When $20 \geqslant \alpha_A/\alpha_B \geqslant 6$, the points are allocated in groups of 3, 5, and 8 in the intervals $(0, L_1)$, (L_1, L_2), $(L_2, 1)$, respectively, where the L values for the appropriate ratio are given in Table VIII. For $6 \geqslant \alpha_A/\alpha_B \geqslant {}^1/_6$, no subdivision is necessary. For $20 \geqslant \alpha_B/\alpha_A \geqslant 6$, the 3, 5, and 8 points are placed in the intervals $(1 - L_2, 1)$, $(1 - L_2, 1 - L_1)$, and $(0, 1 - L_2)$, respectively.

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Energy Levels, Spin Densities, and the Nephelauxetic Effect in Metal Hexafluorides

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The relative electronic energy levels of MF_6^{3-}, where M = Ti, V, Cr, Fe, and Co, are calculated from semiempirical molecular orbital theory. The calculated $\Delta = 10Dq$ values compare well with experimental results. The molecular orbitals indicate less covalent character than previous calculations. Spin density estimates from the 2p orbitals are in good accord with results from nmr and epr measurements. Comparison of calculated and experimental B and β values shows excellent agreement and allows an interpretation of the nephelauxetic effect to be made.

Introduction

In the preceding paper,[1] a method was outlined for the calculation of the relative energy levels of transition metal complexes. This report concerns the application of the procedure to the series MF_6^{3-}, where M = Ti, V, Cr, Fe, and Co. Since full details have already been given, we shall simply summarize the pertinent restrictions.

The calculations are fully specified by the wave functions, internuclear distances, and choice of reduction parameters, R_σ and R_π. The basis set for the metal consisted of the +2 wave functions for the 3d, 4s, and 4p orbitals as tabulated by Richardson and coworkers.[2,3] The fluoride 2p radial function is the same as that used by Shulman and Sugano[4] in their work on $KNiF_3$. With the exception of CrF_6^{3-} where the internuclear distance is known[5] the internuclear distances between the metals and the fluorines were obtained from the tabulation given by Peacock[6] for the neutral compounds MF_3. In each case, octahedral symmetry of fluorines about the metal is evident. In accord with the calculations[1] on TiF_6^{3-}, reduction parameters of $R_\sigma = R_\pi = 0.87$ were employed in the approximation of the two-center interactions for the off-diagonal terms of the secular determinant.

Calculated Energy Levels

The relative values of the energy levels, the self-consistent charges, and the calculated and experimental $\Delta = 10Dq$ values for the five complexes are summarized in Table I. For each system, the levels through t_{1g} are completely filled. The occupation of the $2t_{2g}$ and $2e_g$ levels is then specified by the number of d electrons on the metal distributed in accord with the "weak field" nature of the complexes. It should be noted that the level values are *relative* positions and that the positive values of the $2t_{2g}$ and higher levels result because the potential of the cations was not included in the calculations.

In view of the sensitivity of calculated Δ values to small variations in reduction parameters, the degree of agreement between calculated and experimental results is quite gratifying. As has been shown,[1] minor adjustment of the reduction parameters would have resulted in exact agreement of Δ values with little change in the eigenvector coefficients; these results show that approximate Δ values can be obtained without such adjustment.

The values of the energy levels suggest that charge-transfer transitions from the nonbonding t_{2u} state should not be observable in the visible or ultraviolet regions except in the case of CoF_6^{3-} where the one-electron energy difference $2t_{2g} - t_{2u}$ is 5.20 ev. Of course, this latter quantity does not account for possible electrostatic interaction changes as a result of the charge transfer. Unfortunately, the experimental absorption spectrum for this species[7] is not reported above 20,000 wavenumbers (2.48 ev) so a comparison is not presently possible.

It is also noteworthy that for the titanium complex the transition $2t_{2g} \rightarrow 2a_{1g}$ is expected to appear at 2.41 ev. Since the same vibrations, t_{1u} and t_{2u}, which make the $2t_{2g} \rightarrow 2e_g$ transitions vibronically allowed also make $2t_{2g} \rightarrow 2a_{1g}$ possible, one is tempted to speculate that the higher energy absorption maximum in TiF_6^{3-}

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[1] R. F. Fenske, K. G. Caulton, D. D. Radtke, and C. C. Sweeney, *Inorg. Chem.*, **5**, 951 (1966).

[2] J. W. Richardson, W. C. Nieuwpoort, R. R. Powell, and W. F. Edgell, *J. Chem. Phys.*, **36**, 1057 (1962).

[3] J. W. Richardson, R. R. Powell, and W. C. Nieuwpoort, *ibid.*, **38**, 796 (1963).

[4] R. G. Shulman and S. Sugano, *Phys. Rev.*, **130**, 517 (1963).

[5] K. Knox and D. W. Mitchell, *J. Inorg. Nucl. Chem.*, **21**, 253 (1961).

[6] R. D. Peacock, *Progr. Inorg. Chem.*, **2**, 193 (1960).

[7] F. A. Cotton and M. D. Meyers, *J. Am. Chem. Soc.*, **82**, 5023 (1960).

TABLE I

RELATIVE ELECTRON ENERGY LEVELS IN ELECTRON VOLTS

	TiF_6^{3-} (d^1)	VF_6^{3-} (d^2)	CrF_6^{3-} (d^3)	FeF_6^{3-} (d^5)	CoF_6^{3-} (d^6)
$3t_{1u}$	24.92	27.35	28.35	29.31	30.53
$2a_{1g}$	15.44	14.90	17.57	20.11	22.52
$2e_g$	15.01	13.17	11.23	7.42	6.05
$2t_{2g}$	13.03	11.16	9.18	5.44	4.14
t_{1g}	−1.37	−1.25	−1.21	−1.19	−1.06
t_{2u}	−1.37	−1.25	−1.21	−1.19	−1.06
$2t_{1u}$	−1.62	−1.52	−1.44	−1.42	−1.30
$1t_{2g}$	−2.19	−2.16	−2.17	−2.36	−2.47
$1a_{1g}$	−2.41	−2.35	−2.39	−2.69	−2.79
$1t_{1u}$	−2.48	−2.47	−2.52	−2.70	−2.67
$1e_g$	−3.69	−3.79	−3.91	−4.32	−4.51
Charge	1.92	1.94	1.92	1.96	1.91
10*Dq* (calcd)	1.98	2.01	2.05	1.98	1.92
10*Dq* (exptl)	1.98	1.97	2.05	1.74	1.61

is due in part to the transition to the a_{1g} level. However, since a Jahn-Teller interaction is undoubtedly operative in the excited state of this complex,[8] the two observed absorptions can be explained without recourse to the $2t_{2g} \rightarrow a_{1g}$ transition.

Similarly, the vanadium levels suggest the possibility of the $2t_{2g} \rightarrow 2a_{1g}$ transition at about 3.74 ev. Unfortunately, this region is out of the range of the instrument used to obtain the experimental results[9] on VF_6^{3-}.

TABLE II

EIGENVECTOR COEFFICIENTS AND ELECTRON POPULATIONS OF THE 3d ORBITALS

	$1e_g$		$2e_g$		$1t_{2g}$		$2t_{2g}$					
	$3d\sigma$	$2p\sigma$	$3d\sigma$	$2p\sigma$	$3d\pi$	$2p\pi$	$3d\pi$	$2p\pi$	$G(e_g)$	$G(t_{2g})$	$\bar{a}_{2eg}$	$\bar{a}_{2t_{2g}}$
TiF_6^{3-}	0.270	0.905	0.990	−0.485	0.237	0.922	0.996	−0.446	0.223	0.216	0.87	0.90
VF_6^{3-}	0.303	0.892	0.976	−0.498	0.266	0.914	0.984	−0.450	0.207	0.192	0.85	0.88
CrF_6^{3-}	0.338	0.879	0.961	−0.514	0.296	0.907	0.970	−0.454	0.190	0.167	0.83	0.87
FeF_6^{3-}	0.423	0.841	0.920	−0.564	0.390	0.872	0.930	−0.505	0.159	0.127	0.77	0.80
CoF_6^{3-}	0.474	0.813	0.893	−0.601	0.464	0.834	0.893	−0.565	0.148	0.116	0.72	0.74

One striking aspect of the results in Table I is the essential identity of the self-consistent charges of the complexes. It should be kept in mind that each metal differs in the number of d electrons and their orbital energies. While it is difficult to substantiate directly the validity of the charges, a general value of +1.9 is intuitively satisfying in terms of ionic character tempered somewhat by reduction in charge due to bond formation. Certainly, the calculated charges justify the reasonableness of our choice of +2 metal wave functions for calculation of the integrals. Indirect evidence for the validity of the calculated charges is presented later in this paper.

The similarity of self-consistent charges is all the more intriguing when one considers the increasing covalent character of the complexes as indicated by the trends in eigenvector coefficients and electron populations as indicated in Table II. A general increase of covalency as one proceeds across the row of transition elements is exactly what one would expect to occur. The increase in covalency without substantial charge alteration is possible because of the occupation of the antibonding $2t_{2g}$ and $2e_g$ orbitals by the additional d electrons of the elements with higher atomic number. As bonding increases with the resultant transfer of charge to the metal, by participation of its orbitals in the bonding MO's, the ligand participation in the antibonding orbitals also increases. Hence, the net transfer of charge is not so great for a given degree of covalency for the cobalt complex as it would be for the titanium complex.

Spin Densities

In the interpretation[10,11] of nmr and epr data taken on paramagnetic complexes, it has been postulated that the unpaired spins of an ion are distributed throughout the species in a manner dictated by the coefficients of those molecular orbitals which are occupied by the unpaired electrons. For half-filled subshells in octahedral symmetry, the relationships[10,11] between the spin densities on the ligands and the coefficients in the molecular orbitals are: $f_s = b_s^2/3$, $f_\sigma = b_\sigma^2/3$, and $f_\pi = b_\pi^2/4$, where b_s and b_σ are the coefficients of the 2s and $2p_\sigma$ symmetry-adapted ligand functions in the e_g antibonding orbital and b_π is the coefficient of the ligand $2p_\pi$ functions in the t_{2g} antibonding orbital.

Two of the ions treated in this paper, CrF_6^{3-} and FeF_6^{3-}, have been examined by magnetic resonance techniques. CrF_6^{3-} has been studied by both nmr[12] and epr[13] methods, and essentially the same values were obtained. The nmr results are $f_s = -0.021 \pm 0.01\%$, $f_\sigma - f_\pi = -4.9 \pm 0.8\%$, while the epr values are $f_s = -0.020 \pm 0.01\%$, $f_\sigma - f_\pi = -6.0 \pm 1.0\%$. For the $t_{2g}^3e_g^0$ configuration in this complex, one would predict $f_s = f_\sigma = 0$ and therefore $f_\sigma - f_\pi = -f_\pi$, which is in accord with the observed values. Hence, for CrF_6^{3-}, $f_\pi = 4.9 \pm 0.8$ or $6.0 \pm 1.0\%$. The calculated value of f_π obtained by substitution of the $2t_{2g}$ coefficient into $f_\pi = b_\pi^2/4$ is 5.2% which is within the experimental error of both results.

The epr results[11] for FeF_6^{3-} are $f_s = 0.8 \pm 0.1\%$, $f_\sigma - f_\pi = 3.5 \pm 1.0\%$. In this complex, both the e_g and t_{2g} antibonding orbitals are half-filled so that only the difference in the σ and π spin densities of the 2p orbitals can be obtained. Again from Table II, $f_\sigma - f_\pi = (0.564)^2/3 - (0.505)^2/4 = 4.2\%$, which is also within experimental error. Since the 2s ligand orbitals

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(8) A. D. Liehr and C. J. Ballhausen, *Ann. Phys.*, **3**, 304 (1958).

(9) R. J. H. Clark, *J. Chem. Soc.*, 417 (1964).

(10) R. G. Shulman and S. Sugano, *Phys. Rev.*, **130**, 506 (1963).

(11) L. Helmholz, *J. Chem. Phys.*, **31**, 172 (1959).

(12) R. G. Shulman and K. Knox, *Phys. Rev. Letters*, **4**, 603 (1960).

(13) L. Helmholz, A. V. Guzzo, and R. N. Sanders, *J. Chem. Phys.*, **35**, 1349 (1961).

were not included in the MO calculations presented here, some decrease in the $2p_\sigma$ coefficient would be in order. However, such a decrease would undoubtedly be slight since the 2s participation in the $2e_g$ orbital is relatively small, as indicated by the f_s value, and would primarily tend to decrease the metal contribution to the molecular orbital and not that of the $2p_\sigma$.

The ability to calculate reasonable values of the spin densities from the coefficients of the 2p functions in the e_g and t_{2g} antibonding orbitals suggests that the proposed method for MO calculations properly estimates the degree of both p_σ and p_π bonding in these complexes.

The Nephelauxetic Effect

It is well known that a typical spectrum for weak-field complexes such as the hexafluorides does not, in general, consist of a single absorption maximum which corresponds to the value of Δ. Rather, in terms of crystal field theory, the $2t_{2g} \rightarrow 2e_g$ separation acts as a perturbation on the states which arise from the free-ion configurations. Presuming the calculations give the exact Δ values, prediction of the spectra of the complexes requires that these values be incorporated into the usual secular determinants of the crystal field calculations. One assumption that is implicit in such an approach is that the $2t_{2g}$ and $2e_g$ levels are essentially metal in character. For the hexafluorides reported here, this assumption is quite reasonable as indicated by the values in Table II.

It is a well-established fact[14] that the electrostatic interaction integrals, F_2 and F_4 in Slater–Condon notation[15] or B and C in Racah notation,[16] which are required in a crystal field calculation are substantially reduced from those of the corresponding free ion. This reduction, termed the *nephelauxetic* or *cloud-expanding* effect, has been attributed[17] to two simultaneous causes: (1) the reduction of the effective charge on the metal as a result of electron donation *via* chemical bonding and (2) a covalency effect due to the participation of the metal atomic orbitals in molecular orbitals with the ligands. Both effects would tend to reduce the degree of electrostatic interaction between the electrons in the $2t_{2g}$ and $2e_g$ orbitals.

Since details of the nephelauxetic effect have been thoroughly considered by Jørgensen,[17] one need only summarize certain pertinent conclusions and notations. One experimentally determines the changes in electrostatic interaction associated with electronic transitions in both the free ion and the complex. These changes correspond to certain numerical values for the integrals B and/or C. The ratio $\beta = B(\text{complex})/B(\text{free ion})$ can then be established. Trends in the β values for series of complexes containing various transition metals and/or ligands have been determined[17] and related to the covalency of the species.

Fundamentally, β compares interactions[18] such as

$$K(t_{2g}(xz),\ e_g(x^2 - y^2)) = (t_{2g}(xz),\ e_g(x^2 - y^2)|e_g(x^2 - y^2),\ t_{2g}(xz))$$

where

$$t_{2g}(xz) = ad'_{xz} + (b/2)(y_1 + x_3 + x_4 + y_6)$$

$$e_g(x^2 - y^2) = cd'_{x^2-y^2} + (e/2)(z_1 - z_2 + z_4 - z_5)$$

with the corresponding free-ion integral

$$K(d_{xz},\ d_{x^2-y^2}) = (xz,\ x^2 - y^2|x^2 - y^2,\ xz)$$

As shown in the Appendix, when $|a|$ and $|c|$ are significantly larger than $|b|$ and $|e|$, respectively, the molecular exchange integral is approximately equal to $a^2c^2 \cdot K(d'_{xz},d'_{x^2-y^2})$. The prime notation on the d orbitals indicates that these functions are *not* those of the +3 free ion but more correctly correspond to those wave functions in accord with the self-consistent charge on the metal in the complex. According to these concepts, the B value for the complex would be given by

$$B(\text{complex}) = a^2c^2B(\text{scc})(z' + 2)/(z' + 3)$$

where $B(\text{scc}) = F_2 - 5F_4$ calculated for the free-ion wave functions which correspond to the self-consistent charge of the complex. The ratio $(z' + 2)/(z' + 3)$, where z' is the charge on the ion, is a correction for the fact that SCF wave functions[2,3] are known to give free-ion electrostatic interaction integrals which are too large[17] by approximately

$$B(\text{exptl}) = B(\text{calcd})(z' + 2)/(z' + 3)$$

The corresponding B(free ion) value is then calculated with the SCF wave functions which correspond to the charge on the free ion, +3, again adjusting the calculated value by $(z + 2)/(z + 3)$. Consequently

$$\beta = \frac{a^2c^2B(\text{scc})(z' + 2)/(z' + 3)}{B(\text{free ion})(z + 2)/(z + 3)}$$

One notes that for both B(complex) and β the two effects of charge reduction and molecular orbital participation of the metal in the complex are accounted for in the calculations.

Table III presents the calculated and experimental B and β values for the four complexes containing more than one d electron. Considering the number of approximations in these calculations and in the determination of the molecular orbitals, the agreement is extremely good. One notes particularly that the values of the product a^2c^2 do not correspond to the experimental β values. This indicates the importance of the lower B value as a result of charge reduction on the metal and tends to affirm the method of electron population analysis involving just the 3d orbitals on the metal.

Comparison with Previous Calculations

The energy levels and eigenfunctions for two of the complexes considered here, TiF_6^{3-} and VF_6^{3-}, have

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[14] T. M. Dunn, D. S. McClure, and R. G. Pearson, "Some Aspects of Crystal Field Theory," Harper and Row, New York, N. Y., 1965, p 33.

[15] E. U. Condon and G. H. Shortley, "The Theory of Atomic Spectra," Cambridge University Press, New York, N. Y., 1959.

[16] G. Racah, *Phys. Rev.*, **62**, 438 (1942); **63**, 367 (1943).

[17] (a) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press Ltd., Oxford, 1962, p 134; (b) *Progr. Inorg. Chem.* **4**, 73 (1963).

[18] The notation for the electrostatic interaction integrals is the same as that used in the previous paper.[7]

TABLE III

ELECTROSTATIC INTERACTION AND β VALUES

Complex	B (+3),[a] cm^{-1}	B (+2),[a] cm^{-1}	a^2c^2	B (complex) (calcd), cm^{-1}	B (complex) (exptl), cm^{-1}	β (calcd)	β (exptl)
VF_6^{3-}	890	749	0.92	689	648	0.77	0.75[c]
CrF_6^{3-}	956	818	0.87	712	680	0.74	0.74[d]
FeF_6^{3-}	1084	950	0.73	694	844	0.64	0.77[e]
CoF_6^{3-}	1147	1003	0.63	632	[b]	0.55	[b]

[a] $B(+3)$ and $B(+2)$ are calculated from the corresponding free-ion wave functions and then multiplied by the correction factors, $^5/_6$ and $^4/_5$, respectively. [b] The only observed transition in CoF_6^{3-} is independent of electrostatic interaction. [c] See ref 9. [d] J. Ferguson, K. Knox, and D. L. Wood, *J. Chem. Phys.*, **35,** 2236 (1961). [e] See ref 17.

TABLE IV

COMPARISON OF METAL 3d ORBITAL POPULATIONS AND CALCULATED β VALUES

	VF_6^{3-}		TiF_6^{3-}	
	Present work	Ref 20	Present work	Ref 19
$1e_g$	0.592	0.831	0.508	0.723
$1t_{2g}$	0.708	1.360	0.618	1.232
$2t_{2g}$	1.764	1.547	0.897	0.795
Total	3.064	3.738	2.023	2.750
$\bar{a}(2e_g)$	0.88	0.79	0.87	0.82
$\bar{a}(2t_{2g})$	0.85	0.77	0.90	0.80
$\beta(1)$	0.73[a]	0.60[a]	...	...
B(complex)	689 cm^{-1}	451 cm^{-1}	...	...
$\beta(2)$	0.77[a]	0.51[a]	...	...

[a] $\beta(1)$ is calculated from $\bar{a}(2e_g)\bar{a}(2t_{2g})$ while $\beta(2)$ and B(complex) are calculated by the method outlined in this paper. The experimental value[1] of B(complex) is 648 cm^{-1} and of β is 0.75.

been previously determined[19,20] by the modified version of the Wolfsberg and Helmolz method.[21] A comparison of the methods in terms of quantum mechanical *principles* will be the subject of a future communication, but it is worthwhile to compare closely the *results.* Two questions arise: (1) Do the two methods yield substantially different answers? (2) If they do differ, which, if either, is more correct?

There are, of course, obvious initial differences. The approach used is this paper does not invoke interaction of the 2s ligand orbitals with the metal orbitals,[22] either separately or in the hybrid form of the previous calculations. This eliminates the dilemma of the previous method concerning the high degree of overlap with the "nonbonding" hybrid combination[20,23] yet allows appropriate Δ values to be calculated *via* the 2p orbital interactions, a situation which was not achieved in the previous work.[20] Of course, the reduction factors in our determination for TiF_6^{3-} were adjusted so as to yield a correct Δ, but the values required of these parameters were in keeping with the relationships between point- and spread-charge interactions.[1] Furthermore, they were held constant for the remaining compounds.

The significant differences between the two methods lie in the results obtained for the coefficients of the eigenvectors and in what these coefficients signify in terms of covalency. The covalency differences are reflected in the $2t_{2g}$ and $2e_g$ electron populations and in the evaluation of B(complex) and β. Therefore, our attention is drawn principally to the VF_6^{3-} complex. For comparative purposes, pertinent results are summarized in Table IV. Before discussion of these values some comments on β are necessary.

The authors of the previous work defend the covalency of their results by noting that the experimental β of 0.75 is close to their value of 0.77 for the metal character in the $2t_{2g}$ orbital, listed in Table IV as $\bar{a}(2t_{2g})$. However, as Jørgensen has pointed out,[17] if one uses this fraction to estimate β, it is necessary to *square* it, or more properly to multiply it by $\bar{a}(2e_g)$. In terms of this latter procedure, the previous authors' β should be 0.61 and ours is 0.73 compared to the experimental 0.75 value.

For β at a self-consistent charge of +0.51, calculated according to the method previously outlined in this paper, a value of 0.51 is obtained by use of the coefficients F_k values listed in Tables V and X of ref 20. Even if one assumes that the 3d-orbital population in ref 20 is only 3.75 electrons and consequently B(complex) should be calculated for a charge of +1.25 instead of +0.51, the calculated β is only 0.61. Hence, we repeat our contention[24] that the modified Wolfsberg and Helmholz approach results in excessive covalency and, as the populations of $1t_{2g}$ in Table IV indicate for both VF_6^{3-} and TiF_6^{3-}, attributes more π bonding to the complexes than is probably present.

In answer to the two questions previously posed: there are substantial differences in the results of the two methods and there are good indications that the factors included in the proposed method for the calculation of the matrix elements yield solutions in better accord with experimental evidence.

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Appendix

The electronic transitions which give rise to the absorption spectra of the hexafluoride complexes are, in general, characterized not only by the energy separation Δ but also by changes in electrostatic interaction between the electrons. For example, in CrF_6^{3-} the energy of the transition $^4A_{2g} \rightarrow {}^4T_{1g}$ is $\Delta + 2J(t_{2g}(xy), e_g(z^2)) - 2K(t_{2g}(xz), e_g(z^2)) - 2J(t_{2g}(xz), t_{2g}(xy)) + 2K(t_{2g}(xz), t_{2g}(xy))$. J and K represent the usual coulomb and exchange integrals, but here they involve the molecular orbitals $t_{2g}(xz)$, etc. For example

$$t_{2g}(xz) = a(xz) + \frac{b}{2}(y_1 + x_3 + x_4 + y_6)$$

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[19] H. D. Bedon, S. M. Horner, and S. Y. Tyree, Jr., *Inorg. Chem.*, **3,** 647 (1964).

[20] H. D. Bedon, W. E. Hatfield, S. M. Horner, and S. Y. Tyree, Jr., *ibid.*, **4,** 743 (1965).

[21] M. Wolfsberg and L. Helmholz, *J. Chem. Phys.*, **20,** 837 (1952).

[22] Again, let it be restated that this is not meant to imply a complete absence of interaction but rather that in the hexafluorides this interaction is not appreciable. See ref 1 for a more complete discussion.

[23] R. F. Fenske, *Inorg. Chem.*, **4,** 33 (1965).

$$t_{2g}(xy) = a(xy) + \frac{b}{2}(x_1 + y_2 + y_4 + x_5)$$

Consider the $K(t_{2g}(xz),\ t_{2g}(xy))$ integral for CrF_6^{3-}. In the notation of the previous paper,[1] this integral is $(t_{2g}(xz),\ t_{2g}(xy)|t_{2g}(xy),\ t_{2g}(xz))$. Consequently, evaluation involves the fourth power of the coefficients a and b. If one neglects all three- and four-center integrals such as $(xz,\ y_1|y_3,\ x_3)$ but evaluates all one- and two-center integrals using the +2 wave function for the metal d orbital and the fluoride 2p orbital for the ligands, one obtains

$$K \text{ (in au)} = a^4(0.03099) + a^3b(0.00558) + a^2b^2(0.00178) + ab^3(0.00119) + b^4(0.00971)$$

It is apparent from this calculation that, when $|a|$ is significantly larger than $|b|$, K is dominated by the first term in the expression. From Table II, a = 0.970 and b = −0.454, so K(complete) = 0.0260 au. Since $a^4(0.03099)$ = 0.0274, to a fair degree of approximation the value of K depends only upon the corresponding value of the metal interaction multiplied by the fourth power of the coefficient of the d obital in the molecular orbital. Analogously, interactions involving the t_{2g} and e_g orbitals, whose metal orbital coefficients are a and c, respectively, can be approximated by a^2c^2 times the corresponding metal interaction integral.

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The Spectrum of Potassium Hexachlororhenate(IV) in Fused Salts[1]

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The visible spectrum of K_2ReCl_6 has been investigated in molten dimethyl sulfone, diethylamine hydrochloride, and LiCl–KCl mixtures, at temperatures up to 600°. A splitting of some of the bands has been observed which is dependent on the solvent.

Introduction

The literature reports a number of studies of the electronic spectra of transition metal ions in fused-salt solvents which have given considerable information about complexes and their structures in such media. However, this work has been limited to first-row transition metals.[2] This communication deals with a study of potassium hexachlororhenate(IV) in various fused systems, and the effects of the melt on this octahedral species. We are not concerned with formation of the complex in the melt, as is generally the case when a simple compound is added to the fused salt. Owing to the very large octahedral site stabilization energy of Re(IV) (approximately 84 kcal/mole), the octahedral–tetrahedral equilibrium which has been observed for many of the first-row transition metal ions[3] is not expected. However, interesting information on the nature of ionic interactions with the complex species in the melt can be obtained.

Eisenstein has performed a theoretical analysis of the $ReCl_6^{2-}$ ion, including the spin–orbit interactions.[4] He assigned the energy levels as follows (cm^{-1}, the listed energies are quoted from his paper)

$^4A_2$	(Γ_8)	0	$^2T_1$	(Γ_6)	9,574
$^2T_1$	(Γ_8)	<7700	$^2T_2$	(Γ_7)	14,180
^2E	(Γ_8)	9105	$^2T_2$	(Γ_8)	15,385

The Γ's are representations in the cubic double group. He also tentatively assigned bands at 35,900 and 39,000 cm^{-1} to transitions to the $^4T_2$ and $^4T_1$ levels, respectively, recognizing the possibility that these could be charge-transfer bands masking the ligand field bands.

The detail observed for the transitions $^4A_2\ (\Gamma_8) \rightarrow {}^2E\ (\Gamma_8),\ {}^2T_1\ (\Gamma_6),\ {}^2T_2\ (\Gamma_7)$ is vibrational fine structure.[5]

Experimental Section

The furnace assembly for the Unicam SP700 spectrophotometer with which all spectra were obtained and the method for the preparation of solutions of air-sensitive samples in the LiCl–KCl eutectic have been described previously.[6]

The K_2ReCl_6 was prepared by the method of Rulfs and Meyer,[7] using potassium perrhenate obtained from the S. W. Shattuck Co.

The dimethyl sulfone was Eastman Practical grade, recrystallized from methanol. Diethylamine hydrochloride was prepared by passing HCl gas into a solution of freshly distilled Eastman diethylamine in Fisher Reagent grade benzene.

Stoppered fused-quartz cells of 1-cm light path were used for the spectra of solutions of K_2ReCl_6 in dimethyl sulfone and diethylamine hydrochloride. These and the reference solutions were prepared and maintained under a dry nitrogen atmosphere. The LiCl–KCl studies were done in similar cells which were sealed under vacuum.

The analyses were performed on a Beckman Model DU spec-

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[2] Recent surveys are given by D. M. Gruen in "Fused Salts," B. R. Sundheim, Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1964, Chapter 5, and G. P. Smith in "Molten Salt Chemistry," M. Blander, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, p 427.

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[5] C. K. Jørgensen, *Acta Chem. Scand.*, **9**, 710 (1955).

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