lower sub-shell in octahedral symmetry[10, 11], where at most six electrons can be accommodated, are expected to be particularly simple[12] because each set of degenerate orbitals having the symmetry type γ_k corresponds to exactly one excited term $^2\Gamma_k$, the "hole" having moved from the lower 5d-sub-shell to the filled M. O. (molecular orbitals). Hence, IrCl_6^{--} and IrBr_6^{--} have been favourite examples for the study of electron transfer spectra[13–15]. Due to a rather unexpected effect of nearly pure *j,j*-coupling[13] in $5d^4$, Os (IV) presents nearly the same distribution of electron transfer bands as Ir (IV), only at a higher wavenumber because of the less oxidizing character

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of osmium(IV) and corresponding lower *optical electronegativity* [10, 16] x_{opt}. This argument cannot be extended to Re(IV)[7]. We are now discussing the energy levels expected for substituted chromophores MA_xB_{6-x} of orthoaxial type [17] i. e. all six ligands A and B can be situated on the axes of a Cartesian coordinate system, and we start by considering the unsubstituted hexahalide MA_6.

Unsubstituted Hexahalides MA_6

Until recently, it was assumed [10, 13, 14] that the order of the twelve π orbitals formed by the loosest bound, filled p shell of A was that determined by the number of angular node-planes [18] which also indicates the lowest value of l for central atom orbitals which are able to mix with the combination of ligand orbitals. We call this quantum number "l" and write "s", "p", "d", "f", "g" ... for "l" = 0, 1, 2, 3, 4,... Said in other words, the four sets of π-orbitals have "l" = 4, 3, 2, 1 and the three sets of σ-orbitals "l" = 2, 1, 0. However, in octahedral symmetry, the number of degenerate orbitals is not always $(2l+1)$ like in spherical symmetry [10] but it is 3, 3, 3, 3, 2, 3, 1 in the sets mentioned. The energy difference between the π-orbitals "f" and "d" can be ascribed to the central atom d orbitals forming a bonding M. O. by combination with the latter set (as experimentally verified by the study of hyperfine structure of the paramagnetic resonance curve induced by the iridium and chlorine nuclei [19]). On the other hand, since the central atom g and f orbitals presumably hardly have any importance for the chemical bonding, the energy difference observed between the "g" and "f" π-orbitals must be caused by McClure's effect, i. e. the increased kinetic energy [20, 21] due to the four rather than three angular node-planes. Similar arguments can be extracted from Schmidtke's article on topological matrices [22]. In tetrahedral chromophores MX_4, the loosest bound combination of π-orbitals is "f" having the highest number of angular node-planes [16, 23, 24].

These arguments have always been slightly uncertain in the case of the π-orbitals having "l" = 1. This set is the only one having the same symmetry type (γ_{4u} in Bethe, t_{1u} in Mulliken's nomenclature) as one of the sets of σ-orbitals. The effect on the intensities of transitions to the higher d-sub-shell are spectacular [13]; it is nearly certain that the admixture of σ-character to the π-set [which we hence call $(\pi+\sigma)\gamma_{4u}$] is responsible for nearly all of the electric dipole oscillator strength observed. Thus, it may be argued that one should assign "l" = 3 rather than 1 to the π-combination which has to be orthogonal [25] on the σ-combination "p" and hence develops a node-cone, the M. O. wavefunction having opposite sign for four ligands relative to the two others on one Cartesian axis. It is generally recognized that a node-cone counts for two node-planes.

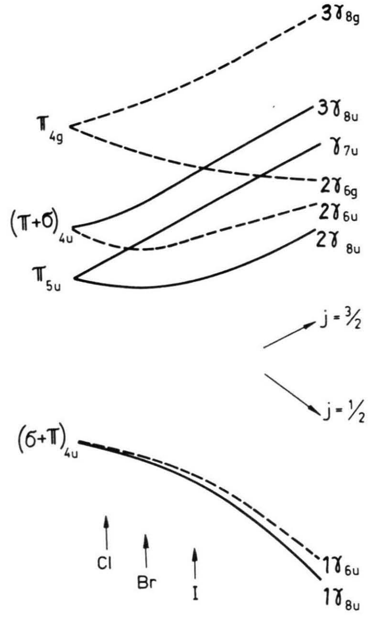

Fig. 1. The energy differences between 8 of the 12 energy levels formed from six halide ligands as a function of their Landé parameter. In the non-relativistic case at the left-hand side, the energy difference between π_{4g} and $(\pi+\sigma)_{4u}$ has been taken as the average for a variety of hexahalide complexes. In our case of Os(IV) and Ir(IV), it is hardly larger [Eq. (9)] than between $(\pi+\sigma)_{4u}$ and π_{5u}. However, since the even and odd levels do not mix, this only shifts the two highest curves. The dashed curves correspond to relativistic orbitals from which transitions to a central atom γ_{7g} orbital have no oscillator strength.

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Said in other words, whereas the lowest "p" σ-orbital has only one node-plane like the angular function (z/r), the π-orbitals of same symmetry type have one node-plane and one node-cone similar to the angular f function $z(5\,z^2-3\,r^2)/r^3$. The question whether this "$\sim$ f" set of symmetry type γ_{4u} or the "f" set of symmetry type γ_{5u} [having node-planes comparable to $z(x^2-y^2)/r^3$] has highest energy becomes a question of whether the stabilizing influence of the central atom empty p orbitals forming bonding combinations with "$\sim$f" are more[13] or less important than the ligand-ligand anti-bonding effect because of the node-cone between π- and σ contributions to "$\sim$f".

Actually, evidence is accumulating[26, 27] that ligand-ligand anti-bonding effects can be of great importance for the loosest bound M. O. In our case, the clearest argument comes from the Faraday effect[28, 29]. According to a kind communication from McCaffery and Schatz[16, 30] there is no doubt that the transition from "$\sim$f" occurs at lower energy, 20.5 kK (1 kK = 1000 cm^{-1}) in $\mathrm{IrCl_6^{--}}$ than from "f" at 23.0 and 24.4 kK because the circular dichroism induced by the external magnetic field has opposite, and known, signs in the two cases.

Figure 1 shows the influence of the relativistic (spin-orbit coupling) effects[10, 13] in the halide ligands represented by increasing values of the Landé parameter ζ_{np} for the halogen[16]. The non-relativistic orbital energy differences are essentially taken from the absorption spectra[13] concording for a large number of hexahalide complexes and from the Faraday effect just discussed. However, their qualitative justification would be:

$$\begin{array}{lll}
\text{"g"} & \pi\,\gamma_{4g}(\mathrm{t_{1g}}) & E = H_\pi + H_{\pi\,\mathrm{ang}} \\
\text{"}\sim\text{f"} & (\pi+\sigma)\,\gamma_{4u}(\mathrm{t_{1u}}) & E = H_\pi + \dfrac{H^2_{\sigma\pi}}{H_\pi - H_\sigma} - H_{\pi\,\mathrm{par}} - \dfrac{H^2_{\pi\mathrm{p}}}{H_\mathrm{p} - H_\pi} \\
\text{"f"} & \pi\,\gamma_{5u}(\mathrm{t_{2u}}) & E = H_\pi + H_{\pi\,\mathrm{par}} \\
\text{"d"} & \pi\,\gamma_{5g}(\mathrm{t_{2g}}) & E = H_\pi - H_{\pi\,\mathrm{ang}} - \dfrac{H^2_{\pi\mathrm{d}}}{H_\mathrm{d} - H_\pi} \\
\text{"d"} & \sigma\,\gamma_{3g}(\mathrm{e_g}) & E = H_\sigma + H_{\sigma\,\mathrm{cis}} - \tfrac{1}{2}H_{\sigma\,\mathrm{trans}} - \dfrac{H^2_{\sigma\mathrm{d}}}{H_\mathrm{d} - H_\sigma} \\
\text{"p"} & (\sigma+\pi)\,\gamma_{4u}(\mathrm{t_{1u}}) & E = H_\sigma - \dfrac{H^2_{\sigma\pi}}{H_\pi - H_\sigma} + \tfrac{1}{2}H_{\sigma\,\mathrm{trans}} - \dfrac{H^2_{\sigma\mathrm{p}}}{H_\mathrm{p} - H_\sigma} \\
\text{"s"} & \sigma\,\gamma_{1g}(\mathrm{a_{1g}}) & E = H_\sigma - 2\,H_{\sigma\,\mathrm{cis}} - \tfrac{1}{2}H_{\sigma\,\mathrm{trans}} - \dfrac{H^2_{\sigma\mathrm{s}}}{H_\mathrm{s} - H_\sigma}
\end{array} \qquad (1)$$

In these equations, H_π and H_σ represent the diagonal elements of energy characterizing non-bonding π- and σ-orbitals. Their difference is partly a ligand field effect influencing the potential, the σ-orbitals being more stabilized by the positive central atom than the π-orbitals. Other reasons may be the orthogonalization conditions in general in the chromophore. The first-order perturbation expressions (proportional to other H), and the second-order expressions (H^2 divided by H_1-H_2) derive from interactions between orbitals having identical energies or highly different energies. In the Wolfsberg–Helmholz model[10, 11] and related treatments, the ligand-ligand bonding effects change the diagonal element for a given symmetry type γ_k as is also the case for the difference between H_π and H_σ. The alternative treatment[31] of non-symmetry-adapted atomic orbitals as starting material would consider the ligand-ligand effects as non-diagonal elements between degenerate orbitals. $H_{\pi\,\mathrm{ang}}$ indicates the non-diagonal element appropriate for two π-orbitals of adjacent ligand atoms in *cis*-position, having orthogonal node-planes. It is expected that this non-diagonal element is larger than $H_{\pi\,\mathrm{par}}$ involving two parallel π-orbitals on two ligands in *cis*-position having the same node-plane. We neglect non-diag-

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onal elements between π-orbitals in ligands in *trans*-position. $H_{\sigma\,\mathrm{cis}}$ is the non-diagonal element between two σ-orbitals on ligands in *cis*-positions and is expected to be much larger than $H_{\sigma\,\mathrm{trans}}$ though WIRTH[32] performed WOLFSBERG–HELMHOLZ calculations for $Co(NH_3)_6^{+3}$ and found a non-negligible overlap integral between the two rather diffuse lone-pairs of ammonia molecules in *trans*-position. The coefficients to the first-order ligand-ligand effects in (1) are found by summing the normalization coefficients of the ligand-ligand overlap integrals in the limit of weak overlap but can also be found considering the topological matrices[22]. The second-order perturbation expressions represent the interactions between central atom and ligand orbitals. It must be recognized that the absorption bands observed only indicate the order of increasing excitation energy "g" < "∼f" < "f" ⋘ "p" and that the position of some of the other orbitals of even parity has not been established[33, 34]. Thus, SYMONS[35] suggested "p" > "s" > "d" for the energies of the three sets of σ-orbitals.

Equation (1) has not taken into account that anti-bonding M. O. are more anti-bonding than the corresponding bonding M. O. are bonding. If the changes of kinetic energy in the bond region are evaluated[21] one would to a certain approximation expect for bonding situations, i. e. negative coefficients in (1),

$$H^2 = \frac{(\varkappa-1)}{2}\left[\mu_{\mathrm{M}}^2 + \mu_{\mathrm{X}}^2 - H_{\mathrm{M}} - H_{\mathrm{X}}\right] S_{\mathrm{MX}}^2 \qquad (2)$$

and for anti-bonding situations

$$H^2 = \frac{\varkappa}{2}\left[\mu_{\mathrm{M}}^2 + \mu_{\mathrm{X}}^2 - H_{\mathrm{M}} - H_{\mathrm{X}}\right] S_{\mathrm{MX}}^2 \qquad (3)$$

and the corresponding square-roots for the first-order perturbations. $\varkappa$ is a constant expected to be somewhat above 1; the case $\varkappa = 1$ occurs if the eigenfunctions are the original combination ψ_{X} of ligand orbitals and the combination made orthogonal to it, i. e. the normalized form of $\psi_{\mathrm{M}} - S_{\mathrm{MX}}\,\psi_{\mathrm{X}}$, where S_{MX} is the overlap integral. The quantities μ_{M} and μ_{X} are the asymptotic values of the exponents for large r, $\psi = k \exp(-\mu r)$, producing a negative local contribution to the kinetic energy[36] and the subtraction of the diagonal elements H_{M} and H_{X} in (2) and (3) represents approximately the effect of positive local kinetic energy $\mathfrak{P}\,\psi^2$ at smaller r values since we can write SCHRÖDINGER's equation for stationary states and real one-electron wave-functions ψ:

$$\mathfrak{P}(x,y,z) + U(x,y,z) = E\,,$$

$$\mathfrak{P} = -\frac{1}{2}\,\frac{\left[\dfrac{\partial^2\psi}{\partial x^2} + \dfrac{\partial^2\psi}{\partial y^2} + \dfrac{\partial^2\psi}{\partial z^2}\right]}{\psi} \qquad (4)$$

U being the potential for electrons and E the eigenvalue, all in atomic units of length 1 bohr and energy 1 hartree = 2 rydberg = 219.5 kK.

It is not suggested that (2) and (3) are quantitatively sufficient; we rather evaluate (1) by comparison with experiment. However, (2) and (3) contain the very important insurance against implosion of molecules and crystals by interpenetration of the atomic cores. Another important point is the influence of MADELUNG potentials on the diagonal elements of such models[37], the local $\mathfrak{P}$ is more negative in a certain region $r_{\mathrm{M}} \sim 3$ bohr because of the more positive U in (4).

It is clear that the energy difference between "∼f" and "f" represented by the wavenumber difference between the two first LAPORTE-allowed absorption bands may vary rather much according to circumstances because of the compensating contributions to the energy of "∼f". Actually, there is good evidence[16, 38–40] that d⁰-complexes such as $TiCl_6^{--}$, $NbCl_6^-$ and WCl_6 have a smaller energy difference, probably corresponding to smaller $H^2{}_{\sigma\pi}/(H_\pi - H_\sigma)$ in the less compressed complexes. At the same time, the transition from "∼f" becomes relatively less intense than from "f". Solvent effects[14] and compression in salts[15] such as Cs_2IrCl_6 seem also to increase the difference between "∼f" and "f".

On the other hand, the energy difference between "g" and "f" represented by the wavenumber difference between the first LAPORTE-forbidden and the second LAPORTE-allowed band stays remarkably constant and is $(H_{\pi\,\mathrm{ang}} - H_{\pi\,\mathrm{par}})$ in the model (1). The

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observed values are 6.8 kK for $TiCl_6^{--}$, 6.8 kK for $RuCl_6^{-3}$, 7.5 kK for WCl_6, 5.8 kK for $OsCl_6^{--}$, 6.2 kK for $OsCl_6^{-3}$ and 6.8 kK for $IrCl_6^{--}$. This is remarkably large quantity for effects of ligand-ligand anti-bonding.

It might be argued that the optical electronegativities x_{opt} ought to be determined from the second LAPORTE-allowed transition since the energy of "f" hardly involves any covalent bonding to the central atom and only very moderate ligand-ligand effects. The present values, which were determined at a time where it was not realized that the first LAPORTE-allowed band is due to a transition from "$\sim$f", are roughly 0.1 unit higher for the central atom than they would be applying "f".

The first-order relativistic effects[10] are proportional to the LANDÉ parameter ζ_{np} of the halogen, which we write ζ for simplicity. The limiting values of the energy levels[13] for very small ζ (RUSSELL-SAUNDERS coupling) and for very large ζ (restoring $j=\frac{3}{2}$ at high and $j=\frac{1}{2}$ at low energy) are

$$\begin{array}{lll}
3\,\gamma_{8g} & \pi_{4g}+\frac{1}{4}\zeta & +\frac{1}{2}\zeta+\frac{3}{4}\pi_{4g}+\frac{1}{4}\pi_{5g} \\
2\,\gamma_{6g} & \pi_{4g}-\frac{1}{2}\zeta & +\frac{1}{2}\zeta+\frac{1}{3}\pi_{4g}+\frac{2}{3}\sigma_{1g} \\
3\,\gamma_{8u} & \pi_{4u}+\frac{1}{4}\zeta & +\frac{1}{2}\zeta+\frac{3}{4}\pi_{4u}+\frac{1}{4}\pi_{5u} \\
2\,\gamma_{6u} & \pi_{4u}-\frac{1}{2}\zeta & +\frac{1}{2}\zeta+\frac{1}{3}\pi_{4u}+\frac{2}{3}\sigma_{4u} \\
\gamma_{7u} & \pi_{5u}+\frac{1}{2}\zeta & +\frac{1}{2}\zeta+\pi_{5u} \\
2\,\gamma_{8u} & \pi_{5u}-\frac{1}{4}\zeta & +\frac{1}{2}\zeta+\frac{1}{12}\pi_{4u}+\frac{1}{4}\pi_{5u}+\frac{2}{3}\sigma_{4u} \\
(\gamma_{7g}) & \pi_{5g}+\frac{1}{2}\zeta & +\frac{1}{2}\zeta+\pi_{5g} \\
(2\,\gamma_{8g}) & \pi_{5g}-\frac{1}{4}\zeta & +\frac{1}{2}\zeta+\frac{1}{12}\pi_{4g}+\frac{1}{4}\pi_{5g}+\frac{2}{3}\sigma_{3g} \\
(1\,\gamma_{8g}) & \sigma_{3g} & -\zeta+\frac{1}{6}\pi_{4g}+\frac{1}{2}\pi_{5g}+\frac{1}{3}\sigma_{3g} \\
1\,\gamma_{8u} & \sigma_{4u} & -\zeta+\frac{1}{6}\pi_{4u}+\frac{1}{2}\pi_{5u}+\frac{1}{3}\sigma_{4u} \\
1\,\gamma_{6u} & \sigma_{4u} & -\zeta+\frac{2}{3}\pi_{4u}+\frac{1}{3}\sigma_{4u} \\
(1\,\gamma_{6g}) & \sigma_{1g} & -\zeta+\frac{2}{3}\pi_{4g}+\frac{1}{3}\sigma_{1g}
\end{array} \tag{5}$$

writing the energies of $\pi\,\gamma_k$ and $\sigma\,\gamma_k$ as π_k and σ_k for brevity and using BETHE's double-group quantum number γ_6, γ_7 and γ_8 with even (g = gerade) and odd (u = ungerade) parity. Fig. 1 gives the variation of the energy levels between the two extremes (5) for a choice of orbital energies π_k and σ_k in reasonable agreement with the observed spectra of hexachloro complexes. The positions of the four levels given in parentheses in (5) are not known but very qualitatively, and since they do not produce any strong absorption bands (the LAPORTE-forbidden transitions may occur[13, 33] in the 30 kK region for $OsCl_6^{--}$ and $IrCl_6^{--}$) they have not been included on Fig. 1. Since the groundlevel of low-spin d^5-systems is Γ_{7g}, i.e. the lower sub-shell has the pure j,j-coupling configuration $\gamma_{8g}^4\,\gamma_{7g}$, the transitions from γ_{6u} orbitals to this γ_{7g}-hole are symmetry-forbidden, and the even orbitals (from which transitions are LAPORTE-forbidden) and γ_{6u} are shown as dashed lines on Fig. 1.

In the gaseous, neutral atoms, the values of ζ known from atomic spectroscopy are in kK:

$$\mathrm{F}\ 0.27 \quad \mathrm{Cl}\ 0.59 \quad \mathrm{Br}\ 2.46 \quad \mathrm{I}\ 5.07 \tag{6}$$

In halide complexes[16], these values are influenced by changing the fractional charge on the halogen and by delocalization effects. These two effects are expected partly to cancel. Further on, (5) neglects the contributions from central atom orbitals.
Thus, in orbitals of the symmetry type γ_{4u}, the contributions from p orbitals of the central atom are

$$\gamma_{8u} \quad +\tfrac{1}{2}a^2\,\zeta_{\mathrm{Mp}} \qquad \gamma_{6u} \quad -a^2\,\zeta_{\mathrm{Mp}} \tag{7}$$

where a is the STEVENS delocalization coefficient equal to $H_{\pi\mathrm{p}}/(H_{\mathrm{p}}-H_{\pi})$ or $H_{\sigma\mathrm{p}}/(H_{\mathrm{p}}-H_{\sigma})$ in the perturbation treatment (1).

After what we may colloquially call the "Virginian revolution", i.e. the establishment from the FARADAY effect[30] that the "$\sim$f" $= (\pi+\sigma)\,\gamma_{4u}$ set of orbitals have higher energy than the "f" $= \pi\,\gamma_{5u}$ set, it is probable that the doublet structure of the second LAPORTE-allowed band (the difference between the two maxima is 1.4 kK in $IrCl_6^{--}$ and 0.7 kK in $OsCl_6^{--}$) is mainly due to the energy difference between $2\,\gamma_{7u}$ and $2\,\gamma_{8u}$ of (5) though it was expected to be only 0.45 kK according to (6). It is possible that $3\,\gamma_{8u}$ and $2\,\gamma_{6u}$ are separated to a larger extent because of (7) but since the transition $2\,\gamma_{6u} \rightarrow 5d\,\gamma_{7u}$ is symmetry-forbidden we do not expect it to be spectacular though a weak band seems to occur for $IrCl_6^{--}$ in certain organic solvents producing narrower bands than the aqueous solution[14].

$IrBr_6^{--}$ is in fairly good agreement with Fig. 1 assuming π_{4u} 3.5 kK and π_{5u} 6.7 kK below π_{4g} (all values 5.0 kK higher than for $IrCl_6^{--}$) and $\zeta = 2.4$ kK (see Table 2). The transitions from the filled M.O. to the higher sub-shell 5d γ_{3g} are not restricted to γ_{8u} components of γ_{4u} orbitals since $\gamma_{6u} \rightarrow \gamma_{8g}$ is also symmetry-allowed as electric dipole radiation. However, it is beyond doubt[13, 34] that $(\pi+\sigma)\,\gamma_{4u} \rightarrow 5d\,\gamma_{3g}$ presents a much higher intensity because of the σ-intermixing than does the equally symmetry-allowed $\pi\,\gamma_{5u} \rightarrow 5d\,\gamma_{3g}$. Hence, the relativistic orbitals $3\,\gamma_{8u}$ and $2\,\gamma_{8u}$ are expected to divide the intensity of the broad absorption bands, at 31.5 and 37.0 kK in the case of $IrBr_6^{--}$, according to the σ-character. It is worth emphasizing that the difference 5.5 kK is more than $2\,\zeta_{Br}$ of (6) and could not be readily explained by a relativistic splitting of one $\pi\,\gamma_k$ set. However, on Fig. 1, it is caused partly by the energy difference between π_{4u} and π_{5u}. Actually, the $5d^6$-complex $PtBr_6^{--}$ has three bands at 27.0, 31.8 and 33.3 kK, and the hexaiodides three maxima (OsI_6^{--} 26.8, 30.0 and 35.6 kK; PtI_6^{--} 20.25, 22.75 and 29.15 kK). The middle of these three transitions can be explained by $2\,\gamma_{6u}$ acquiring some σ-character.

We mentioned above the extraordinary similarity between low-spin d^4-systems such as Os(IV) and low-spin d^5-systems such as Os(III) and Ir(IV) due to the somewhat accidental validity of $\gamma_k \rightarrow \gamma_{7g}$ results in both cases[13]. The individual bands of $OsBr_6^{--}$ can be recognized as corresponding to those obtained by adding 5.7 kK to the wavenumbers of $IrBr_6^{--}$ [4 kK in the case of $(\pi+\sigma) \rightarrow 5d\,\gamma_{3g}$]. Actually, the agreement is better than concerning the shift 12 – 13 kK between the isoelectronic $OsBr_6^{-3}$ and $IrBr_6^{--}$.

It is interesting to compare Fig. 1 with OsI_6^{-3} and OsI_6^{--} having three Laporte-allowed $\pi \rightarrow 5d\,\gamma_{5g}$ transitions[41] roughly equidistant with the difference 3 kK. This is qualitatively in agreement with the positions expected for $3\,\gamma_{8u}$, $2\,\gamma_{7u}$ and $2\,\gamma_{8u}$ but only if the effective value of ζ is somewhat above the value 5.07 kK for the isolated iodine atom (6). The intermediate coupling has progressed so strongly toward the *j,j*-extreme that the difference between $2\,\gamma_{7u}$ and $2\,\gamma_{8u}$ is not much below the difference $\frac{3}{4}\pi_{5u} - \frac{1}{12}\pi_{4u} - \frac{2}{3}\sigma_{4u}$ from (5) which would be expected to be some 8 kK, since the broad band $1\,\gamma_{8u} \rightarrow 5d\,\gamma_{3g}$ has been identified[13] at 44.6 kK for OsI_6^{--}, i. e. 17.8 kK above $3\,\gamma_{8u} \rightarrow 5d\,\gamma_{3g}$ (the analogous distance is 19.5 kK for PtI_6^{--}). The difference between $3\,\gamma_{8u}$ and $1\,\gamma_{8u}$ in the *j,j*-limit (5) is $\frac{3}{2}\zeta + \frac{7}{12}\pi_{4u} - \frac{1}{4}\pi_{5u} - \frac{1}{3}\sigma_{4u}$, and suggests that $\pi_{4u} - \pi_{5u} \sim 3$ kK and $\pi_{5u} - \sigma_{4u} \sim 12$ kK appropriate for hexachloro complexes cannot be far off for hexaiodo complexes either. This discrepancy cannot be removed within the frame of our model, because the two distances between adjacent bands in the visible are known to be nearly identical.

However, we should not believe that we have understood everything. It is striking that each of the Laporte-allowed transitions in OsI_6^{-3} and OsI_6^{--} correspond to two adjacent, very narrow bands[41] having a distance of some 0.3 to 0.7 kK. This may be a vibronic phenomenon connected either with a dynamic Jahn-Teller effect or with some higher-order relativistic effect. Comparable difficulties occur for the additional bands of $IrBr_6^{--}$, one of the two bands 13.4 or 14.3 kK and the broad band at 19.7 kK which moves to 18.5 kK in many organic solvents[14]. However, one of the even levels given in parentheses in (5) might be the origin of the latter absorption band.

Tetragonal *trans*-MA_4B_2

Eisenstein[42] indicated the symmetry types of central atom and ligand π- and σ-orbitals in many different chromophores. The type *trans*-MA_4B_2 having the symmetry D_{4h} can be considered as the superposition of quadratic MA_4 and linear MB_2. We use Bethe's nomenclature for tetragonal symmetry, giving Mulliken's nomenclature in parenthesis, as derived from octahedral symmetry. The even or odd parity is added as a further specification if D_{4h} and O_h are considered rather than D_4 and O:

$$\begin{aligned}
&\gamma_1(a_1) = \gamma_{t1}(a_1), && \gamma_6 = \gamma_{t6},\\
&\gamma_2(a_2) = \gamma_{t3}(b_1), && \gamma_7 = \gamma_{t7},\\
&\gamma_3(e) \;\,= \gamma_{t1}(a_1) + \gamma_{t3}(b_1), && \gamma_8 = \gamma_{t6} + \gamma_{t7}.\\
&\gamma_4(t_1) = \gamma_{t2}(a_2) + \gamma_{t5}(e), &&\\
&\gamma_5(t_2) = \gamma_{t4}(b_2) + \gamma_{t5}(e), &&
\end{aligned} \tag{8}$$

Using the coordinates given in Table 4 of ref.[43] the non-relativistic orbitals given in Table 1 have well-defined symmetry types γ_{tk} and their energy and the first-order relativistic splitting can be calculated. It is sufficient to consider the diagonal sum rule and the invariance of squared elements of the secular determinant [Eq. (93) of ref.[43]] in order to obtain these results. It has previously been shown[11, 13, 16] that in cubic symmetry, the orbitals γ_6 consist of $(\omega = \frac{1}{2})$ components of the p-shell of the ligands and γ_7 exclusively of $(\omega = \frac{3}{2})$, having the contribution $+\frac{1}{2}\zeta$.

In Table 2, the observed and calculated energy levels of iridium(IV) chloro-bromo complexes are compared, and in Table 3, a similar comparison is made for osmium(IV). The agreement is satisfactory in spite of the following difficulties:

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Symmetry type cubic	Symmetry type tetragonal	Wavefunction	Non-relativistic energy	First-order relativistic correction			non-diagonal elements
$\pi\,\gamma_{4g}$	γ_{t5g}	$A\,z_1-A\,z_2-B\,x_5+B\,x_6$	$\frac{1}{2}H_{A\pi}+\frac{1}{2}H_{B\pi}+H_{AB\pi\,\mathrm{ang}}$	γ_{t7g}	$+\frac{1}{4}\zeta_B$	←	$\frac{\sqrt{2}}{4}\zeta_A$
		$A\,z_3-A\,z_4-B\,y_5+B\,y_6$		γ_{t6g}	$-\frac{1}{4}\zeta_B$	←	
	γ_{t2g}	$A\,y_1-A\,y_2-A\,x_3+A\,x_4$	$H_{A\pi}+H_{AA\pi\,\mathrm{ang}}$	γ_{t6g}	0		
$\pi\,\gamma_{4u}$	γ_{t5u}	$A\,y_1+A\,y_2+B\,y_5+B\,y_6$	$\frac{1}{2}H_{A\pi}+\frac{1}{2}H_{B\pi}-H_{AB\pi\,\mathrm{par}}$	γ_{t7u}	$+\frac{1}{4}\zeta_B$		$\frac{\sqrt{2}}{4}\zeta_A$
		$A\,x_3+A\,x_4+B\,x_5+B\,x_6$		γ_{t6u}	$-\frac{1}{4}\zeta_B$	←	
	γ_{t2u}	$A\,z_1+A\,z_2+A\,z_3+A\,z_4$	$H_{A\pi}-H_{AA\pi\,\mathrm{par}}$	γ_{t6u}	0	←	
$\pi\,\gamma_{5u}$	γ_{t5u}	$A\,y_1+A\,y_2-B\,y_5-B\,y_6$	$\frac{1}{2}H_{A\pi}+\frac{1}{2}H_{B\pi}+H_{AB\pi\,\mathrm{par}}$	γ_{t7u}	$+\frac{1}{4}\zeta_B$	←	$\frac{\sqrt{2}}{4}\zeta_A$
		$A\,x_3+A\,x_4-B\,x_5-B\,x_6$		γ_{t6u}	$-\frac{1}{4}\zeta_B$		
	γ_{t4u}	$A\,z_1+A\,z_2-A\,z_3-A\,z_4$	$H_{A\pi}+H_{AA\pi\,\mathrm{par}}$	γ_{t7u}	0	←	
$\sigma\,\gamma_{4u}$	γ_{t5u}	$A\,\sigma_3-A\,\sigma_4$	$H_{A\sigma}+\frac{1}{2}H_{AA\sigma\,\mathrm{trans}}$	γ_{t7u}	0		
		$A\,\sigma_1-A\,\sigma_2$		γ_{t6u}	0		
	γ_{t2u}	$B\,\sigma_5-B\,\sigma_6$	$H_{B\sigma}+\frac{1}{2}H_{BB\sigma\,\mathrm{trans}}$	γ_{t6u}	0		

Table 1. Energies of the filled M.O. in *trans*-MA_4B_2. The results can be applied to MA_5B removing the parity of the group-theoretical quantum numbers and, when the ligand A replaces B on one of the positions 5 or 6, replacing ζ_B by $(\zeta_A+\zeta_B)/2$.

Symmetry type									
cubic non-relativistic	$\pi\gamma_{4g}$			$(\pi+\sigma)\gamma_{4u}$			$\pi\gamma_{5u}$		
tetragonal non-relativistic	γ_{t5g}		γ_{t2g}	γ_{t5u}		γ_{t2u}	γ_{t5u}		γ_{t4u}
tetragonal relativistic	γ_{t7g}	γ_{t6g}	γ_{t6g}	γ_{t7u}	γ_{t6u}	γ_{t6u}	γ_{t7u}	γ_{t6u}	γ_{t7u}
$IrCl_6^{--}$ obs.[13]		17.0			20.5			23.0, 24.4	
$IrCl_5Br^{--}$ obs.[8]	14.23	—	—	18.8	19.65	—	22.05	—	23.6
calc.	15.5	16.1	17.0	19.0	19.6	20.5	22.2	22.8	23.7
trans-$IrCl_4Br_2^{--}$ obs.[9]	13.66	—	—	17.24	—	—	21.64	—	23.53
calc.	13.9	15.1	17.0	17.4	18.6	20.5	20.6	21.8	23.7
trans-$IrCl_2Br_4^{--}$ obs.[9]	—	12.05	—	16.56	14.8	20.08	18.08	21.14	22.27
calc.	14.5	11.8	14.7	18.0	15.3	18.2	18.5	21.2	21.4
$IrClBr_5^{--}$ obs.[8]	—	12.4	—	15.62	14.5	—	17.68	18.95	20.6
calc.	12.9	11.6	13.9	16.4	15.1	17.4	18.2	20.2	20.1
$IrBr_6^{--}$ obs.[13]	11.6		13.4	14.3, 14.9		—	17.15	18.35, 19.7	
calc.	11.4		13.2	14.9		16.7	17.5	19.3	
fac-$IrCl_3Br_3^{--}$ obs.[9]	13.17		15.43	17.68		—	20.5	22.32	
calc.	14.2		15.1	17.7		18.6	20.6	21.5	
cubic relativistic	γ_{8g}		γ_{6g}	γ_{8u}		γ_{6u}	γ_{7u}	γ_{8u}	

Table 2. Assignments of absorption bands of iridium (IV) complexes.

Symmetry type									
cubic non-relativistic	$\pi\gamma_{4g}$			$(\pi+\sigma)\gamma_{4u}$			$\pi\gamma_{5u}$		
tetragonal non-relativistic	γ_{t5g}		γ_{t2g}	γ_{t5u}		γ_{t2u}	γ_{t5u}		γ_{t4u}
tetragonal relativistic	γ_{7tg}	γ_{t6g}	γ_{t6g}	t7u	γ_{t6u}	γ_{t6u}	γ_{t7u}	γ_{t6u}	γ_{t7u}
$OsCl_6^{--}$ obs.[13]		23.9			27.0			29.3, 30.0	
$OsCl_5Br^{--}$ obs.[8]	21.23	—	—	(25.0)	26.32	—	(28.6)	—	29.6
calc.	22.1	22.7	23.9	25.3	25.9	27.0	28.1	28.7	29.7
trans-$OsCl_4Br_2^{--}$ obs.[9]	(20.28)	—	—	23.64	(25)	—	—	(28.4)	29.58
calc.	20.2	21.4	23.9	23.5	25.3	27.0	26.4	27.6	29.7
trans-$OsCl_2Br_4^{--}$ obs.[9]	—	(18.3)	—	22.57	20.7	(25.8)	23.75	(27.0)	28.17
calc.	20.8	17.5	21.0	24.1	21.0	24.3	24.1	27.0	27.3
$OsClBr_5^{--}$ obs.[8]	18.76	—	—	21.68	(20)	—	23.53	—	26.63
calc.	18.9	17.4	19.8	22.3	20.9	23.2	23.9	26.0	25.9
$OsBr_6^{--}$ obs.[13]	17.3		(19.0)	20.45		22.6	23.7		25.0
calc.	17.1		18.9	20.6		22.4	23.2		25.0
fac-$OsCl_3Br_3^{--}$ obs.[9]	19.7		(21.5)	23.75		—	26.45		28.1
calc.	20.5		21.4	23.8		24.7	26.4		27.3
cubic relativistic	γ_{8g}		γ_{6g}	γ_{8u}		γ_{6u}	γ_{7u}		γ_{8u}

Table 3. Assignments of absorption bands of osmium (IV) complexes.

1) It has been assumed that energies such as $H_{\mathrm{AB}\,\pi\,\mathrm{ang}}$ are the arithmetic means of the corresponding values in MA_6 and MB_6. It might have been argued that they would be smaller and reduce to a kind of second-order perturbation because of the different diagonal energies $H_{\pi\mathrm{A}}$ and $H_{\pi\mathrm{B}}$. However, a closer analysis shows that in octahedral chromophores, the normalization coefficients of the wavefunctions in Table 1 are given by symmetry alone in the limit of A and B not being particularly different. If the electronegativities of A and B are indeed very different, the two sets of orbitals γ_{t5u} originating from the cubic symmetry types $\gamma_{4\mathrm{u}}$ and $\gamma_{5\mathrm{u}}$ are redistributed in such a way that e. g. the linear combination $(\mathrm{By}_5+\mathrm{By}_6)$ has much higher energy than $(\mathrm{Ay}_1+\mathrm{Ay}_2)$. Because the normalization coefficient is $\sqrt{2}$ times larger, the relativistic splitting of the former set corresponds to γ_{t7u} at $+\frac{1}{2}\zeta_{\mathrm{B}}$ and γ_{t6u} at $-\frac{1}{2}\zeta_{\mathrm{B}}$. In the case of complexes such as *trans*-$\mathrm{M(NH_3)_4B_2}$ where the second set does not exist at all, ligands such as $\mathrm{NH_3}$ having only a σ-bonding lone-pair and no π-lone-pairs, the same situation occurs. The same arguments hold for the two sets γ_{t5g} in *trans*-$\mathrm{MA_4B_2}$.

2) In Tables 2 and 3, the calculated levels are derived from the first-order relativistic treatment alone, assuming $\zeta_{\mathrm{Cl}}=0$ and $\zeta_{\mathrm{Br}}=2.4$ kK, and the σ-admixture (estimated to $a^2\sim 0.2$ from intensities [13]) to γ_{t4u} has been neglected, except as a contribution to the diagonal energy $\pi_{4\mathrm{u}}$.

This approximation of RUSSELL–SAUNDERS coupling seems to be satisfactory in chloro-bromo complexes, whereas it would not work for iodides, as we discussed in connection with Fig. 1. Actually, the agreement is slightly less convincing for $\mathrm{IrBr_6}^{--}$ than for the mixed complexes. The excitation energies of the non-relativistic orbital sets relative to the $5\mathrm{d}\,\gamma_{7\mathrm{g}}$ hole were taken to be in kK:

	$-\pi_{4\mathrm{g}}$	$-\pi_{4\mathrm{u}}$	$-\pi_{5\mathrm{u}}$	
$\mathrm{OsCl_6}^{--}$	23.9	27.0	29.7	
$\mathrm{OsBr_6}^{--}$	17.7	21.2	24.4	(9)
$\mathrm{IrCl_6}^{--}$	17.0	20.5	23.7	
$\mathrm{IrBr_6}^{--}$	12.0	15.5	18.7	

essentially in order to obtain agreement with the observed spectra of the hexachloro complexes. The corresponding excitation energies were taken to be 5.0 kK lower in $\mathrm{IrBr_6}^{--}$ than in $\mathrm{IrCl_6}^{--}$ and 5.7 kK higher in $\mathrm{OsBr_6}^{--}$ than in $\mathrm{IrBr_6}^{--}$.

We do not attempt to describe the roughly linear variations of the broad and intense electron transfer bands above 30 kK corresponding to transitions from the three $\gamma_{8\mathrm{u}}$ (cubic symmetry) relativistic orbital sets of (5) to the upper $5\mathrm{d}\,\gamma_{3\mathrm{g}}\,(\gamma_{8\mathrm{g}})$ sub-shell. The main interest of the observation of these bands [8, 9] would be the detection of weak transitions from orbitals such as $(\mathrm{By}_5+\mathrm{By}_6)$ in *trans*-$\mathrm{MA_4B_2}$ discussed above. YAMATERA [44] discussed thoroughly such transitions in $\mathrm{Co(NH_3)_5X^{++}}$ and similar complexes [16]. However, LAPORTE-forbidden transitions between the two sub-shells $5\mathrm{d}\,\gamma_{5\mathrm{g}}$ and $5\mathrm{d}\,\gamma_{3\mathrm{g}}$ and transitions from low-lying M. O. to $5\mathrm{d}\,\gamma_{5\mathrm{g}}$ interfere with the detection of weak transitions to $5\mathrm{d}\,\gamma_{3\mathrm{g}}$. It is recognized [13] that even the LAPORTE-allowed transition $\sigma\,\gamma_{4\mathrm{u}}\rightarrow \mathrm{d}\,\gamma_{5\mathrm{g}}$ is remarkably weak, and there is only one certain case where it has been identified, viz. the low-spin $4\mathrm{d}^5$ complex $\mathrm{Ru(NH_3)_6}^{+3}$ having a band with moderate intensity $(\varepsilon=530)$ [16, 45] at 36.2 kK. Another interesting phenomenon is the weak and very broad shoulder of $\mathrm{IrBr_6}^{--}$ at 24 kK which persists [8] in $\mathrm{IrClBr_5}^{--}$.

Orthoaxial Chromophores of Lower Symmetry

We have no safe theoretical reason to believe that the approximation of *holohedrized symmetry* [17, 25, 31] can be applied to electron transfer bands. However, experimental evidence [8, 9] and the results of the first-order relativistic calculation in Tables 2 and 3 seem to indicate that it is still a fairly good approximation. The assumption of $\zeta_{\mathrm{Cl}}=0$ assures that our first-order calculation gives excitation energies for $\mathrm{MCl_5Br}^{--}$ which are exactly the mean values for $\mathrm{MCl_6}^{--}$ and *trans*-$\mathrm{MCl_4Br_2}^{--}$. On the other hand, the non-diagonal element between the two levels having identical $\gamma_{\mathrm{t}k}$ and deriving from the same cubic γ_k in Table 1 is the same in $\mathrm{MClBr_5}^{--}$ and *trans*-$\mathrm{MCl_2Br_4}^{--}$ but act on diagonal elements at slightly different positions. Consequently, a perfect linear extrapolation is not possible from these chromophores to $\mathrm{MBr_6}^{--}$.

Actually, the observed absorption bands [8, 9] in most cases vary in a fairly linear fashion from $\mathrm{MCl_6}^{--}$ over $\mathrm{MCl_5Br}^{--}$ to *trans*-$\mathrm{MCl_4Br_2}^{--}$. However, the very first LAPORTE-forbidden transition of

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MCl_5Br^{--} has a somewhat lower wavenumber, about 1 kK, than expected. This is much less than one would predict from the difference 6 kK between the excitation energies of chloro and bromo complexes of the same central atom. This discrepancy can be explained by the dilemma mentioned above: if γ_{t5g} orbitals really change from $(\mathrm{A}\, z_1 - \mathrm{A}\, z_2 - \mathrm{B}\, x_5 + \mathrm{B}\, x_6)$ to $(\mathrm{B}\, x_5 - \mathrm{B}\, x_6)$, they are easier to excite because of the lower electronegativity of B, but this effect is counter-acted by the absence of A – B ligand-ligand anti-bonding effects, and we know from the unsubstituted hexahalides that $(H_{\pi\,\mathrm{ang}} - H_{\pi\,\mathrm{par}})$ is some 6 to 7 kK. In other words, the first electron transfer band of MCl_5I^{--} is expected to be much closer to that of *trans*-$MCl_4I_2^{--}$ than to that of MCl_6^{--} because the optical electronegativities of Cl^- and I^- correspond to a larger energy difference, 15 kK.

A clear-cut case of holohedrized symmetry[17] O_h of *fac*-MA_3B_3 (having the conventional symmetry C_{3v}) can also be recognized in Tables 2 and 3. We treat *fac*-$OsCl_3Br_3^{--}$ and *fac*-$IrCl_3Br_3^{--}$ as the hexa-complexes of a hypothetical ligand having $\zeta = (\zeta_{Cl} + \zeta_{Br})/2$, or for the argument, 1.2 kK. It turns out that the wavenumbers of the absorption maxima are very satisfactorily predicted (though ζ could very well be 2 kK), and that no additional bands are observed in this region. There is a very pronounced intensification of LAPORTE-forbidden transitions [the iridium(IV) complex has $\varepsilon = 880$ for the first band and osmium(IV) $\varepsilon = 2320$]. In close analogy to the corresponding internal transitions in partly filled d-shells, the complexes *cis*-$MCl_4Br_2^{--}$ and *cis*-$MCl_2Br_4^{--}$ also lacking a centre of inversion have ε-values for LAPORTE-forbidden bands approaching the values in *fac*-$MCl_3Br_3^{--}$. It is typical for the concept of holohedrized symmetry that it is approximately valid for the energy levels, but that relatively minor modifications of the wavefunctions are able to mitigate the selection rules for intensity.

At present, we do not judge it worthwhile to attempt similar calculations for the residual complexes[8, 9] *cis*-$MCl_4Br_2^{--}$, *mer*-$MCl_3Br_3^{--}$ and *cis*-$MCl_2Br_4^{--}$ having lower symmetries. However, the success encountered for *fac*-$MCl_3Br_3^{--}$ makes it plausible to consider the holohedrized tetragonal symmetry of the *cis*-complexes having either two chloride or two bromide ligands on the tetragonal axis and the mean (Cl + Br) on the four positions in the equatorial plane. The approximate result of applying the treatment of Table 1 to this situation is that each cubic γ_k is split $-\frac{1}{2}$times as much in *cis*-MA_4B_2 as in the corresponding *trans*-MA_4B_2 in close analogy to the well-known results for internal d-shell transitions.

Conclusions

The excited energy levels of electron transfer transitions removing one of the 24 π-electrons mainly concentrated on the six ligands to the partly filled 5d-shell of the central atom have been described in mixed chloro-bromo complexes which can be separated by electrophoretic techniques[8, 9, 46]. The electronegativities of chloride and bromide are not sufficiently different to mask the strong effects of interaction between the six ligands. In a way, the situation would be much simpler in complexes such as $RuCl_5I^{-3}$ or IrF_5Br^{--} with great electronegativity differences comparable with known cases such as[16, 45] $Ru(NH_3)_5X^{++}$ or[44] $Co(NH_3)_5X^{++}$. It would be of great theoretical importance to study the absorption spectra of complexes such as[47] yellow WF_5Cl. We shall attempt to prepare and separate the mixed complexes of the series $OsCl_xI_{6-x}^{--}$, $OsF_xBr_{6-x}^{--}$ and $IrF_xBr_{6-x}^{--}$. In the case of Os(IV) it seems to be possible to isolate some species of the type $OsF_xI_{6-x}^{--}$.

It is interesting to note that straw-yellow IrF_6^{--} is known[48, 49] to have an internal $5d^5$-transition at 31.6 kK and an electron transfer band at 47.0 kK. It has been argued[49] that a pink modification exists having a moderately strong band ($\varepsilon \sim 250$) at 19.0 kK. It is quite conceivable that this sample contained a substituted impurity such as IrF_5Cl^{--} or $F_5IrOIrF_5^{-4}$.

From the point of view of M. O. theory, mixed aqua-halide complexes are similar to the situation of very weakly reducing ligands, and indeed, a comparable behaviour is observed for ruthenium(III)[16] and rhodium(III) complexes[50] which are relatively

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easier to separate than mixed hexahalides. However, bromo and iodo complexes have much narrower absorption bands, mainly because of the higher mass of the ligands [43], and hence, it is possible to identify adjacent energy levels with much higher confidence.

The close similarity between the osmium (IV) and iridium (IV) complex of a given set of ligands yields the interesting information that not only is the groundstate of Os (IV) a nearly pure *j,j*-coupling sub-shell configuration [7, 13] but also that the effects of interelectronic repulsion between the partly filled 5d-shell and the lower orbitals do not separate individual terms of a given M. O. configuration to any large extent. This is not trivial because the first excited levels of MnO_4^- are spread over some 5 kK, and apparently belonging to the same excited configuration [23].

The first-order effect of changing the ligands for either Os (IV) or Ir (IV) is to shift the complicated group of excited levels to an extent roughly proportional to the relative content of chloride and bromide. However, the geometrical isomers have structures of this group at least as different as two complexes of different composition. It has been shown that the concept of holohedrized symmetry [17, 25] can be applied to electron transfer spectra with the same success as to internal transitions in the partly filled d-shell in octahedral orthoaxial complexes.

γ-Radiolyse von flüssigem Kohlenoxid bei -196 °C

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The radiation chemistry of liquid carbon monoxide at -196 °C and mixtures of CO with various gases has been investigated. In the γ-radiolysis of pure CO CO_2 is formed with $G(CO_2)=0.18$. The addition of CH_4, C_2H_4, O_2, and NO leads to the formation of C_3O_2 which is not observed in the γ-radiolysis of pure CO.

In the case of $CO-CH_4$ mixtures the following reacting products were identified: C_2H_6, C_2H_2, H_2CO, H_2C_2O (Ketene), CO_2 and C_3O_2. Results of experiments with $CO-CH_4-{}^{13}CH_4$ and $CO-CH_4-CD_4$ mixtures and measurements of the dependence of $G(CO_2)$, $G(C_3O_2)$, $G(C_2H_2)$ and $G(C_2H_6)$ on the concentration of CH_4 have shown that ethane is formed by energy transfer from CO to CH_4 or by reaction of CH_4 with excited CO and that C_3O_2 and C_2H_2 are formed by reaction of free carbon atoms which are formed in the presence of methane.

Von photochemischen Untersuchungen her ist bekannt, daß sich Kohlenoxid bei Bestrahlung mit den Linien 1236 Å und 1295 Å [1] sowie mit der Linie 2062 Å [2] unter Bildung von Kohlendioxid und Kohlensuboxid zersetzt. Dagegen beobachtet man bei der γ-Radiolyse des Kohlenoxids [3, 4] zwar die Bildung von Kohlendioxid mit $G(CO_2)=2{,}0$, anstelle von Kohlensuboxid findet man jedoch ein festes braunes Reaktionsprodukt. Dieses ist im Gegensatz zu thermisch oder strahlenchemisch polymerisiertem Kohlensuboxid in allen untersuchten Lösungsmitteln nicht löslich. Es ist anzunehmen, daß es sich bei diesem Reaktionsprodukt um eine innige Mischung von Kohlensuboxid und freiem Kohlenstoff handelt. Die Bildung von monomerem Kohlensuboxid ist bei der γ-Radiolyse des Kohlenoxids auch nicht zu erwarten, da Messungen in unserem Laboratorium ergeben haben, daß Kohlensuboxid unter dem Einfluß ionisierender Strahlung mit $G(-C_3O_2)=10^5$ polymerisiert. Bei der Bestrahlung von verflüssigtem reinem Kohlenoxid bei -196 °C beobachtet man ebenfalls die Bildung von Kohlendioxid. Kohlensuboxid ist unter diesen Bedingungen nicht nachweisbar.

Setzt man jedoch dem verflüssigten Kohlenoxid Fremdgase zu, so wird je nach Art des zugesetzten Gases Kohlensuboxid gebildet. Die Radiolyseprodukte verschiedener Gasmischungen sind in Tab. 1 zusammengefaßt.

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