Electron affinities can be taken as approximate IP's. As the ionization energies of anionic species are fairly low, the higher excited states are easily attained. A reasonable guess can be made about these excited states and their energies by comparing them to those of other isoelectronic cases for which the required information is known. As shown in part II, values calculated on this basis are well suited to the MO calculations, as the results are excellent. A more detailed treatment of anionic species will appear in a subsequent publication.

Results and Discussion. To exemplify the proposed method, the evaluation of BOIE's of 3d, 4s, and 4p orbitals of Ni are documented elsewhere.[27] A comparison of the overall VOIE's of Ni and their respective charge dependence calculated by the present method and those by Basch, *et al.* is shown in Table IV.

$(\mathrm{BOIE})_{n\rightarrow n+1}$ attains a limiting value when the highest term of the configurations considered is reached. Thus, when the electron attains the highest term of the configurations, the $(\mathrm{BOIE})_{n\rightarrow n+1}$ would be independent of charge. One implication is that if the charge on the atom gives a limiting energy which exceeds that corresponding to the highest term of the configurations considered, the bonding may "involve" orbitals other than those already considered. In other words, the charge on the atom would depend, among other things, on the orbitals involved in bonding.

By the present method of evaluation of orbital ionization energies, it will be possible to attain more accurate information regarding the participation of virtual orbitals in bonding. To support this contention, a comparison between observed and calculated molecular properties which show a critical dependence on atomic charge distribution is presented and discussed in detail in part II. Also discussed in part II are the implications and consequences of the very significant difference in the numerical values of calculated properties using the proposed BOIE's and those using the usual VOIE's.

It is obvious that the proposed method relies heavily on a knowledge of spectroscopic states. In cases where such data are incomplete, or lacking, it is possible to arrive at suitable information by acceptable extrapolation techniques. Although the latter procedure will of necessity lack the accuracy of experimental data, this in no way will impair the basic approach to the calculation of VOIE proposed here.

[27] A listing of BOIE's as a function of charge for the 3d, 4s, and 4p orbitals of Ni will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-73-1590.

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Investigations in Semiempirical Molecular Orbital Methods. II. Computational Results for Octahedral Fluorides TiF_6^{3-}, CrF_6^{3-}, FeF_6^{3-}, and NiF_6^{4-}

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A new parameter-free method for doing semiempirical molecular orbital calculations has been applied to octahedral fluoro complexes MF_6^{n-} ($M = Ti^{3+}, Cr^{3+}, Fe^{3+}, Ni^{2+}$). Calculations of ligand field splittings, superhyperfine coupling constants, and spin densities are found to be in excellent agreement with experiment. In all cases the results obtained are at least as good as the best SCF calculations done on these complexes thus far.

Introduction

A new approach to performing semiempirical molecular orbital calculations on inorganic coordination complexes and molecules has been developed in part I of this series.[1] In this part of the series we present computational results on the model systems TiF_6^{3-}, CrF_6^{3-}, FeF_6^{3-}, and NiF_6^{4-} (in the salt $KNiF_3$). This selection is based on the fact that in these particular species it is possible to compare the results of this study with those of other theoretical studies having varying degrees of sophistication. Also these complexes allow a comparison to be made between the experimental and calculated data regarding ligand field splitting ($10Dq$), charge-transfer spectra, superhyperfine coupling constants and spin densities (derived from epr and nmr), and net atomic charges (derived from X-ray absorption). Consequently a very crucial test of the accuracy and applicability of the method is thus provided.

Method of Calculation

Details of the computational approach have already been given previously.[1] Thus only the basic features of the method will be reiterated here.

The diagonal elements of the Hamiltonian are

$$\mathbf{H}^{\mathrm{M}}{}_{ii} = \epsilon_i(q_{\mathrm{M}})_i - n(q_{\mathrm{L}} + q_{\mathrm{ex}})(1/R_{\mathrm{ML}}) + q'_{\mathrm{L}}\frac{\langle r_{\mathrm{d}}{}^4\rangle}{6R_{\mathrm{ML}}{}^5}F_{\mathrm{M}} \quad (1)$$

$$\begin{aligned}\mathbf{H}^{\mathrm{L}}{}_{jj} = {} & \epsilon_j(q_{\mathrm{L}})_j - q_{\mathrm{M}}/R_{\mathrm{ML}} - [q_{\mathrm{L}} + q_{\mathrm{ex}}]\left[\frac{n-2}{(R_{\mathrm{LL}})_{\mathrm{C}}} + \right.\\ & \left. 1/(R_{\mathrm{LL}})_{\mathrm{T}}\right] - \frac{q_{\mathrm{M}}\langle r_{\mathrm{p}}{}^2\rangle}{5R_{\mathrm{ML}}{}^3} - q'_{\mathrm{L}}(\langle r_{\mathrm{p}}{}^2\rangle/5)\left[\frac{n-2}{(R_{\mathrm{LL}})_{\mathrm{C}}} + \right.\\ & \left. 1/(R_{\mathrm{LL}})_{\mathrm{T}}\right] + \frac{q'_{\mathrm{L}}N_i{}^2}{2}\left\{(\mathrm{IF})_{\mathrm{C}}\left[1/(R_{\mathrm{LL}})_{\mathrm{C}} - \langle\frac{1}{r_{\mathrm{p}}}\rangle\right] + \right.\\ & \left. (\mathrm{IF})_{\mathrm{T}}\left[1/(R_{\mathrm{LL}})_{\mathrm{T}} - \langle\frac{1}{r_{\mathrm{p}}}\rangle\right]\right\} \quad (2)\end{aligned}$$

where $\mathbf{H}^{\mathrm{M}}{}_{ii}$ and $\mathbf{H}^{\mathrm{L}}{}_{jj}$ refer to the metal and ligands, respec-

[1] Part I: A. Dutta-Ahmed and E. A. Boudreaux, *Inorg. Chem.*, 12, 1590 (1973).

tively, while the off-diagonal elements $\mathbf{H}^{\mathrm{ML}}{}_{ij}$ (between metal and ligands) and $\mathbf{H}^{\mathrm{LL}}{}_{ij}$ (between ligands) are

$$\mathbf{H}^{\mathrm{ML}}{}_{ij} = (\mathrm{G}^{\mathrm{ML}}{}_{ij}/2)\left[\mathbf{H}^{\mathrm{M}}{}_{ii} + \mathbf{H}^{\mathrm{L}}{}_{jj} - (q_{\mathrm{M}}\langle\frac{1}{r_i}\rangle_{\mathrm{M}}/2) + q'_{\mathrm{L}}\langle\frac{1}{r_{i1}}\rangle_{\mathrm{L}} + \frac{q_{\mathrm{M}} + q'_{\mathrm{L}}}{2R_{\mathrm{ML}}}\right] \qquad (3)$$

$$\mathbf{H}^{\mathrm{LL}}{}_{ij} = (G^{\mathrm{LL}}{}_{ij}/2)[(\mathbf{H}_{\mathrm{L}}')_i + (\mathbf{H}_{\mathrm{L}}')_j + N_iN_j\{\sum_{t\neq u}\sum C_{it}C_{iu}S'_{\mathrm{C}}/(R_{\mathrm{LL}})_{\mathrm{C}} + \sum_{t'\neq u'}\sum C_{it'}C_{iu'}S'_{\mathrm{T}}/(R_{\mathrm{LL}})_{\mathrm{T}}\}] \qquad (4)$$

All other quantities contained in eq 1-4 have previously been defined in part I.[1]

The wave functions required for calculating the group overlaps, $G^{\mathrm{ML}}{}_{ij}$ and $G^{\mathrm{LL}}{}_{ij}$, were taken as the optimized Slater type functions for the 3d, 4s, and 4p orbitals of the metals in the 1+ state[2] and Clementi functions for the 2s and 2p orbitals of fluoride.[3]

All computations were performed on a PDP-10 computer, with the **G** matrices calculated initially and subsequently incorporated in the calculation of the **H** matrices. The VOIE's required in the **H** matrices were derived according to the procedure given in part I.[1] Finally the calculated MO's were iterated to a self-consistency of ±0.01 unit of atomic charge and orbital population utilizing Lowdin orthogonalization.[4]

A series of comparative calculations were also made on the $\mathrm{FeF_6}^{3-}$ complex for the purpose of assessing the importance of each of the following features: (a) choice of VOIE's, (b) ligand field splitting terms, (c) the electrostatic potential of the external environment, and (d) Lowdin *vs.* Mulliken method of population. The results of this analysis are treated in greater detail in the discussion part of this paper.

Although it is not to be expected that the methodology of the present procedure is directly comparable to that of other methods totally computational in approach, it is appropriate to provide at least a brief account of the kinds of most exacting calculations that have been made thus far on the systems under consideration. In this way it is possible to attain a fuller appreciation of the merits of the much simpler and most direct approach presented here.

The work of De Laat[5] consists of an unrestricted HF-SCF study on $\mathrm{TiF_6}^{3-}$ using several choices of basis functions for Ti^{3+} and F^-. A variety of calculations were made wherein all but three- and four-center two-electron integrals were calculated exactly, but the latter were treated with different approximations. No attempt was made to take explicit account of the influence of the external potential.

Offenhartz[6] did an HF-SCF study on $\mathrm{FeF_6}^{3-}$, $\mathrm{CrF_6}^{3-}$, and $\mathrm{NiF_6}^{4-}$, using strictly 3d ionic wave functions in an attempt to calculate $10Dq$. The results, however, were generally quite poor. In a later publication considerable improvement in calculating $10Dq$ of these same complexes was made with an open-shell SCF method.[7]

An approximate SCF method was derived by Fenske, *et al.*,[8] and applied to $\mathrm{MF_6}^{3-}$ (M = Ti, V, Cr, Fe, Co) complexes, which bears some similarity to the present method. The former, however, involves computation of all integrals and hence requires parameterization in certain instances. No consideration was given to the external potential, and the Mulliken method was employed to obtain charges and orbital populations. In spite of various criticisms,[9] results obtained by this method appear to be generally in good agreement with experiment.

Richardson and coworkers[10] reported SCF calculations on $\mathrm{MF_6}^{n-}$ (M = Ti^{3+}, Cr^{3+}, Fe^{2+}, Ni^{2+}) complexes using 1s through 2p orbitals for F^- and 1 s through 4p orbitals for M. Calculated values of $10Dq$ were found to be in better agreement with experiment with 4s and 4p metal orbitals rather than without. However, attempts to calculate the magnetic hyperfine constants, A_s and $A_\sigma - A_\pi$, yielded poor results.

In a recent study Brown and Burton[11] reported spin-unrestricted HF-SCF calculations on $\mathrm{MF_6}^{n-}$ (M = Cr^{3+}, Fe^{3+}, Mn^{4+}, Ni^{2+}) complexes. The Slater type orbitals which were employed in the atomic basis included the 3d, 4s, and 4p functions of M, while those of F^- were limited to the 2p. Electrostatic effects of the lattice environment were included and shown to have marked influences on atomic charges and charge densities. Although no attempt was made to determine $10Dq$, calculated spin densities were found to be in reasonable agreement with experiment in most cases, but the results for $\mathrm{NiF_6}^{4-}$ were poor.

Finally, the $\mathrm{NiF_6}^{4-}$ ion has perhaps been the object of the most varied and exacting calculations made thus far on an inorganic complex ion. One of the most recent works is a complete *ab initio* HF-SCF study by Wachters, both with and without the external potential.[12] Also Moskowitz and coworkers[13] reported both restricted and unrestricted *ab initio* calculations on the isolated cluster. The results of both studies are reasonably successful in reproducing most observed physical properties.

Results and Discussion

The results of these calculations are presented in Tables I-VI, where the aforementioned physical properties and computed results are compared both with experiment and with the calculations of other workers. It is to be noted that agreement of the present results with experiment is consistently excellent.

An inspection of Table I reveals that the relative order of energies of the highest occupied orbitals in the O_h point group are: $(3t_{1u})^6(2a_{1g})^2(2t_{2g})^a(3e_g)^b$, where a and b of course depend upon the particular metal atom in the $\mathrm{MF_6}^{n-}$ complex. The other orbitals have variable ordering but in many cases the energy spacings are quite close together. The atomic orbital composition of the highest MO's is given in terms of Lowdin eigenvectors, which are presented in Table II together with the net orbital populations and atomic charges. The most significant feature is that the $2t_{2g}$ and $3e_g$ levels are not essentially pure M(3d) in character but rather contain significant admixtures of F(2p) character which increases regularly with increasing atomic number of M. In other words, the degree of covalency in the bonding changes appreciably with M, though these changes do not parallel those expected on the basis of electronegativity arguments alone. This has a substantial bearing on the inter-

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(2) (a) J. W. Richardson, W. C. Nieuwpoort, R. R. Powell, and W. F. Edgell, *J. Chem. Phys.*, 36, 1057 (1962); (b) J. W. Richardson, R. R. Powell, and W. C. Nieuwpoort, *ibid.*, 38, 796 (1963).

(3) E. Clementi, *J. Chem. Phys.*, 40, 1944 (1964); IBM Report RJ-256.

(4) See Appendix I in part I.

(5) F. L. M. A. H. De Laat, Doctoral Thesis, Eindhoven, The Netherlands, 1968.

(6) P. O. Offenhartz, *J. Chem. Phys.*, 47, 2951 (1967).

(7) P. O. Offenhartz, *J. Amer. Chem. Soc.*, 91, 5699 (1969).

(8) R. F. Fenske, K. G. Coulton, D. D. Radtke, and C. C. Sweeney, *Inorg. Chem.*, 5, 960 (1966).

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(10) J. W. Richardson, D. M. Vaught, T. F. Saules, and R. R. Powell, *J. Chem. Phys.*, 50, 3633 (1969).

(11) R. D. Brown and P. G. Burton, *Theor. Chim. Acta*, 18, 309 (1970).

(12) A. J. H. Wachters, Doctoral Thesis, Groningen, 1971.

(13) J. W. Moskowitz, C. Hollister, and C. J. Hornback, *J. Chem. Phys.*, 53, 2570 (1970).

Table I. Relative Electron Energy Levels[a]

	TiF_6^{3-} ($3d^1$)	CrF_6^{3-} ($3d^3$)	FeF_6^{3-} ($3d^5$)	NiF_6^{4-} ($3d^8$)
$4t_{1u}$	35.030	22.999	−36.633	66.093
$3a_{1g}$	−27.505	−45.963	−94.718	−55.712
$(3e_g)^b$	−84.095	−100.535	−114.510	−107.967
$(2t_{2g})^a$	−99.951	−113.210	−124.597	−114.912
$(2a_{1g})^2$	−140.209	−139.095	−139.709	−117.704
$(3t_{1u})^6$	−143.285	−141.027	−143.949	−120.715
$(2e_g)^4$	−146.908	−147.245	-150.987^b	-127.691^b
$(t_{2u})^6$	−152.817	−149.974	-151.639^b	-126.172^b
$(t_{2g})^6$	−153.018	-151.850^b	-153.631^b	−128.501
$(2t_{1u})^6$	−153.308	-153.368^b	-149.948^b	−132.086
$(t_{1g})^6$	−154.452	-151.576^b	-153.133^b	-127.113^b
$(e_g)^4$	−240.920	−237.901	−234.379	−223.629
$(t_{1u})^6$	−258.638	-268.798^b	-246.421^b	-254.843^b
$(a_{1g})^2$	−262.089	-261.604^b	-245.006^b	-236.123^b

[a] Energies are in kK (1000 cm^{-1}). [b] Note the change in relative order of the levels.

Table II. Transformed Lowdin Eigenvector Coefficients[a]

	Eigenvectors			
Orbitals	TiF_6^{3-}	CrF_6^{3-}	FeF_6^{3-}	NiF_6^{4-}
$3e_g$				
M(3dσ)	0.885	0.784	0.731	0.542
F(2pσ)	0.088	0.197	0.256	0.455
F(2s)	0.027	0.019	0.013	0.002
$2t_{2g}$				
M(3dπ)	0.862	0.800	0.777	0.655
F(2pπ)	0.138	0.200	0.223	0.345
$2a_{1g}$				
M(4s)	0.001	0.001	0.049	0.020
F(2pσ)	0.998	0.997	0.951	0.979
F(2s)	0.001	0.002	0.000	0.001
$2t_{1u}$				
M(4p)	0.001	0.000	0.004	0.000
F(2pσ)	0.745	0.970	0.993	0.860
F(2pπ)	0.254	0.029	0.002	0.139
F(2s)	0.001	0.001	0.001	0.001

[a] These are the squares of the Lowdin eigenvectors transformed to the original basis.

pretation of spectral assignments and other physical properties, which thus far have been based primarily on ligand field arguments involving nearly pure 3d orbital character.

Atomic Charges and Populations. As stated earlier atomic charges and orbital populations were iterated to self-consistency by utilizing Lowdin orthogonalization. The results are presented in Table III, which also includes other calculated data according to Fenske, *et al.*,[8] Brown, *et al.*,[11] and others[5,13] plus some recent experimental information acquired through X-ray absorption studies.[14] These latter studies lead to charges of 1.33+ on Fe in K_3FeF_6 and 1.53+ on Cr in K_3CrF_6, which appear to be reliable to an accuracy of 10%. The calculated values of 1.388+ for Fe in FeF_6^{3-} and 1.525+ for Cr in CrF_6^{3-} obtained by the present method are in excellent agreement with the experimental data.

The population analyses show that although the major charge density is in the 3d orbitals, small but significant contributions are found in the 4s and 4p orbitals. The fluorine 2s and 2p orbitals, on the other hand, are nearly fully populated.

Electronic Spectra. Although numerous attempts have been made to correlate observed electronic spectra with those assignments made from MO theory, the general conclusion made thus far is that it is difficult to obtain accurate results in the absence of a detailed calculation of both the ground and excited states involved. The main problem is that even if the geometries of the ground and excited states are essentially unchanged, the differences in spin properties of the two states are sufficient to account for discrepancies in results that are based merely on the ground state MO configuration. Only in those instances where the differences in spin interactions in the excited compared to the ground state are small or accidentally cancel each other, should close agreement between calculated and observed spectra be anticipated.

With the present method, however, the concept of an average effective spin can be readily applied to both ground and excited states, and thus it should be possible to attain a reasonably accurate account of spectra for at least most observable electronic transitions. The only drawback is that this procedure will not account for possible changes in symmetries of excited states. In the latter instances completely separate calculations would be required.

Although it is not the purpose of this paper to treat the calculation of spectra in any detail, the calculated results for both ligand field (10*Dq*) and charge-transfer (ligand to metal; $3t_{1u} \rightarrow 3e_g$, $t_{2u} \rightarrow 2t_{2g}$, $t_{2u} \rightarrow 3e_g$) bands of the MF_6^{n-} complexes considered here are given in Table IV.

The very important effect of the "spin-pairing" energy correction is clearly demonstrated in that the data in column 4 of Table IV bring the calculated values of 10*Dq* into nearly exact agreement with the observed ones. However, in the case of charge-transfer bands, the "spin-pairing" correction is only of the order <1 kK and hence is of little consequence in these cases. From among the various likely choices for assignments there appears to be at least one that is in good agreement with the observed data.

There are further difficulties, however, in attempts to match calculated and observed charge-transfer spectra. The experimental data are questionable since in most cases wherein the MF_6^{n-} complexes are involved, assignments are made on the basis of incompletely resolved peaks.[15] Also, the observed bands are quite broad, spanning at least 10 kK or more, and suggest the likelihood of more than one transition, even though the assignments are always labeled $L(\pi_u) \rightarrow M(t_{2g})$. Furthermore, even in the cases where it may be assumed that the assignments are essentially correct, the involved transitions are from ligand orbitals, which are nonbonding, to metal orbitals, which are at least partially bonding in character. Thus it is quite possible that the geometries of the excited states are sufficiently different from that of the ground state, thus accounting for any appreciable discrepancy between the calculated and observed data.

It is of interest to point out that the results of the present calculations give a good match between calculated and observed bands for the complete spectra of all the MF_6^{n-} complexes treated here, if one is willing to accept different assignments from those reported in the literature. This will be treated in greater detail in a future communication.

Spin Densities. The extent to which electron spin is transferred from a metal atom onto the ligands has for a long time been accepted as direct experimental evidence for covalent bonding in MF_6^{n-} complexes. The basic equations for this interaction are well established[16] and are derived from the hyperfine interaction of an electron on the metal atom with

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(14) G. Leonhardt and A. Meisel, *J. Chem. Phys.*, 52, 6189 (1970).

(15) G. C. Allen, G. A. M. El-Sharkawy, and K. D. Warren, *Inorg. Chem.*, 10, 2538 (1971); (b) G. C. Allen and K. D. Warren, *Struct. Bonding (Berlin)*, 9, 49 (1971).

(16) W. Marshall and R. Stuart, *Phys. Rev.*, 123, 2048 (1961); (b) A. Abragam, "Principles of Nuclear Magnetism," Clarendon Press, Oxford, 1962, p 172.

Table III. Orbital Populations and Atomic Charges

	Total populations					Atomic charges	
	M(4p)	M(4s)	M(3d)	F(2s)	F(2p)	M	F
TiF_6^{3-}							
Fenske, *et al.*[a]			2.046		5.820	1.92+	0.82−
De Laat[b]	(0.085)[f]		1.333	(7.935)[f]		2.61+	0.94−
This work	0.066	0.003	2.248	1.982	5.799	1.683+	0.781−
CrF_6^{3-}							
Fenske, *et al.*[a]			4.088		5.820	1.92+	0.82−
Brown, *et al.*[d]	−0.004	0.172	4.716		5.648	1.124+	0.648−
This work	0.011	0.001	4.463	1.987	5.767	1.525+	0.754−
Obsd[c]						1.53+	
FeF_6^{3-}							
Fenske, *et al.*[a]			6.014		5.827	1.96+	0.83−
Brown, *et al.*[d]	0.000	0.366	5.534		5.850	2.100+	0.850−
This work	0.209	0.102	6.300	1.986	5.745	1.388+	0.731−
Obsd[c]						1.33+	
NiF_6^{4-}							
Brown, *et al.*[d]	0.023	0.373	8.034		5.921	1.524+	0.921−
Moskowitz, *et al.*[e]	0.062	0.071	8.023	1.985	5.986	1.826+	0.971−
This work	0.005	0.042	8.916	1.999	5.841	1.038+	0.840−

[a] See ref 8. [b] See ref 5. [c] G. Leonhardt and A. Meisel, *J. Chem. Phys.*, **52**, 6189 (1970). [d] See ref 11. [e] See ref 13. [f] s and p orbitals considered as composite units.

Table IV. Electronic Spectra[a]

	One-electron $2t_{2g} \rightarrow 3e_g$					
	Uncor	Cor[b]	10*Dq*	$3t_{1u} \rightarrow 2t_{2g}$ $3t_{1u} \rightarrow 3e_g$	$t_{2u} \rightarrow 2t_{2g}$ $t_{2u} \rightarrow 3e_g$	$\pi_u \rightarrow t_{2g}$
TiF_6^{3-}						
De Laat[c]			15.37			
Fenske, *et al.*[d]			15.97			116.16
This work	15.85	15.49	15.49	43.33 59.18	52.87 68.72	
Obsd			15.3, 19.3[f]			47.7[f]
CrF_6^{3-}						
Fenske, *et al.*[d]			16.54			
Offenhartz[h]			6.88 (12.7)			
This work	12.68	16.44	16.44	27.82 40.50	36.76 49.44	
Obsd			16.10[i] 15.20[j]			7.50[f]
FeF_6^{3-}						
Fenske, *et al.*[d]			15.97			
Offenhartz[h]			7.30 (13.9)			
This work	10.08	13.64	13.64	19.35 29.44	27.04 37.13	
Obsd			13.35[f]			37.0, 47.6[f]
NiF_6^{4-}						
Moskowitz, *et al.*[e]			6.09			
Offenhartz[h]			4.04 (7.25)			
This work	6.94	7.30	7.30	5.81 12.75	11.26 18.20	
Obsd			7.25[g]			?

[a] All energies are in kK (1000 cm^{-1}). [b] Corrected for spin interaction as discussed in part I. [c] See ref 5. [d] See ref 8. [e] See ref 13. [f] G. C. Allen, G. A. M. El-Sharkawy, and K. D. Warren, *Inorg. Chem.*, **10**, 2538 (1971); G. C. Allen and K. D. Warren, *Struct. Bonding (Berlin)*, 9, 49 (1971). [g] K. Knox, R. G. Shulman, and S. Sugano, *Phys. Rev.*, **130**, 512 (1963). [h] See ref 6 and 7. [i] D. L. Wood, J. Ferguson, K. Knox, and J. F. Dillon, *J. Chem. Phys.*, **39**, 890 (1963). [j] C. K. Jorgensen "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, London, 1962.

the nuclear moment of the ligand. The important relations are

$$f_s = 2SA_s/A_{2s}$$

$$f_\sigma - f_\pi = 2S(A_\sigma - A_\pi)/A_{2p}$$

where A_s and $A_\sigma - A_\pi$ are hyperfine interaction parameters obtained from experiment, A_{2s} and A_{2p} are analogous quantities for the fluoride ion, S is the total spin of the metal ion, and the f parameters are fractional spin densities.[17] The A_s parameter arises from the well-known Fermi contact interaction which is a function of $|\phi_s^{(0)}|^2$, the square of the radial wave function of an s orbital at the fluorine nucleus, which gives the s-electron density at the nucleus; A_σ and A_π, on the other hand, are functions of the operator $1/r^3$ for the fluorine 2p orbitals.

Additional expressions relating spin densities to molecular orbital coefficients have been derived by Shulman and Sugano,[17] *i.e.*

$$f_s = C_{e_g}/3$$

$$f_\sigma = f_\pi = C_{e_g}/3 - C_{e_{2g}}/4$$

where the C_{e_g} and $C_{t_{2g}}$ are the coefficients for the highest occupied e_g and t_{2g} orbitals.

It is important to point out that the evaluation of f_s and $f_\sigma - f_\pi$ from observed data has been made using the total spin, S, of the free metal ion. However, this should rather be the "true spin" of the metal in the MF_6^{n-} complex which is correctly represented by the net effective spin obtained

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

Table V. Fluorine Superhyperfine Interaction Parameters (f, %; A, $\times 10^4$ cm^{-1})

	This work	Obsd Reported	 Corrected[a]	Other works
CrF_6^{3-}				
f_s				
f_σ				−2.192[d]
f_π	4.989			−0.2550[d]
$f_\sigma - f_\pi$	−4.989	−6.0 ± 1.0[b]	−4.8 ± 0.8	−4.742[d]
		−4.9 ± 0.8[c]	−3.9 ± 0.6	
A_s				
$A_\sigma - A_\pi$	−8.918	−4.5 ± 1.0[b]		
		−7.2 ± 1.2[c]		
FeF_6^{3-}				
f_s	0.433	0.8 ± 0.1[c,e]	0.61 ± 0.08	
f_σ	8.547			6.336[d]
f_π	5.570			1.196[d]
$f_\sigma - f_\pi$	2.977	3.40 ± 1.0[e]	2.66 ± 0.76	5.140[d]
A_s	17.171	25 ± 1[e]		
$A_\sigma - A_\pi$	3.370	3 ± 1[e]		
NiF_6^{4-}				
f_s	0.083[f]	0.538[g]	0.847	0.46[h]
f_σ	15.177[f]			2.86,[h] 0.455[d]
f_π	8.614[f]			−0.003[d]
$f_\sigma - f_\pi$	6.563[f]	3.78[g]	5.954	2.86,[h] 0.458[d]
A_s	4.487[f]	33.9[g]		34.48[h]
$A_\sigma - A_\pi$	8.938[f]	8.8[g]		8.10[h]

[a] Corrected for spin interaction as discussed in part I. [b] L. Helmholz, A. V. Guzzo, and R. N. Sanders, *J. Chem. Phys.*, 35, 1349 (1961). [c] T. P. P. Hall, W. Hayes, R. W. H. Stevenson, and T. Wilkens, *ibid.*, 38, 1977 (1963). [d] See ref 11. [e] L. Helmoholz, *J. Chem. Phys.*, 31, 172 (1959). [f] See text regarding adjustments to these values. [g] K. Knox, R. G. Shulman, and S. Sugano, *Phys. Rev.*, 130, 512 (1963). [h] See ref 12.

Table VI. Comparative Calculations on FeF_6^{3-} [a]

	Method A	Method B	Method C	Method E
Total populations				
Fe(3d)	7.131	7.421	6.189	6.300
Fe(4s)	0.011	−0.306	0.055	0.102
Fe(4p)	0.043	−0.954	0.220	0.209
F(2s)	1.999	2.166	1.980	1.986
F(2p)	5.637	5.641	5.776	5.745
Charge on Fe	0.815+	1.838+	1.536+	1.388+
Charge on F	0.636−	0.806−	0.756−	0.731−
10*Dq*, kK	5.87	15.31	3.08	13.64
f_s, %	0.045	0.213	0.564	0.433
$f_\sigma - f_\pi$, %	2.83	3.79	0.558	2.977

[a] Methods: A, VOIE of H. Basch, A. Viste, and H. B. Gray, *Theor. Chim. Acta*, 3, 458 (1965); *J. Chem. Phys.*, 44, 10 (1966); B, Mulliken population analysis; C, no ligand field splittings; D, no external potential (no values are given for this method owing to nonconvergence of the calculations); E, complete method.

from the population analysis as derived part I.[1] Thus the observed values of f_s and $f_\sigma - f_\pi$ reported in the literature should be corrected for net effective spin as demonstrated by La Mar in a recent publication.[18]

Since the calculations of spin densities and hyperfine interaction constants provide a very sensitive test as to the accuracy of molecular wave functions, we have made such calculations using the present MO method. The results are summarized in Table V. The calculated values of f_s and $f_\sigma - f_\pi$ are found to be generally in excellent agreement with the "spin-corrected" experimental values. Similarly, the calculated values of A_s and $A_\sigma - A_\pi$ obtained from the f parameters, together with the net effective spins for each complex, are in equally good agreement with experiment. The only case for which there is any major discrepancy is in the values of f_s and A_s for NiF_6^{4-}. Structurally speaking, NiF_6^{4-} unlike the other MF_6^{n-} complexes considered here, does not exist as an isolated entity. Actually the $KNiF_3$ crystal does contain NiF_6^{4-} octahedral clusters, but these are linked through continuous -F-Ni-F-Ni-F- chains which give rise to an antiferromagnetic exchange interaction.[19] This interaction has been treated theoretically by Wachters,[12] whose results show that as a consequence of this exchange the coefficient of the fluorine 2s orbital in the $3e_g$ MO should be increased by a factor of 10, while that of the nickel 3d orbital remains essentially unchanged. Thus there must be a proportional decrease in the coefficient of the fluorine 2pσ orbital. The new values of these coefficients for the 2s and 2pσ orbitals in the $3e_g$ MO are 0.02480 and 0.43300, respectively. From these data the new calculated values of the superhyperfine parameters are $f_s = 0.83$, $f_\sigma - f_\pi = 5.82$, $A_s = 33.225$, and $A_\sigma - A_\pi = 8.602$, all of which are in nearly exact agreement with the experimental results.

Comparative Studies. As stated earlier, further calculations were made to determine the sensitivity of the method to the following: (a) choice of VOIE's, (b) effect of external lattice potential, (c) ligand field splitting terms, and (d) method of population analysis. Four separate calculations, each of which contained only one of these variations, were made of FeF_6^{3-}. The results presented in Table VI are compared on the basis of total orbital populations, atomic charges, 10*Dq*, and f_s and $f_\sigma - f_\pi$ parameters.

In method A, the only change in the calculation is that the VOIE's were obtained from the tables of Basch, *et al.*,[20] who assumed a regular quadratic dependence on charge. It is readily seen that the results are very poor in regard to atomic charges, 10*Dq*, and the f_s parameter. In method B, the only variation is that the population was carried out according to the commonly employed Mulliken method. The result is unreasonable negative populations in the Fe 4s and 4p orbitals, and a population that exceeds the limit of 2 in the F 2s orbital. Also, the atomic charges are too high, as are the values of 10*Dq* and $f_\sigma - f_\pi$. Ligand field splitting terms are ignored in method C, which leads to values of 10*Dq* and $f_\sigma - f_\pi$ that are too low. The variation made in method D was the elimination of the external potential, Q_{ex}. As expected, high orbital energies result and the calculation never showed any signs of converging to reasonable values of populations and charges even after 28 cycles of iteration. Finally, method E is the present procedure in its entirety. Obviously it is possible to attain consistently good results for all the calculated quantities considered here, only if all of the factors which are implicit features of the model are included *in totum.* Thus it appears that all of these factors are essential to attain an adequate molecular orbital representation of the bonding and to interpret the manner in which this is related phenomenologically to various experimental data.

Conclusion

The results of the present work on first-row transition metal-hexafluoro complexes are found to be at least as good as those of the best SCF calculations made thus far, including *ab initio.* Hence there is no reason to expect that the same method would not provide equally good results on other complexes and molecules not considered here.

It has been shown that every feature of the model is essential to its success, and in no instance does it appear that any

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one of these can be neglected without leading to drastic consequences. The implication is that the extent of success of other semiempirical methods, which rely on parameterization, depends on the effectiveness of the parameters to compensate for those quantities which are inherent in the bonding, *i.e.*, neighbor atom potentials, ligand field splittings, environmental charge effects, electron pairing, etc. Although the relative importance of any one, or all of these quantities, is very much a function of the particular environmental influences on the atoms forming the bonds, they must all be integrated to achieve a unified and physically reasonable molecular orbital representation. In methods that are totally computational, this is achieved through the mathematics of the model, but in semiempirical or empirical models these quantities must be explicitly included, which may or may not be possible through the use of arbitrary scaling parameters.

Finally, the success of the present method shows that it is indeed possible to achieve meaningful results through a simplified MO approach without having to resort to the very costly and limited applications of the *ab initio* method. Calculations utilizing the present method are now in progress on other types of systems to provide a further test and will be presented in forthcoming publications.

Registry No. TiF_6^{3-}, 19694-53-2; CrF_6^{3-}, 15276-04-7; FeF_6^{3-}, 17595-31-2; NiF_6^{4-}, 18918-81-5.

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Sharp-Line Luminescence and Absorption for the Hexabromoosmate(IV) Ion in Single Crystals of Cesium Hexabromozirconate(IV) at 20°K

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Strong sharp-line luminescence has been observed for the (5d^4) hexabromoosmate(IV) ion in single cubic crystals of the host lattice cesium hexabromozirconate(IV) at 20°K. In the visible and near-infrared regions luminescence is found within the t_{2g}^4 configuration between the $\Gamma_1({}^1A_{1g})$ excited state and the four spin-orbit components of the ${}^3T_{1g}$ ground state. Additional bands are observed in absorption. The major portion of the vibrational structure for each of the band systems is assigned to the ungerade modes of the $OsBr_6^{2-}$ complex in the lattice. The weak vibrational structure may be interpreted in terms of a magnetic dipole mechanism and Jahn–Teller coupling. Good agreement is obtained with available infrared results. The value of the magnetic susceptibility can be calculated from the optical data and is in good agreement with the available susceptibility data for Cs_2OsBr_6.

Introduction

A great amount of luminescence data is available for 3d and 4f transition metal substances. In contrast, little work has been reported in the literature on the luminescence spectra of 4d and 5d transition metal complexes with two exceptions. First, Reinberg and Parker[2,3] have reported the sharp-line luminescence of $ReCl_6^{2-}$ and $OsCl_6^{2-}$ doped in single crystals of Cs_2ZrCl_6 and Cs_2HfCl_6 at 4°K using phase-sensitive detection methods. Second, we have reported recently[4] the sharp-line luminescence and absorption spectra at 20°K for $ReBr_6^{2-}$ doped in Cs_2ZrBr_6. The luminescence reported for the $ReBr_6^{2-}$ ion is sufficiently intense that the absorption and the luminescence were recorded simultaneously on photographic plates without phase-sensitive instrumentation. In this paper we discuss the sharp-line luminescence and absorption spectra for the 5d^4 system of $OsBr_6^{2-}$ doped as an impurity in the Cs_2ZrBr_6 lattice at 20°K. This system is of interest because selection rules can be derived that describe the nature of vibrational–electronic coupling in d–d type transitions.

Dorain, Patterson, and Jordan[5] have reported the optical absorption spectra for $OsCl_6^{2-}$ doped into Cs_2ZrCl_6, Cs_2HfCl_6, and K_2PtCl_6 at 4°K. Transitions with energies greater than 20,000 cm^{-1} were assigned as of the type $t_{2g}^4 \rightarrow t_{2g}^3e_g$. Within the t_{2g}^4 configuration the $\Gamma_1({}^3T_{1g}) \rightarrow \Gamma_1({}^1A_{1g})$ transition was observed at 17,091 cm^{-1}, the $\Gamma_1({}^3T_{1g}) \rightarrow \Gamma_5({}^1T_{2g})$ transition at 10,733 cm^{-1}, and the $\Gamma_1({}^3T_{1g}) \rightarrow \Gamma_3({}^1E_g)$ transition at 11,083 cm^{-1}. Also, the energies of the low-lying states arising from the t_{2g}^4 configuration were calculated by means of an intermediate coupling crystal field model. Reinberg[3] has reported luminescence for $OsCl_6^{2-}$ in Cs_2ZrCl_6 at 4°K. Vibronic structure could only be assigned for the $\Gamma_1({}^1A_{1g}) \rightarrow \Gamma_1({}^3T_{1g})$ transition. Excellent agreement was obtained between the predicted energies of Dorain, Patterson, and Jordan and the Reinberg experimental results for the states arising out of the t_{2g}^4 configuration. Recently, Allen and coworkers[6] have discussed the electronic spectra of OsX_6^{2-} (X = F, Cl, Br, I).

Experimental Section

Cesium hexabromozirconate(IV) was prepared from zirconium tetrabromide (Alfa Inorganics) and cesium bromide (Alfa Inorganics). Stoichiometric amounts of zirconium tetrabromide and cesium bromide were placed in a 9-mm Vycor tube and dried *in vacuo* at 110° for 24 hr. The sealed evacuated Vycor tube was then lowered through a Bridgeman furnace preheated to 800°. The product was allowed to anneal at 500° for 12 hr before the furnace was turned off and the tube was cooled slowly to room temperature. The tube was opened in a drybox and any black impurities were removed with a razor blade. The clearest portions were collected in a new Vycor tube which, after being evacuated and sealed, was passed

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