Table I. Computed Values of the Equilibrium Constant, K_c, for the Dissociation of the HF_2^- Ion at Different Concentrations of KHF_2 in Water

Concn of KHF_2, C^a	$K_c{}^a$	Concn of KHF_2, C^a	$K_c{}^a$
0.25	0.246	2.25	0.105
0.50	0.240	2.50	0.104
0.75	0.220	2.75	0.100
1.00	0.137	3.00	0.100
1.25	0.135	3.25	0.097
1.50	0.120	3.50	0.090
1.75	0.105	3.75	0.085
2.00	0.106	4.00	0.083

[a] In moles/kg of water.

The chemical shift changes of ^{19}F in solutions of NH_4HF_2 do not depend entirely on the equilibrium represented by eq 1. It is evident from the dilution shift in NH_4F solutions that solutions containing the NH_4^+ ion which can hydrolyze and form hydrogen bonds with F^- are much more complex. The hydrolytic equilibria and hydrogen-bonding effects which lead to a low-field shift in NH_4F solutions also effect in a more complex manner the chemical shift changes in the NH_4HF_2 solutions. It is interesting to note, however, that the chemical shift of ^{19}F at infinite dilution is probably about the same for NH_4HF_2 and KHF_2 solutions. From this study we are able to compare chemical shifts of ^{19}F in different hydrogen-bonded environments. If we take the shift of F^- ion at infinite dilution in water as zero (some hydrogen-bonded solvation is occurring in this case), then the chemical shift of a hypothetical isolated HF molecule in water is +20.5 ppm to high field, the HF_2^- ion is +36.4 ppm to high field, and the chemical shift in anhydrous liquid HF is +76.1 ppm.[13] If, as seems reasonable, we assume that the chemical shift becomes diamagnetic monotonically as the hydrogen bond strength to a fluorine atom increases, then this indicates hydrogen bond strengths in the order: $(HF)_n$(anhydrous liquid) > $HF_2^-(H_2O)_x$ > $HF(H_2O)_y$ > $F^-(H_2O)_z$. The subscripts n, x, y, and z can be regarded as unknown solvation numbers.

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[13] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959.

Intensities of Forbidden Transitions in Octahedral Complexes

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Abstract: This work concerns the relative intensities of Laporte forbidden ligand field transitions of octahedrally coordinated transition metal complexes in which the charge-transfer transitions are from the ligand to the metal. Within the framework of a one-electron approximation, it is shown from theoretical considerations that the ligand field transitions in such complexes vibronically mix with those ligand-to-metal transitions in which the final states involve the e_g and not the t_{2g} orbital of the metal. Relative intensities of ligand field transitions within a complex are correlated with the observed ligand-to-e_g transition. Correlations of intensities between corresponding transitions for analogous chloro and bromo complexes are also obtained.

It has long been recognized[1] that the portions of the absorption spectra of octahedral transition metal complexes associated with the ligand field transitions are Laporte forbidden since both the ground and excited states are of the same parity (g → g). That weak absorptions are actually observed has been attributed to vibrational perturbations which "mix" electronic states of even and odd parity. The forbidden dipole transition is said to "borrow" intensity from an allowed g → u transition.

Early explanations[2,3] of the Laporte forbidden transitions in metal complexes were carried out in the framework of a crystal-field model. Consequently, the state of odd parity was presumed to be the metal p orbital above the partially filled d orbitals, *e.g.*, the 4p level for the first transition row. Englman[4] was the first to attempt a calculation on the basis of a molecular orbital (MO) model in which the g → u transition involved a "charge transfer," that is, the molecular orbitals of even and odd parities were primarily associated with the metal and ligand atomic orbitals, respectively. Although Englman concluded that the allowed transitions in aquo complexes were from the metal to the ligand, there is substantial agreement that in complexes with electron-donor ligands it is the ligand-to-metal transitions which give rise to the observed absorptions. One can say only that his correlation of ligand field transitions with the *edge* of the first intense absorption band was possibly fortuitous. In this connection, it should be noted that in Englman's tabulation, he presumes that all first observed transitions occur from the $2t_{2g}$ metal orbital which is not reasonable for those ions, Fe^{+2} through Cu^{+2}, in which the $2e_g$ metal orbital is occupied (see Figure 1).

It is worthwhile to reexamine Englman's postulates in the light of ligand-to-metal charge-transfer transitions involving electron-donor ligands. According to first-order perturbation theory, the contribution of odd parity states, C_i, to the even parity ground and excited

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[1] C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, and references therein.

[2] C. J. Ballhausen and A. D. Liehr, *Mol. Phys.*, 2, 123 (1959).

[3] S. Koide and M. H. L. Pryce, *Phil. Mag.*, 3, 607 (1959).

[4] R. Englman, *Mol. Phys.*, 3, 48 (1960).

states, A and B, respectively, is given by

$$|\mathrm{A}'\rangle = |\mathrm{A}\rangle + \sum_i |\mathrm{C}_i\rangle\langle \mathrm{C}_i|\mathcal{H}_\mathrm{V}|\mathrm{A}\rangle/(E_\mathrm{A} - E_{\mathrm{C}_i}) \quad (1)$$

$$|\mathrm{B}'\rangle = |\mathrm{B}\rangle + \sum_i |\mathrm{C}_i\rangle\langle \mathrm{C}_i|\mathcal{H}_\mathrm{V}|\mathrm{B}\rangle/(E_\mathrm{B} - E_{\mathrm{C}_i}) \quad (2)$$

were $\mathcal{H}_\mathrm{V}$ is the part of the vibrational perturbation Hamiltonian which is odd in the electronic coordinates; E_A, E_B, and E_{C_i} are the energies of the respective states. For the present purposes, we can ignore the explicit dependence on the vibrational quantum numbers. The matrix element of the transition probability can then be written as

$$\langle \mathrm{A}'|P|\mathrm{B}'\rangle = \sum_i \frac{\langle \mathrm{A}|P|\mathrm{C}_i\rangle\langle \mathrm{C}_i|\mathcal{H}_\mathrm{V}|\mathrm{B}\rangle}{E_\mathrm{B} - E_{\mathrm{C}_i}} + \sum_i \frac{\langle \mathrm{B}|P|C_i\rangle\langle \mathrm{C}_i|\mathcal{H}_\mathrm{V}|\mathrm{A}\rangle}{E_\mathrm{A} - E_{\mathrm{C}_i}} \quad (3)$$

where P is the dipole operator, $e\sum_j \vec{r}_j$, the summation being over all electrons j.

For nonzero matrix elements, the Slater determinants associated with A and B can differ from C by only one electron since both P and $\mathcal{H}_\mathrm{V}$ are one-electron operators. Consider the forbidden and allowed transitions in the one-electron MO formalism which, of course, corresponds to the strong field approximation of ligand field theory. For simplicity, one can write a portion of the Slater determinants associated with the various states, ignoring all other electrons not involved in changes.

$$\begin{aligned} \mathrm{A} &= |\ldots(2\mathrm{t}_{1\mathrm{u}})(2\mathrm{t}_{2\mathrm{g}})| \\ \mathrm{B} &= |\ldots(2\mathrm{t}_{1\mathrm{u}})(2\mathrm{e}_\mathrm{g})| \\ \mathrm{C} &= |\ldots(2\mathrm{e}_\mathrm{g})(2\mathrm{t}_{2\mathrm{g}})| \\ \mathrm{D} &= |\ldots(2\mathrm{t}_{2\mathrm{g}})(2\mathrm{t}_{2\mathrm{g}})| \end{aligned}$$

The ground-state determinant, A, represents a state in which the $1\mathrm{a}_{1\mathrm{g}}$ through $2\mathrm{t}_{1\mathrm{u}}$ orbitals of Figure 1 are completely occupied, and there is at least one electron in the $2\mathrm{t}_{2\mathrm{g}}$ orbital. The excited-state determinant, B, is achieved by the $2\mathrm{t}_{2\mathrm{g}} \rightarrow 2\mathrm{e}_\mathrm{g}$ transition from the ground state. The determinants C and D represent excited states obtained by the charge-transfer transition of an electron from the $2\mathrm{t}_{1\mathrm{u}}$ orbital to the $2\mathrm{e}_\mathrm{g}$ and $2\mathrm{t}_{2\mathrm{g}}$ orbitals, respectively.[5]

Insertions of the above determinants into eq 3 immediately show that transitions to the $2\mathrm{t}_{2\mathrm{g}}$ orbital do not contribute to the Laporte forbidden ligand field transitions since B and D differ by more than one electron, and consequently $\langle \mathrm{D}|\mathcal{H}_\mathrm{V}|\mathrm{B}\rangle$ and $\langle \mathrm{B}|P|\mathrm{D}\rangle$ are zero. Therefore, within the one-electron approximation for transition metal complexes with electron-donor ligands *the ligand field transitions borrow their intensity from the charge-transfer transitions to the* $2\mathrm{e}_\mathrm{g}$ *orbital only.* This means that, in those complexes where the $2\mathrm{t}_{2\mathrm{g}}$ orbital is only partly occupied, the intensities of the ligand field bands should *not* be correlated with the allowed bands of lowest energy since they correspond to transitions to the $2\mathrm{t}_{2\mathrm{g}}$ orbitals.

To proceed further, it is worthwhile to examine the matrix elements which arise in $\langle \mathrm{A}'|P|\mathrm{B}'\rangle$ from A, B, and C.

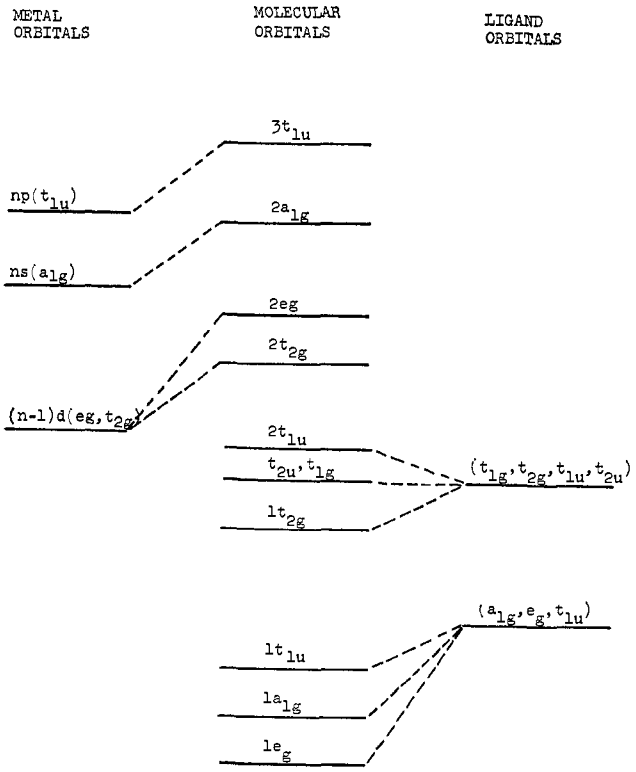

Figure 1. Octahedral energy levels for electron-donor complexes. The diagram is qualitative only. A dashed line connects an atomic orbital to that molecular orbital in which it has the greatest participation.

$$\frac{\langle \mathrm{A}|P|\mathrm{C}\rangle\langle \mathrm{C}|\mathcal{H}_\mathrm{V}|\mathrm{B}\rangle}{E_\mathrm{B} - E_\mathrm{C}} = \frac{\langle (2\mathrm{t}_{1\mathrm{u}})_1|P|(\mathrm{e}_\mathrm{g})_1\rangle\langle (2t_{1\mathrm{u}})_1|\mathcal{H}_\mathrm{V}|(t_{2\mathrm{g}})_1\rangle}{E_\mathrm{C} - E_\mathrm{B}} \quad (4)$$

$$\frac{\langle \mathrm{B}|P|\mathrm{C}\rangle\langle \mathrm{C}|\mathcal{H}_\mathrm{V}|\mathrm{A}\rangle}{E_\mathrm{A} - E_\mathrm{C}} = \frac{\langle (2\mathrm{t}_{1\mathrm{u}})_1|P|(\mathrm{t}_{2\mathrm{g}})_1\rangle\langle (2\mathrm{t}_{1\mathrm{u}})_1|\mathcal{H}_\mathrm{V}|(\mathrm{e}_\mathrm{g})_1\rangle}{E_\mathrm{C} - E_\mathrm{A}} \quad (5)$$

Both eq 4 and 5 contribute to the intensity expression, but there are several reasons to presume that, contrary to Englman's postulates, eq 4 represents the dominant contribution. First of all, the denominator of eq 4 will be substantially smaller than that of eq 5, the difference being the energy of the d–d transition. Furthermore, Jørgensen[6] has shown that charge-transfer transitions to the e_g orbital are from 4 to 20 times more intense than those to the $\mathrm{t}_{2\mathrm{g}}$ orbital. Hence $\langle (2\mathrm{t}_{1\mathrm{u}})_1|P|(\mathrm{e}_\mathrm{g})_1\rangle$ is much larger than $\langle (2\mathrm{t}_{1\mathrm{u}})_1|P|(\mathrm{t}_{2\mathrm{g}})_1\rangle$. Thus, it will be assumed in what is to follow that the matrix element of the transition probability is given by

$$\langle \mathrm{A}'|P|\mathrm{B}'\rangle \approx \sum_i \frac{\langle \mathrm{A}|P|\mathrm{C}_i\rangle\langle \mathrm{C}_i|\mathcal{H}_\mathrm{V}|\mathrm{B}\rangle}{E_\mathrm{B} - E_{\mathrm{C}_i}} \quad (6)$$

Two sets of calculations will be presented to affirm the reasonableness of the foregoing discussion: (1) relative intensities between different states for the same complex; (2) relative intensities between the corresponding hexachloro and hexabromo complexes.

States within a Complex

Unfortunately, there are few octahedral complexes in which both the ligand field and ligand-to-$2\mathrm{e}_\mathrm{g}$ bands are

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[5] The placement of the $2\mathrm{t}_{1\mathrm{u}}$ level above the $\mathrm{t}_{2\mathrm{u}}$ in Figure 1 is in accord with recent theoretical and experimental results. The arguments to follow are independent of the assumption as to which of the two orbitals is the source of the charge-transfer transitions.

[6] C. K. Jørgensen, *Mol. Phys.*, **2**, 309 (1959).

observed. Consider those complexes in which the $2t_{2g}$ orbital is only partly occupied. The ligand field transitions generally occur in the range of frequencies from 15 to 25 kK, where 1 kK equals 1000 cm^{-1}. If the first charge-transfer bands, $2t_{1u} \rightarrow 2t_{2g}$, are not to mask the ligand field bands, they must occur at higher frequencies, say 35 kK. But the energy of the charge-transfer transition of interest, $2t_{1u} \rightarrow 2e_g$, is only slightly less than the sum of the $2t_{1u} \rightarrow 2t_{2g}$ and $2t_{2g} \rightarrow 2e_g$ transitions, which places the $2t_{1u} \rightarrow 2e_g$ band beyond the accessible ultraviolet region. When the $2t_{1u} \rightarrow 2e_g$ transition is of low enough energy for detection, the intense $2t_{1u} \rightarrow 2t_{2g}$ transitions are of energy comparable to the much weaker ligand field transitions, and the latter are either not observed or appear as slight shoulders on the intense bands.

The above dilemma does not exist for those species in which the $2t_{2g}$ is fully occupied. Such is the case for the cobalt,[7] iridium,[8] and rhodium[8] complexes given in Table I. Each possesses a strong field d^6 configuration, $2t_{2g}^6$, so that the first observed charge-transfer band must be to the $2e_g$ orbital with an energy greater than the $2t_{2g} \rightarrow 2e_g$ transition, yet still at a detectable frequency.

Table I. Intensities to States within a Complex

Complex	State	Frequency, kK	Intensity (exptl) × 10^4	$f(T_1)/f(T_2)$ Exptl	Calcd
$Co(NH_3)_6^{+3}$	$^1T_1$	21.2[a]	104	1.00	1.19
	$^1T_2$	29.4	104	...	...
	CT[d]	52.6	~4000	...	...
$Co(en)_6^{+3}$	$^1T_1$	21.5[a]	129	0.98	1.02
	$^1T_2$	29.6	132	...	...
	CT	47.2	~3000	...	...
$Co(C_2O_4)_3$	$^1T_1$	16.7[a]	27	0.90	1.06
	$^1T_2$	23.8	30	...	...
	CT	41.1	~3000	...	...
$RhCl_6^{-3}$	$^1T_1$	19.3[b]	140	1.08	1.08
	$^1T_2$	24.3	130	...	...
	CT	39.2[c]	8000	...	...
$IrCl_6^{-3}$	$^1T_1$	24.1[b]	125	1.04	1.80
	$^1T_2$	28.1	120	...	...
	CT	48.5[c]	10500	...	...
$RhBr_6^{-3}$	$^1T_1$	18.1[b]	250	1.00	1.41
	$^1T_2$	22.2	250	...	...
	CT(1)	30.1[c]	2000	...	...
	CT(2)	33.9	3000	...	...
$IrBr_6^{-3}$	$^1T_1$	22.4	370	1.15	1.83
	$^1T_2$	25.8	320	...	...
	CT(1)	36.8	2500	...	...
	CT(2)	41.1	5000	...	...

[a] Reference 7. [b] Reference 8. [c] Reference 6. [d] CT symbolizes the charge-transfer state to the $2e_g$ orbital.

Each of the complexes of Table I displays Laporte forbidden transitions from the $^1A_{1g}$ ground state to $^1T_{1g}$ and $^1T_{2g}$ excited states. Both states arise from the $|\ldots(t_{2g})^5(e_g)^1|$ configuration. It is possible to calculate the oscillator strengths to these excited states by consideration of only one of the wave functions associated with them and then multiply each result by three. Thus

$$^1T_{1g}(1) = \{\overset{+}{(xy)}(x^2 \overset{+}{-} y^2)\}$$

$$^1T_{2g}(1) = \{\overset{+}{(xy)}\overset{+}{(z^2)}\}$$

In the above "determinants," the states are represented by the d-orbital component of the t_{2g} "hole" (xy), and the d-orbital component of the occupied e_g orbital, $(x^2 - y^2)$ or (z^2). Thus

$$\{\overset{+}{(xy)}(x^2 \overset{+}{-} y^2)\} = |\ldots\overset{-}{(xz)}\overset{-}{(yz)}\overset{-}{(xy)}\overset{+}{(xz)}\overset{+}{(yz)}(x^2 \overset{+}{-} y^2)|$$

In an analogous fashion, one can represent the determinants which arise from the allowed transition of an electron from the $2t_{1u}$ orbital to the e_g orbital[9]

$$\psi_1 = \{\overset{+}{(z)}\overset{+}{(z^2)}\}$$

$$\psi_2 = \{\overset{+}{(y)}\overset{+}{(z^2)}\}$$

$$\psi_3 = \{\overset{+}{(x)}\overset{+}{(z^2)}\}$$

$$\psi_4 = \{\overset{+}{(y)}(x^2 \overset{+}{-} y^2)\}$$

$$\psi_5 = \{\overset{+}{(x)}(x^2 \overset{+}{-} y^2)\}$$

Application of perturbation theory to mix the above functions with $T_{1g}(1)$ and $T_{2g}(1)$ yields

$$|T_{1g}(1)'\rangle = |T_{1g}(1)\rangle + (E_C - E_{T_1})^{-1}|(y)(x^2 - y^2)\rangle\langle y|\mathcal{H}_V|xy\rangle + |(x)(x^2 - y^2)\rangle\langle x|\mathcal{H}_V|xy\rangle$$

$$|T_{2g}(1)'\rangle = |T_{2g}(1)\rangle + (E_C - E_{T_2})^{-1}|(y)(z^2)\rangle\langle y|\mathcal{H}_V|xy\rangle + |(x)(z^2)\rangle\langle x|\mathcal{H}_V|xy\rangle$$

Then

$$\langle ^1A_{1g}|P|T_{1g}(1)\rangle' = \{\langle(y)|P|(x^2 - y^2)\rangle\langle(y)|\mathcal{H}_V|(xy)\rangle + \langle(x)|P|(x^2 - y^2)\rangle\langle(x)|\mathcal{H}_V|(xy)\rangle\}(E_C - E_{T_1})^{-1}$$

while

$$\langle ^1A_{1g}|P|T_{2g}(1)\rangle' = \{\langle(y)|P|(z^2)\rangle\langle(y)|\mathcal{H}_V|(xy)\rangle + \langle(x)|P|(z^2)\rangle\langle(x)|\mathcal{H}_V|(xy)\rangle\}(E_C - E_{T_2})^{-1}$$

Because of the differences in normalization constants of the $(x^2 - y^2)$ and (z^2) orbitals, it is easily shown that

$$\langle(y)|P|(x^2 - y^2)\rangle^2 = \langle(x)|P|(x^2 - y^2)\rangle^2 = 3\langle(y)|P|(z^2)\rangle^2 = 3\langle(x)|P|(z^2)\rangle^2$$

Hence

$$\langle ^1A_{1g}|P|T_{1g}(1)'\rangle^2 = 3Q^2I^2/(E_C - E_{T_1})^2 \qquad (7)$$

$$\langle ^1A_{1g}|P|T_{2g}(1)'\rangle^2 = Q^2I^2/(E_C - E_{T_2})^2 \qquad (8)$$

where $Q^2 = \langle(y)|P|(z^2)\rangle^2$ and $I^2 = \langle(x)|\mathcal{H}_V|(xy)\rangle^2 = \langle(y)|\mathcal{H}_V|(xy)\rangle^2$.

Since the oscillator strength, f, for an even–even transition[1] is equal to

$$f = 1.085 \times 10^{11}(E_A - E_B)|\langle A|P|B\rangle|^2 \qquad (9)$$

with appropriate summation of the excited states and averaging of the initial states, then

$$\frac{f(^1T_{1g})}{f(^1T_{2g})} = \frac{3(E_{A_{1g}} - E_{T_{1g}})(E_{T_{2g}} - E_C)^2}{(E_{A_{1g}} - E_{T_{2g}})(E_{T_{1g}} - E_C)^2} \qquad (10)$$

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(7) A. V. Kiss and D. V. Czegledy, *Z. Anorg. Allgem. Chem.*, **235,** 407 (1938).

(8) C. K. Jørgensen, *Acta Chem. Scand.*, 10, 501 (1956).

(9) The transition from the $2t_{1u}$ orbital was chosen for illustrative purposes since the three spatial MO's can be conveniently represented by their metal p-orbital constituent. The same arguments hold for the wave functions of the t_{2u} orbitals.

Thus, the intensity ratios of the two transitions are seen to be dependent on the energy differences and independent of the forms of the matrix elements. As seen from the results of Table I, the factor of 3 which favors an increased intensity for the $^1T_{1g}$ transition is compensated for by the fact that the $^1T_{2g}$ level is at a higher energy than the $^1T_{1g}$ level.

Equation 10 is applicable only when there is one charge transfer-band, C, which is accessible from the ground state and near enough to the T_{1g} and T_{2g} levels to permit appreciable mixing. Thus, for the cobalt complexes and the chloride complexes in Table I, eq 10 is a reasonable approximation. However, in both $RhBr_6^{-3}$ and $IrBr_6^{-3}$ there are two charge-transfer bands, presumably $t_{2u} \rightarrow 2e_g$ and $2t_{1u} \rightarrow 2e_g$, within about 4000 cm^{-1} of one another. If one makes the assumption that $\langle C|\mathcal{H}_V|B\rangle = \langle D|\mathcal{H}_V|B\rangle$, where C and D are the two allowed excited states, then eq 7, 8, and 10 must be modified and one obtains

$$\frac{f(^1T_{1g})}{f(^1T_{2g})} = \frac{3(E_D - E_{T_{2g}})^2(E_C - E_{T_{2g}})^2[(E_D - E_{T_{1g}})^2 + (E_C - E_{T_{1g}})^2]}{(E_D - E_{T_{1g}})^2(E_C - E_{T_{1g}})^2[(E_D - E_{T_{2g}})^2 + (E_C - E_{T_{2g}})^2]} \quad (11)$$

Equation 11 was used to calculate the intensity ratios for the two bromide complexes given in Table I.

Such semiempirical intensity calculations within a given complex are helpful in identifying absorption maxima. For example, in $PtCl_6^{-2}$, also a d^6 configuration, there are two low-intensity transitions[10] at 22.1 and 28.3 kK with oscillator strengths of 9 × 10^{-4} and 70 × 10^{-4}, respectively. The observed charge-transfer band is at 38.2 kK. Insertion of these values into eq 10 yields a calculated value for the ratio, $f(T_1)/f(T_2)$, of 0.88 compared to the experimental ratio of 0.13. This suggests that the two bands do not correspond to the same type of d-to-d transition, in accord with Jørgensen's assignment[10] that the first is a spin-forbidden transition to the $^3T_{1g}$ state, made allowed by the substantial spin-orbit coupling in platinum.

Relative Intensities between Complexes

While the ligand-to-$2e_g$ charge-transfer bands of hexachloro complexes[6] are more intense than their hexabromo[6] counterparts, the reverse is generally true for the ligand field transition.[8,10] This reversal can be correlated with the greater energy separation between the ligand field and charge-transfer bands in the chloro complexes compared to those of the bromo complexes. Some examples are given in Table II.

If one again applies perturbation theory to the excited state, B, of eq 9 and mixes in the allowed state C, one obtains

$$f = 1.085 \times 10^{11}(E_A - E_B)\langle A|P|C\rangle^2 \times \langle C|\mathcal{H}_V|B\rangle^2/(E_C - E_B)^2$$

But the oscillator strength for the allowed transition A → C is given by

$$f' = 1.085 \times 10^{11}(E_A - E_C)\langle A|P|C\rangle^2$$

so one can write

$$f = f'(E_A - E_B)\langle C|\mathcal{H}_V|B\rangle^2/(E_A - E_C)(E_C - E_B)^2 \quad (12)$$

Table II. Relative Intensities between Chloro and Bromo Complexes

Complex	Transition designation	Frequency, kK	Intensity × 10^4 Exptl	Intensity × 10^4 Calcd
$PtCl_6^{-2}$	(1)[a]	22.1[c]	9	...
	(2)	28.3	70	...
	(3)[b]	38.2	5,700	...
$PtBr_6^{-2}$	(1)	19.1	15	25
	(2)	23.0	200	202
	(3)	27.0	1,500	...
	(4)	32.0	5,000	...
$IrCl_6^{-3}$	(1)	24.1[d]	125	...
	(2)	28.1	120	...
	(3)	48.5	10,500	...
$IrBr_6^{-3}$	(1)	22.4	370	220
	(2)	25.8	320	340
	(3)	36.8	2,500	...
	(4)	41.1	5,000	...
$RhCl_6^{-3}$	(1)	19.3[d]	140	...
	(2)	24.3	130	...
	(3)	39.2	8,000	...
$RhBr_6^{-3}$	(1)	18.1	250	210
	(2)	22.2	250	223
	(3)	30.1	2,000	...
	(4)	33.9	3,000	...
$IrCl_6^{-2}$	(1)	17.4[c]	50	...
	(3)	43.1	6,700	...
$IrBr_6^{-2}$	(1)	13.6	84	70
	(3)	31.5	2,000	...
	(4)	37.0	4,500	...
$RuCl_6^{-3}$	(1)	19.2[c]	7	...
	(3)	43.6	5,500	...
$RuBr_6^{-3}$	(1)	15.3	18	14
	(3)	35.0	4,300	...
	(4)	(40.0)	5,000	...

[a] (1) and (2) designate ligand field transitions. [b] (3) and (4) designate charge-transfer transitions to the $2e_g$ orbital. All such transitions were obtained from ref 6. [c] Reference 10. [d] Reference 8.

If more than one charge-transfer band can contribute, say C and D, then f is the sum of two expressions given by eq 12. The only experimental unknown in eq 12 is $\langle C|\mathcal{H}_V|B\rangle^2$. If one makes the assumption that $\langle C|\mathcal{H}_V|B\rangle^2$ is dependent only on the metal (that is, that the change in the effective potential on a metal electron as a result of the vibrational modes of the system is essentially the same for all ligands), then it is possible to predict the intensities of the transitions for one ligand from those of another. Of course, such an assumption is dubious at best and is reasonable only if the energy differences constitute a major factor in the forbidden intensities. That such seems to be the case is indicated by the results given in Table II. The value of $\langle C|\mathcal{H}_V|B\rangle^2$ was determined from the appropriate energies and intensities of transitions in a chloride complex. Equation 12 was then used to calculate the intensity of the corresponding transition in the bromide complex. Because of the proximity of the two charge-transfer bands in the bromide complexes, both were taken into account in the calculation of the bromide oscillator strengths. Considering the approximations involved in the calculations, the results are in very good accord with the experimental values.

Summary

This work has attempted to show that ligand field transition intensities in electron-donor complexes should be correlated with the allowed ligand-to-$2e_g$

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(10) C. K. Jørgensen, *Acta Chem. Scand.*, 10, 518 (1956).

transitions. The intensities are quite sensitive to the energy separations between the allowed and forbidden bands.

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Substitution Reactions of Tetracarbonyl-1,5-cyclooctadienemolybdenum(0)

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Abstract: The complex $Mo(CO)_4(C_8H_{12})$ undergoes substitution reactions with 1,2-bis(diphenylphosphino)-ethane, α,α'-dipyridyl, 1,10-phenanthroline, triphenylphosphine, triphenylarsine, and triphenylstibine to yield the products $Mo(CO)_4L_2$ or $Mo(CO)_4D$, where L is a monodentate ligand and D a bidentate ligand. The reactions proceed according to the two-term rate law: rate $= k_1[Mo(CO)_4(C_8H_{12})] + k_2[Mo(CO)_4(C_8H_{12})][L]$ (or [D] in the case of the bidentate ligands). The possible reaction mechanism and the reactivities of the entering groups toward molybdenum carbonyl complexes are discussed.

Extensive kinetic investigations on some octahedral complexes of group VI metal carbonyls (Cr, Mo, W) have shown that generally the replacement of weak basic groups by relatively strong bases (dipyridyl or substituted dipyridyl) increases the lability of the CO groups. As an example, $Cr(CO)_4(dipy)$ reacts readily with phosphites to form *cis*-$Cr(CO)_3L(dipy)$, whereas under the same conditions $Cr(CO)_6$ is quite inert.[1,2] However, the replacement of CO groups by phosphines or phosphites does not affect markedly the lability of the CO; *i.e.*, in the language of Pearson, the "harder" the base the more labile the CO groups are. As an example, $Re(CO)_4BrL$ undergoes a more rapid dissociation of a CO group when L is pyridine than in the case of the analogous complex in which L is triphenylphosphine.[3] This is consistent with the important conclusion of Jørgensen that a "soft" ligand coordinated to a metal ion can confer "softness" on it,[4] and this makes the release of a "soft" coordinated ligand, such as CO, more difficult.

In some ways, the kinetic behavior of metal carbonyl complexes of chromium, molybdenum, and tungsten is significantly different. Thus, the reaction of $Cr(CO)_4(dipy)$ with phosphites (L) to yield *cis*-$Cr(CO)_3L(dipy)$ proceeds according to a first-order rate law, whereas the analogous metal carbonyls of Mo and W (M) undergo, under the same conditions, substitution reactions with phosphites, which lead to both *cis*-$M(CO)_3L(dipy)$ and *trans*-$M(CO)_4L_2$. For these reactions, a two-term rate law is followed.

$$\text{rate} = k_1[M(CO)_4(dipy)] + k_2[M(CO)_4(dipy)][L]$$

This immediately suggests that the coordinated dipyridyl is much less inert in the latter complex than in the analogous chromium complex. The simple dissociative path (characterized by k_1) for the release of a carbon monoxide group depends slightly on the nature of the central atom, the rate of reaction varying in the order $Cr \simeq Mo > W$.[1] Moreover, on going from apolar to dipolar aprotic solvents, the values of k_1 do not depend appreciably upon the nature of the solvent, in agreement with the fact that neutral species arise from dissociation of the uncharged complexes.

This work is a development of a previous study on the substitution reactions of tetracarbonyl-1,5-cyclooctadienemolybdenum(0).[5] The present paper deals with kinetic investigations on substitution reactions of $Mo(CO)_4(C_8H_{12})$ with entering groups having nitrogen, phosphorus, arsenic, and antimony as donor atoms, in benzene or 1,2-dichloroethane solution. The object was to investigate, first, the possible reaction mechanism and, second, the factors which enhance the reactivity of the entering groups toward molybdenum carbonyl complexes.

Experimental Section

Materials. $Mo(CO)_4(C_8H_{12})$ was prepared following the method given in the literature.[6] The 1,2-bis(diphenylphosphino)ethane was prepared according to Chatt and Hart.[7] The method of Stiddard was used to prepare $Mo(CO)_4(bipy)$.[8] The compounds *cis*-$Mo(CO)_4[P(C_6H_5)_3]_2$, *cis*-$Mo(CO)_4[As(C_6H_5)_3]_2$, and *cis*-$Mo(CO)_4[Sb(C_6H_5)_3]_2$ were prepared by adding, under nitrogen, a *n*-heptane solution of the ligand to a *n*-heptane solution of $Mo(CO)_4(C_8H_{12})$. The identity and purity of all these compounds were confirmed by their carbon, hydrogen, and nitrogen analyses and by their infrared spectra.

Triphenylphosphine, triphenylarsine, and triphenylstibine, commercial reagent grade, were recrystallized from petroleum ether. α,α'-Dipyridyl and 1,10-phenanthroline, as reagent grade, were used without further purification. Thiophene-free benzene was refluxed over sodium wire and then fractionally distilled. Purification of 1,2-dichloroethane was effected by fractional distillation.

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