tion of temperature is presented. From these data the values calculated are[7] $\Delta H^* = 6.662 \pm 0.077$ kcal/mol and $\Delta S^* = -16.22 \pm 0.27$ eu.

The variation of the rate parameter with change in ionic strength is presented in Table III.

If the assumption is made that reaction 1 proceeds *via* an outer-sphere path and that the thermodynamic driving force is not large enough to preclude an adiabatic process, it is feasible to use the Marcus cross relations[8] for this reaction. The result of such a calculation[9] $\Delta F^* = 11.0$ kcal/mol is in surprising agreement with the observed value $\Delta F^* = 11.5$ kcal/mol.

The electron-exchange reaction between Np(V) and Np(VI) involves ions of similar charge and structure as those considered in this investigation. A comparison of the dynamic parameters of these systems is of interest in view of the difference in $\Delta F^\circ$ for these reactions, *ca.* 0 compared to $-10.61$ kcal/mol. The relevant values for Am(VI) + Np(V) and Np(VI) + Np(V) are as follows: $k$ ($M^{-1}$ sec$^{-1}$) = $2.5 \times 10^4$, 96; $\Delta H^*$ (kcal/mol) = $6.66 \pm 0.08$, $7.6 \pm 0.4$; $\Delta S^*$ (eu) = $-16.2 \pm 0.3$, $-23.7 \pm 1.5$. It is apparent, although a rationale is not as obvious, that the difference in thermodynamic driving force is reflected in a lower value for the enthalpy of activation and a more positive value of the entropy of activation in the net reaction. This latter point is reflected in the values for $S^*$ (eu) of $-42.2$ and $-49.9$ for the respective $\mathrm{Am^{VI}}$–$\mathrm{Np^{V}}$ and $\mathrm{Np^{VI}}$–$\mathrm{Np^{V}}$ activated complexes. A qualitative explanation of this result is to postulate a different number of water molecules in the respective activated complexes.

**Registry No.** Am, 7440-35-9; Np, 7439-99-8.

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[7] There were 132 data points correlated by the functional form referenced in K. Reinschmidt, J. C. Sullivan, and M. Woods, *Inorg. Chem.*, 12, 1639 (1973).

[8] R. A. Marcus, *Annu. Rev. Phys. Chem.*, 15, 155 (1964).

[9] For Np(V)–Np(VI), $\Delta F^* = 14.85$ kcal/mol: D. Cohen, J. C. Sullivan, and J. C. Hindman, *J. Amer. Chem. Soc.*, 76, 352 (1954). For Am(V)–Am(VI), $\Delta F^* = 16.86$ kcal/mol, estimated from unpublished data from this laboratory.

# Correspondence

## Orbital Energies as Ligand Field Parameters in the Weak-Field Approximation. Application to the Paramagnetic Anisotropy of Bis(2,4-pentanedionato)bis(pyridine)cobalt(II)

AIC40222K

*Sir*:

In the strong-field approach to ligand field theory (LFT) it is a well-established procedure to treat the one-electron d-orbital energies or the energies of the "mainly d" MO's as parameters. In this approach the real d orbitals, $d^{\text{real}} = d_{z^2}$, $d_{yz}$, $d_{xz}$, $d_{xy}$, $d_{x^2-y^2}$, form the basis set and interelectronic interaction effects may be accounted for by computing matrix elements of the type $\langle \Phi | 1/r_{12} | \Phi' \rangle$ between Slater determinantal wave functions $\Phi$ based thereon. If it is desired to calculate magnetic properties, for example, $g$ values, the spin–orbit coupling interaction must be added, as can be done with some additional effort by calculating matrix elements of the type $\langle \Phi | \xi \hat{l}\cdot\hat{s} | \Phi' \rangle$, where $\xi$ is the spin–orbit coupling constant. Examples of procedures of this sort abound in the literature.[1]

On the other hand, orbital energies have not generally been employed as parameters in weak-field calculations. In the weak-field approach it is the free-ion term states, which themselves incorporate interelectronic interaction effects, upon which the ligand field perturbation is allowed to act. In this case the basis set involves the many-electron wave functions of the $|L,M_L,S,M_S\rangle$ type. The genesis of the parameters involved in a weak-field calculation most often is a point-charge or point-dipole model.[2] Since these electrostatic models have been shown to be fallacious,[3] these parameters are best viewed as physically meaningless phenomenological variables.

It is the purpose of this correspondence to propose an alternative LF parameterization scheme which involves physically meaningful parameters, namely, one-electron orbital energies. This scheme is applicable to many but not all point symmetries. Furthermore, I wish to outline a generally applicable, symmetry-independent procedure for calculating spectral and magnetic properties for complexes with $d^n$ configurations[4] using the weak-field formalism and including spin–oribit coupling.

**The Effective Perturbation Method and Orbital Energies.** I recently proposed[5] a new approach to ligand field calculations, which I called the effective perturbation method (EPM). The EPM represents a formal mathematical way of using the results of one-electron MO calculations on transition metal complexes to obtain LF parameters for use in weak-field calculations. Very briefly, the method proceeds as follows. The five eigenfunctions of the "mainly d" MO's are truncated to remove all but the metal 3d contributions. The resulting $5 \times 5$ nonorthonormal matrix of column eigenvector coefficients is then symmetrically orthonormalized *via* Lowdin's procedure[6] to yield a $5 \times 5$ matrix $\mathbf{C}$, the orthonormal matrix of column eigenvectors which most nearly resembles the original MO coefficient matrix in a least-squares sense.[7] If $\mathbf{E}$ is a $5 \times 5$ diagonal matrix whose elements consist of the MO energies, then the desired LF matrix elements $\langle d_i^{\text{real}} | \hat{V}_{\text{LF}} | d_j^{\text{real}} \rangle$ are those of the $5 \times 5$ matrix $\mathbf{V}_{\text{eff}}^{\text{real}}$ as defined by eq 1. It is clear that if the real d orbitals are eigen-

$$\mathbf{V}_{\text{eff}}^{\text{real}} = \mathbf{C}\mathbf{E}\tilde{\mathbf{C}} \qquad (1)$$

functions of the LF operator $\hat{V}_{\text{LF}}$, then the $\mathbf{C}$ matrix be-

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[1] See, for example: (a) A. H. Maki, N. Edelstein, A. Davison, and R. H. Holm, *J. Amer. Chem. Soc.*, 86, 4580 (1964); (b) W. DeW. Horrocks, Jr., G. R. Van Hecke, and D. DeW. Hall, *Inorg. Chem.*, 6, 694 (1967).

[2] For a recent thorough discussion of LF parameters of this sort see M. Gerloch and R. C. Slade, "Ligand-Field Parameters," Cambridge University Press, Cambridge, U. K., 1973.

[3] For a discussion of this point with regard to 3d electrons see D. S. McClure in "Phonons in Perfect Lattices and Lattices with Point Imperfections," R. W. H. Stevenson, Ed., Oliver and Boyd, Edinburgh, 1966, pp 314–376, and with regard to f electrons see D. J. Newman, *Advan. Phys.*, 20, 197 (1971).

[4] The methods outlined are applicable to $f^n$ configurations as well.

[5] W. DeW. Horrocks, Jr., *J. Amer. Chem. Soc.*, 94, 656 (1972).

[6] P. O. Lowdin, *J. Chem. Phys.*, 18, 365 (1950); *Advan. Phys.*, 5, 1 (1956).

[7] B. C. Carlson and J. M. Keller, *Phys. Rev.*, 105, 102 (1958).

comes the unit diagonal matrix 1 and the equality expressed by eq 2 follows. This identity will hold whenever each of

$$\mathbf{V}_{\mathrm{eff}}^{\mathrm{real}} = \mathbf{E} \qquad (2)$$

the five real d orbitals belongs to a *different* irreducible representation of the point group involved with the exception, of course, that two or three d orbitals may form the basis for a single multidimensional irreducible representation. Inspection of the point group character tables[8] reveals that the equality of eq 2 will hold for the following 26 point groups to which I refer as *group A*: $C_5, C_6, C_7, C_8, D_4, D_5, D_6, C_{4v}, C_{5v}, C_{6v}, C_{3h}, C_{5h}, C_{6h}, D_{3h}, D_{4h}, D_{5h}, D_{6h}, D_{2d}, D_{4d}, D_{5d}, D_{6d}, S_8, T_d, O_h, C_{\infty v}, D_{\infty h}$. Thus for complexes belonging to the above point groups the orbital energies themselves, along with a specification as to which real d orbital each corresponds, can serve as LF parameters. On the other hand, for the following 16 point groups, two or more d orbitals belong to the same irreducible representation and orbital energies by themselves are not sufficient to parameterize a LF calculation. These I call *group B*: $C_1, C_s, C_i, C_2, C_3, C_4, D_2, D_3, D_{3d}, C_{2v}, C_{3v}, C_{2h}, C_{4h}, D_{2h}, S_4, S_6$. For this latter set of point groups an additional parameter or parameters are necessary to specify the extent of symmetry-allowed mixing between d orbitals belonging to the same irreducible representation (*i.e.*, a specification of the nonzero, off-diagonal elements of matrix **C**). It is for molecules in these point groups that the EPM is particularly powerful since the results of an MO calculation can be used to specify both the orbital energies and the extent of symmetry-allowed orbital mixing.

**Many-Electron Weak-Field Calculations.** The many-electron basis functions $|L,M_{\mathrm{L}},S,M_{\mathrm{S}}\rangle$ are readily expressed as linear combinations with *real* coefficients of Slater determinantal functions composed of the one-electron *complex* d orbitals $|m_l\rangle$.[9] The necessary matrix-elements $\langle L,M_{\mathrm{L}}\cdot|V_{\mathrm{LF}}|L',M_{\mathrm{L}}'\rangle$ may be readily evaluated in terms of the $\langle m_l\cdot|V_{\mathrm{LF}}|m_l'\rangle$ matrix elements.[10] In order to apply the LF parameterization scheme described in the previous section it is merely necessary to transform from the real to the complex d orbital basis. $\mathbf{V}^{\mathrm{complex}}$, whose elements are the desired quantities $\langle m_l|\hat{V}_{\mathrm{LF}}|m_l'\rangle$, is readily calculated *via* the similarity transformation of eq 3, where **T** is the matrix which

$$\mathbf{V}^{\mathrm{complex}} = \mathbf{T}^{-1}\mathbf{V}^{\mathrm{real}}\mathbf{T} \qquad (3)$$

transforms the set of complex d orbitals into the $\mathrm{d}^{\mathrm{real}}$ set. It should be noted that the elements of $\mathbf{V}^{\mathrm{complex}}$ will all be real numbers for LF's of group A symmetry, but in general will be complex numbers for molecules belonging to point groups B.

Proceeding with the weak-field calculation, diagonalization of the $N \times N$ ligand field matrix between orbital states $|L,M_{\mathrm{L}}\rangle$ yields the $N$ orbital energies. In the weak-field formalism, matrix elements of the spin–orbit coupling perturbation $\lambda k\hat{L}\cdot\hat{S}$ ($\lambda$ is the many-electron spin–orbit coupling constant, $k$ is the orbital reduction factor) are easily evaluated between the $|L,M_{\mathrm{L}},S,M_{\mathrm{S}}\rangle$ basis functions. If magnetic properties are to be calculated the $N \times N$ matrix of LF elements is added appropriately to the $M \times M$ matrix of spin–orbit coupling (note that $\hat{V}_{\mathrm{LF}}$ connects only states of the same $S$ and $M_{\mathrm{S}}$) and the resulting $M \times M$ matrix is diagonalized yielding the final energies and eigenfunctions from which $g$ values and magnetic susceptibility tensor components may be evaluated *via* Van Vleck's equation as is described elsewhere.[11] The final section of this article describes an application of this procedure.

**Generality of the Methodology.** Before proceeding with an example illustrative of the use of orbital energies as LF parameters I wish to note two generalizations. First, the point group symmetry aspects of the use of orbital energies as LF parameters apply as well to strong and weak calculations. Thus, in strong-field calculations on molecules in class B symmetry groups it is improper, without supportive arguments or corroborative evidence, to *assume* that a particular energy level corresponds solely to a particular real d orbital. This aspect is discussed further in conjunction with the illustrative example in the final section of this article. Second, the simple, real to complex basis transformation procedure described above may be equally well applied to other ligand field models. For instance, a 5 × 5 $\mathbf{V}^{\mathrm{real}}$ matrix can be obtained using a generalized point-charge model in a real d orbital basis such as has been described by Companion and Komarynsky.[12] Likewise, the more realistic angular overlap model approach[13] will yield the elements of a matrix corresponding to $\mathbf{V}^{\mathrm{real}}$. No matter what one-electron model is chosen, be it an LCAO-MO calculation, a point-charge perturbation, or an angular overlap model, the results can be straightforwardly applied to many-electron problems by the procedure outlined above. Computer programs have been written in this laboratory[14] to implement such calculations of spectral and magnetic properties for the $\mathrm{d}^1$–$\mathrm{d}^4$ and $\mathrm{f}^1$–$\mathrm{f}^6$ electron and vacancy configurations. The calculations are independent of symmetry and are applicable to any molecule belonging to a class A point group. Programs applicable to class B molecules, which involve complex arithmetic, are currently being developed.[15]

**Caveat Concerning the Meaning of Orbital Energies.** If orbital energies are to be employed as LF parameters, a remark or two concerning their physical interpretation may be appropriate here. While most chemists have an intuitive understanding of the concept of orbital energies, there is some difficulty and ambiguity in placing them on a rigorous quantum mechanical basis and relating them to observable quantities. Demuynck, *et al.*,[16] have recently reported extensive *ab initio* calculations on $\mathrm{d}^9$ $\mathrm{CuCl_4}^{2-}$ species and have discussed some of the problems involved. For one thing, they found that the energy differences between the "mainly d" MO's obtained from their calculations on the ground-state complex were not the same as the excitation energies of the unpaired electron obtained from differences between separate calculations performed on the ground and various excited states. These discrepancies, which involve even a change in orbital order, can be ascribed principally to electron relaxation effects which occur upon excitation of the unpaired electron to the orbital in question. Differences between the coulomb and exchange interactions involving the unpaired electron and the closed-shell electrons between the ground and excited states may also be somewhat responsible. Weak-

(8) F. A. Cotton, "Chemical Applications of Group Theory," 2nd ed, Wiley-Interscience, New York, N. Y., 1971, Appendix III.

(9) See for instance W. DeW. Horrocks and D. DeW. Hall, *Coord. Chem. Rev.*, **6**, 147 (1971).

(10) See for instance M. Tinkham, "Group Theory and Quantum Mechanics," McGraw-Hill, New York, N. Y., 1964, p 162 ff.

(11) See ref 9, p 154 ff.

(12) A. L. Companion and M. A. Komarynsky, *J. Chem. Educ.*, **41**, 257 (1964).

(13) C. E. Schaffer, *Struct. Bonding (Berlin)*, **5**, 68 (1968), and references therein.

(14) $\mathrm{d}^n$ programs: E. S. Greenberg, Ph.D. Thesis, The Pennsylvania State University, 1973. $\mathrm{f}^n$ programs: D. R. Sudnick, M.S. Thesis, The Pennsylvania State University, 1973.

(15) D. Burlone, work in progress, this laboratory.

(16) J. Demuynck, A. Veillard, and V. Wahlgren, *J. Amer. Chem. Soc.*, **95**, 5563 (1973).

field LF calculations are, of course, designed to account for coulomb and exchange interactions between states of the *partially filled shell*, but electronic relaxation effects and differential interactions with closed-shell electrons upon excitation are not considered. Thus, from the LF point of view, it may be appropriate to think of orbital energies as *one-electron excitation energies*, which include the above-mentioned factors, rather than according to their more conventional specification. For systems with more than one unpaired electron a rigorous definition of such one-electron excitation energies may be difficult to achieve.

**Bis(2,4-pentanedionato)bis(pyridine)cobalt(II), Co(acac)$_2$(py)$_2$.** We recently reported[17] the measurement of the principal magnetic susceptibilities of this compound and the calculation of nuclear magnetic resonance dipolar shifts therefrom. No interpretation of the results in terms of the electronic structure of the complex was offered. The present section will illustrate the use of orbital energies as LF parameters in interpreting these results. In the solid state[18] Co(acac)$_2$(py)$_2$ consists of a planar Co(acac)$_2$ moiety with two axial py ligands, the planes of which are mutually perpendicular. The molecular symmetry is $C_{2v}$. In the nickel analog[19] the axial py ligands are coplanar and the molecular symmetry is $D_{2h}$, which is the effective point symmetry of the metal and the six ligand atoms in either complex. Both $C_{2v}$ and $D_{2h}$ are group B (*vide supra*) point groups and mixing of the $d_{z^2}$ and $d_{x^2-y^2}$ orbitals is allowed by symmetry. In the present case it is expected that this mixing will be negligible. This is because these orbitals are well separated in energy (~10,000 cm$^{-1}$) and the results show (*vide infra*) that deviations from idealized $D_{4h}$ symmetry, in which $d_{z^2}$ and $d_{x^2-y^2}$ belong to different irreducible representations, are small ($d_{xz}$ and $d_{yz}$, degenerate in $D_{4h}$, are split by only 165 cm$^{-1}$). These considerations justify the use of orbital energies as LF parameters in the present $C_{2v}$ case, although in many instances, *e.g.*, for pseudotetrahedral $C_{2v}$ complexes, this would not be so. For the present discussion the coordinate system of ref 17 will be adopted. The $z$ axis coincides with the N-Co-N bond axis and the $x$ axis bisects the two chelate rings.

The calculation involves the $^4$F and $^4$P term states of the d$^7$ (three-vacancy) configuration. As described in an earlier section the one-electron orbital energies serve to define the one-electron matrix elements of the type $\langle m_l | \hat{V}_{\mathrm{LF}} | m_l' \rangle$ between the complex d orbitals. From these quantities the 10 X 10 matrix of elements of the type $\langle L,M_L | \hat{V}_{\mathrm{LF}} | L',M_L' \rangle$ ($L$ = 1, 3) is readily computed. The quantity 15$B$, where $B$ is the Racah parameter, is added to the three diagonal elements which correspond to the excited $^4$P state ($L$ = 1). Diagonalization of this 10 X 10 matrix yields the energies of the many-electron orbital states. The elements of this 10 X 10 matrix are added appropriately to the elements of the 40 X 40 matrix of spin-orbit coupling whose elements are $\langle L,M_L,S,M_S | k\lambda\hat{L}\cdot\hat{S} | L,M_L',S,M_S' \rangle$. Diagonalization of the resulting 40 X 40 matrix yields the energies and eigenfunctions from which the magnetic properties are calculated using Van Vleck's equation.[11] Thus the parameters of the calculation are four orbital energies (the lowest may be arbitrarily set equal to zero), $B$, $k$, and $\lambda$. It is desired to fit both the magnetic data and the electronic absorption spectrum,[20] the chief features of the latter being a broad band centered about 10,100 cm$^{-1}$ (assigned to $^4T_1 \rightarrow {}^4T_2$(F) in $O_h$ symmetry) and almost continuous absorption above 20,000 cm$^{-1}$. The following parameters yield the fit to the principal magnetic susceptibilities and their temperature dependencies[21] shown in Figure 1: $d_{yz}$ 0 cm$^{-1}$, $d_{xz}$ 165 cm$^{-1}$, $d_{x^2-y^2}$ 360 cm$^{-1}$, $d_{z^2}$ 10,200 cm$^{-1}$, $d_{xy}$ 11,700 cm$^{-1}$, $B$ 750 cm$^{-1}$, $k\lambda$ 161 cm$^{-1}$, $k$ 0.73. The zeroth-order ground configuration is thus $(yz)^2(xz)^2(x^2-y^2)^1(z^2)^1(xy)^1$. The ground manifold consists of six Kramers doublets in the range 0-952 cm$^{-1}$ with significant thermal population at room temperature of the lowest three lying at 0, 262, and 387 cm$^{-1}$. A series of six Kramers doublets corresponding to the $^4T_2$(F) state in $O_h$ symmetry is calculated to lie in the 9600-10,600-cm$^{-1}$ range with the remaining eight levels lying between 19,600 and 21,300 cm$^{-1}$. These results are consistent with the observed electronic spectrum.[20] It should be noted that the magnetic properties are quite insensitive to the energies of the $d_{z^2}$ and $d_{xy}$ orbitals and to the value of $B$; hence these parameters have not been determined with any accuracy. The results serve to illustrate the subtlety of the magnetic anisotropy phenomenon in hexacoordinate cobalt(II) complexes. The observed anisotropy is due to a total splitting of the "t$_{2g}$" orbitals of only 360 cm$^{-1}$. The observed temperature dependencies of the principal susceptibilities could only be satisfactorily fit using a $k\lambda$ product corresponding to 90% of the free-ion value. While this appears to be high considering the value of $k$ (0.73) required to describe the

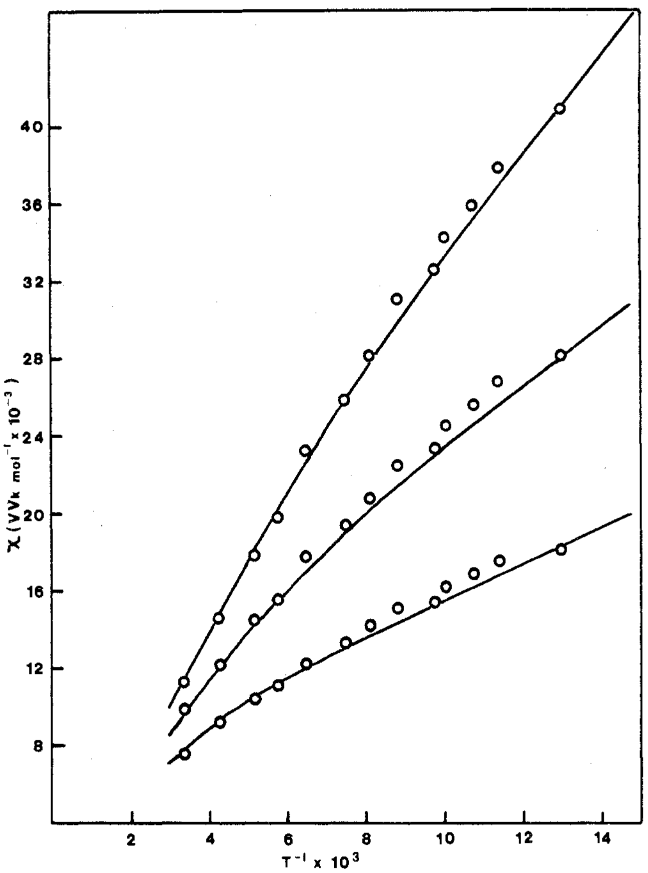

**Figure 1.** Plot of the principal magnetic susceptibilities (1 VVk ≡ 10$^{-6}$ cgsu; see ref 9) of Co(acac)$_2$(py)$_2$ *vs.* $T^{-1}$. The open circles are the data points taken from ref 21; the solid lines are the calculated values using the parameters stated in the text. Upper trace, $\chi_y$; middle trace, $\chi_x$; lower trace, $\chi_z$.

(17) W. DeW. Horrocks, Jr., and D. DeW. Hall, *Inorg. Chem.*, 10, 2368 (1971).

(18) R. C. Elder, *Inorg. Chem.*, 7, 1117 (1968).

(19) R. C. Elder, *Inorg. Chem.*, 7, 2316 (1968).

(20) J. T. Hashagen and J. P. Fackler, Jr., *J. Amer. Chem. Soc.*, 87, 2821 (1965).

(21) D. DeW. Hall, Ph.D. Thesis, Princeton University, 1971.

susceptibility tensor, it may be in part due to the necessarily static nature of the calculation. No explicit account is taken of molecular vibrations, their effects on the energy levels, and their fluctuation over a temperature range.

The zeroth-order electronic configuration derived here is consistent with the electron spin delocalization observed in nmr experiments on the $M(acac)_2(py)_2$ ($M = Co, Ni$) complexes. Thus for $M = Ni$ the unpaired electrons occupy the $d_{z^2}$ and $d_{xy}$ orbitals while for $M = Co$ they occupy the $d_{x^2-y^2}$, $d_{z^2}$, and $d_{xy}$ orbitals. None of these orbitals have $\pi$ symmetry with respect to the axial pyridine ligands, a result consistent with the observed $\sigma$-only spin delocalization pattern in this ligand for both the cobalt and nickel systems.[22,23] The results also suggest an explanation for the large observed difference in contact shift pattern[17] for the protons of the acac moiety between the cobalt and nickel systems. In the nickel case this delocalization would arise from an in-plane interaction with $d_{xy}$ while for cobalt both $d_{xy}$ and $d_{x^2-y^2}$ are available for interaction with acac orbitals of the appropriate symmetry. It should be kept firmly in mind that the actual ground electronic configuration contains significant admixtures of "excited-state configurations" and thermal population effects are also of importance.

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[22] W. DeW. Horrocks, Jr., and D. L. Johnston, *Inorg. Chem.*, 10, 1835 (1971).

[23] W. DeW. Horrocks, Jr., *Inorg. Chem.*, 12, 1211 (1973).