

## Molecular Orbital Theory for Octahedral and Tetrahedral Metal Complexes

HAROLD BASCH, ARLEN VISTE,\* AND HARRY B. GRAY

*The Department of Chemistry, Columbia University, New York, New York*

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Self-consistent charge and configuration (SCCC) molecular orbital calculations are reported for 32 selected octahedral and tetrahedral first-row transition-metal complexes containing halide and chalcogenide ligands. It is found that for the range of metal oxidation states II through IV,  $F_\sigma$ , chosen to fit the experimental  $\Delta$ , is a function of only the metal atomic number for constant  $F_\pi$ . In the range of formal metal oxidation numbers V through VII,  $F_\sigma$  is also a function of oxidation number.

Calculated and observed trends in covalency,  $\Delta$  values, and first L→M charge-transfer energies are compared. The conclusion is drawn that the molecular orbital method, in its present formulation, gives a reasonable account of the ground states and low excited states in simple metal complexes.

## INTRODUCTION

THE semiempirical molecular orbital theory in the Wolfsberg-Helmholz framework<sup>1</sup> has been revived in recent calculations on a wide variety of molecules.<sup>2-18</sup> Such diverse molecular properties as geometric configurations,<sup>4,5,9</sup> electric-dipole moments,<sup>10</sup> transition moments,<sup>1,3,11</sup> electronic spectra,<sup>1-3,10-13,15-18</sup> charge distributions, and ionization potentials have been calculated with varying degrees of success. In particular, this reasonably simple MO approach has been of great value in interpreting various electronic structural properties of transition-metal complexes. Although the initial results are encouraging, there have been too few

attempts at a critical evaluation of the method. A good start in evaluation of the generality of the simple MO method has been made by Cotton and Haas,<sup>13</sup> who studied the variation of the so-called  $F$  factor in exactly fitting the  $\Delta$  values in a series of octahedral ammine complexes. Also, Fenske and Sweeney<sup>11,12</sup> have studied  $\text{MnO}_4^-$  and  $\text{TiF}_6^{3-}$  in detail. Recently, Boer, Newton, and Lipscomb<sup>14</sup> have calculated theoretical  $F$  factors for the  $\text{B}_2$  and BH molecules.

It is clear that the steady development of a satisfactory MO theory for transition-metal complexes depends upon making detailed studies and improvements in the existing approximate schemes. In particular, there is the obvious need for a standard and consistent method of choosing the parameters of the calculation that can be transferred from one molecule to another. For this purpose we have chosen to calculate 32 octahedral and tetrahedral complexes containing first-row transition metals and one-atom ligands. The complexes were selected to explore the possibility that, using essentially the same set of initial assumptions, the variation of  $\Delta$  and ligand-to-metal (L→M) charge transfer with (1) geometry, (2) ligand, (3) metal oxidation number, and (4) metal atomic number could be made the function of a single parameter, the  $F$  factor.

## METHOD

The method as used in this investigation is similar to that applied in the calculation of  $\text{MnO}_4^-$ .<sup>7</sup> As usual, the secular equation to be dealt with is of the form,

$$|H_{ij} - G_{ij}E| = 0. \quad (1)$$

The matrix elements are between properly normalized (with ligand-ligand overlap) symmetry basis functions,  $\chi_i^{\mu\alpha}$ . The  $\chi_i^{\mu\alpha}$ 's include atomic orbitals of the metal and linear combinations of ligand atomic (or molecular) orbitals;  $G_{ij}$  is the group overlap matrix,

$$G_{ij} = (\chi_i^{\mu\alpha} | \chi_j^{\nu\beta}) = G_{ij}^{\mu\nu} \delta_{\alpha,\beta}. \quad (2)$$

\* Present address: Augustana College, Sioux Falls, South Dakota.

<sup>1</sup> M. Wolfsberg and L. Helmholz, *J. Chem. Phys.* **20**, 837 (1952).

<sup>2</sup> (a) R. Hoffman and W. N. Lipscomb, *J. Chem. Phys.* **36**, 2179, 3489; **37**, 520 (1962); (b) R. Hoffman, *ibid.* **39**, 1397 (1963); **41**, 2474, 2480, 2745 (1964).

<sup>3</sup> C. J. Ballhausen and H. B. Gray, *Inorg. Chem.* **1**, 111 (1962).

<sup>4</sup> L. L. Lohr, Jr., and W. N. Lipscomb, *J. Chem. Phys.* **38**, 1607 (1963); *J. Am. Chem. Soc.* **85**, 240 (1963); *Inorg. Chem.* **2**, 911 (1963); *ibid.* **3**, 22 (1964).

<sup>5</sup> T. Jordan, H. W. Smith, L. L. Lohr, Jr., and W. N. Lipscomb, *J. Am. Chem. Soc.* **85**, 846 (1963).

<sup>6</sup> H. Bedon, S. M. Horner, and S. Y. Tyree, Jr., *Inorg. Chem.* **3**, 647 (1964).

<sup>7</sup> A. Viste and H. B. Gray, *Inorg. Chem.* **3**, 1113 (1964).

<sup>8</sup> S. I. Shupack, E. Billig, R. J. H. Clark, R. Williams, and H. B. Gray, *J. Am. Chem. Soc.* **86**, 4594 (1964).

<sup>9</sup> E. A. Boudreaux, *Inorg. Chem.* **3**, 506 (1964); *J. Chem. Phys.* **40**, 246 (1964).

<sup>10</sup> H. A. Pohl, R. Rein, and K. Appel, *J. Chem. Phys.* **41**, 3385 (1964).

<sup>11</sup> R. F. Fenske and C. C. Sweeney, *Inorg. Chem.* **3**, 1105 (1964).

<sup>12</sup> R. F. Fenske, *Inorg. Chem.* **4**, 33 (1965).

<sup>13</sup> F. A. Cotton and T. E. Haas, *Inorg. Chem.* **3**, 1004 (1964).

<sup>14</sup> F. P. Boer, M. D. Newton, and W. N. Lipscomb, *Proc. Nat. Acad. Sci. (U.S.)* **52**, 889 (1964).

<sup>15</sup> A. Latham, V. C. Hascall, and H. B. Gray, *Inorg. Chem.* **4**, 788 (1965).

<sup>16</sup> P. T. Manoharan and H. B. Gray, *J. Am. Chem. Soc.* **87**, 3340 (1965).

<sup>17</sup> W. E. Hatfield, H. D. Bedon, and S. M. Horner, *Inorg. Chem.* **4**, 1181 (1965).

<sup>18</sup> J. Halper, W. D. Closson, and H. B. Gray, *Theoret. Chim. Acta* (to be published).

$H$  is the Hamiltonian matrix,

$$H_{ij} = (\chi_i^{\mu\alpha} | \mathcal{H} | \chi_j^{\nu\beta}) = H_{ij}^{\mu\nu} \delta_{\alpha,\beta}, \quad (3)$$

with  $\mathcal{H}$  as the one-electron Hamiltonian operator.<sup>19</sup> The superscripts  $\alpha$  and  $\mu$  label the row and irreducible representation, respectively, to which the  $\chi_i^{\mu\alpha}$ 's belong. The  $\delta$  function shows that there are no nonzero matrix elements between basis functions belonging to different representations, or different rows of the same representation.

(a)  $H_{ii}$ . The diagonal-Hamiltonian matrix elements  $H_{ii}$  are approximated as the negative values of valence orbital ionization potentials (VOIP's). The VOIP for the transition  $M_a^{q-1} \rightarrow M_b^{q+1}$ , corresponding to the ionization of an electron from configuration  $M_a$  to form configuration  $M_b$ , is computed from the formula,

$$\text{VOIP}(q) = I(q) + E(M_b) - E(M_a), \quad (4)$$

where  $q$  is the charge on the atom,  $I(q)$  is the ground-state ionization potential of  $M_a^{q-1}$  (not necessarily resulting in  $M_b^{q+1}$ );  $E(M_b)$  and  $E(M_a)$  are the  $E_{Av}$ 's of the two configurations,  $M_b$  and  $M_a$ , where a particular  $E_{Av}$  is the weighted mean of the energies of all the multiplet terms arising from a given configuration relative to the ground state of the atom or ion in question. The weighting factor is equal to the total degeneracy (spin  $\times$  orbital) of the term. After averaging over the  $J$  components, we have, for example,

$$E_{Av}(p^2) = \frac{1}{15} [9E(^3P) + 5E(^1D) + E(^1S)]. \quad (5)$$

The evaluation of  $E_{Av}$ 's for the pertinent configurations, where missing terms prevent a direct averaging can be done straightforwardly by using the equations of Slater<sup>20</sup> relating the energies of the individual multiplets to  $E_{Av}$  in terms of the Slater-Condon parameters. For example,

$$E_{Av}(p^2) = \begin{cases} E(^3P) + 3F_2(p\bar{p}) \\ E(^1D) - 3F_2(p\bar{p}) \\ E(^1S) - 12F_2(p\bar{p}) \end{cases}. \quad (6)$$

In these cases one can derive an  $E_{Av}$  for each Russell-Saunders term which theoretically should be identical for all the terms within one given configuration. However, the  $E_{Av}$ 's actually differ in some configurations by a few thousand  $\text{cm}^{-1}$ . In all such instances the  $E_{Av}$ 's derived from the different terms were averaged. Term energies and ionization potentials were taken from

<sup>19</sup> C. C. J. Roothaan, *Rev. Mod. Phys.* **23**, 69 (1951).

<sup>20</sup> J. C. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill Book Company, Inc., New York, 1960), Vol. 1, Chap. 14 and Appendix 12a; Vol. 2, Appendix 22.

Moore.<sup>21</sup> Slater-Condon parameters were taken from the literature<sup>22,23</sup> or obtained by a least-squares fit of the relevant spectral data.

For the metal, three different orbital  $H_{ii}$ 's are required:  $3d$ ,  $4s$ , and  $4p$ . The VOIP for a given metal orbital is considered as a linear combination of three different configurations in order to adequately represent fractional populations. For instance, for  $4s$  the three configurations are taken to be  $d^{n-1}s$ ,  $d^{n-2}s^2$ , and  $d^{n-2}s\bar{p}$ . All the configurations are calculated as functions of charge and from the resulting nine VOIP curves, the metal  $3d$ ,  $4s$ , and  $4p$   $H_{ii}$ 's can easily be evaluated.<sup>7</sup>

For the ligands, with valence orbitals  $s$  and  $\bar{p}$ , the same procedure can be followed, requiring four VOIP curves. However, we have considered only the configuration  $s^2\bar{p}^n$ ; i.e., fractional population was considered only in the  $\bar{p}$  level. The additional constraint was imposed that  $n$  be equal to the occupancy of the  $\bar{p}$  level in the ground-state configuration of the neutral ligand, as in one calculation of  $\text{MnO}_4^-$ .<sup>7</sup> Richardson and Rundle<sup>24</sup> also found that the ligand  $H_{ii}$ 's were relatively insensitive functions of charge.

Valence state ionization energies of potentials (VSIE's or VSIP's) have been computed by Skinner, Pritchard, and Pilcher,<sup>25-27</sup> and Hinze and Jaffé.<sup>28</sup> These methods assume a hybridized state of the atom, implying a particular spatial orientation of the orbital favorable for bond formation. Such a concept is not necessary in MO theory. It is for this reason that we suggest the name valence-orbital ionization potentials for the energies calculated from  $E_{Av}$  values.<sup>29</sup> In addition, the VOIP's can be derived as naturally continuous functions of charge on the atom and, using Mulliken's prescription for summing populations,<sup>30</sup> the  $H_{ii}$ 's can be adjusted for variations of charge on the metal atom. Thus, the major advantage of the VOIP's is perhaps their simplicity. Finally, a clear relationship between  $H_{ii}$ 's, VOIP's, and the concept of electronegativity has recently been established.<sup>31,32</sup>

<sup>21</sup> C. E. Moore, "Atomic Energy Levels," Natl. Bur. Std. Circ. No. 467 (1958), Vols. 1, 2, and 3.

<sup>22</sup> J. Hinze and H. H. Jaffé, *J. Chem. Phys.* **38**, 1834 (1963). The  $F_k$  and  $G_k$  taken from Hinze and Jaffé differ by a multiplicative constant from the  $F^k$  and  $G^k$  used by Slater (Ref. 20).

<sup>23</sup> J. S. Griffith, *The Theory of Transition Metal Ions* (Cambridge University Press, Cambridge, 1961).

<sup>24</sup> J. W. Richardson and R. E. Rundle, U.S. Atomic Energy Commission, ISC-830, 1956.

<sup>25</sup> H. A. Skinner and H. O. Pritchard, *Trans. Faraday Soc.* **49**, 1254 (1953).

<sup>26</sup> H. O. Pritchard and H. A. Skinner, *Chem. Rev.* **55**, 745 (1955).

<sup>27</sup> G. Pilcher and H. A. Skinner, *J. Inorg. Nucl. Chem.* **24**, 937 (1962).

<sup>28</sup> J. Hinze and H. H. Jaffé, *J. Am. Chem. Soc.* **84**, 540 (1962); *Can. J. Chem.* **41**, 1315 (1963); *J. Phys. Chem.* **67**, 1501 (1963).

<sup>29</sup> H. Basch, A. Viste and H. B. Gray, *Theoret. Chim. Acta* (to be published).

<sup>30</sup> R. S. Mulliken, *J. Chem. Phys.* **23**, 1833 (1955).

<sup>31</sup> C. K. Jørgensen, *Orbital in Atoms and Molecules* (Academic Press Ltd., London, 1962), Chap. 7.

<sup>32</sup> G. Klopman, *J. Am. Chem. Soc.* **86**, 1463, 4550 (1964).

TABLE I. Average energies of configurations<sup>a,b</sup> (in 1000 cm<sup>-1</sup>).

Metal	<i>n</i>	<i>d<sup>n</sup></i>	<i>d<sup>n-1</sup>s</i>	<i>d<sup>n-1</sup>p</i>	<i>d<sup>n-2</sup>s<sup>2</sup></i>	<i>d<sup>n-2</sup>sp</i>	<i>d<sup>n-2</sup>p<sup>2</sup></i>
Sc	3	38.3	16.3	36.1	0.0	20.2	46.1
Ti	4	40.7	18.1	39.4	5.8	27.4	55.3
V	5	40.3	20.9	46.0	12.2	40.5	76.4
Cr	6	55.3	36.5	59.2	30.8	56.1	
Mn	7	58.2	42.9	71.3	39.3	69.3	104.3
Fe	8	40.4	25.1	50.8	27.1	50.8	
Co	9	27.9	13.1	42.2	19.3	46.8	
Ni	10	14.7	1.4	30.2	10.4	41.5	
Cu	11	...	0.0	30.7	12.0	46.5	
Zn	12	...	...	...	0.0	36.1	80.6

<sup>a</sup> Relative to ground-state multiplet.<sup>b</sup> For neutral atom first-row transition metals.

(b)  $H_{ij}$ . The off-diagonal Hamiltonian matrix elements are approximated using Eq. (7),

$$H_{ij} = -\frac{1}{2}F_m G_{ij}[\text{VOIP}_i + \text{VOIP}_j], \quad (7)$$

which contains an adjustable parameter  $F_m$ , called the  $F$  factor. The subscript  $m$  is used to differentiate among  $\sigma$ ,  $\pi$ ,  $\dots$ , etc.  $-$  type interactions. In most applications of the method to date, it has been necessary to use  $F_m$  greater than one and also to use separate values for  $F_\sigma$  and  $F_\pi$  in order to achieve reasonable results.

(c) Implicit in the previous discussion is the neglect of all nonvalence atomic orbitals. The designation, "valence" in this context is necessarily arbitrary. For example, the metal  $3p$  orbital has a finite, albeit small, overlap with the ligand functions and, if included in the calculation, would probably have some effect, particularly on the antibonding MO levels. Omitting the nonvalence atomic orbitals may be unduly optimistic,<sup>14</sup> but nevertheless seems necessary if simplicity is to be preserved. The valence orbitals used in these calculations are, therefore,  $3d$ ,  $4s$ , and  $4p$  for the metal, and  $ns$  and  $np$  on the ligand.

(d) The treatment of group overlap integrals, normalizations, and correction factors relating the  $H_{ii}$ 's to the  $H'_{ii}$ 's has been given in detail in a previous paper.<sup>7</sup>

## RESULTS

VOIP's for the  $3d$ ,  $4s$ , and  $4p$  valence orbitals of the metals Sc through Zn have been determined from the average energies of the pertinent configurations.<sup>29</sup> The data have been smoothed by a least-squares quadratic fit across the transition series. For more efficient computer programming the resulting VOIP's are represented quadratically,

$$\text{VOIP}(q) = Aq^2 + Bq + C, \quad (8)$$

where  $q$  is the charge. The  $A$ ,  $B$ , and  $C$  parameters,

together with some neutral atom  $E_w$ 's, are presented in Tables I and II. For the ligands, only the configuration  $s^2p^n$  of the neutral atom was used and these VOIP's are listed in Table III. In all calculations the ligand  $p_\sigma$  was assumed more stable (by 10 000 cm<sup>-1</sup>) than  $p_\pi$ , and the latter was set equal to the value found in Table III. This adjustment is derived from inspection of theoretically calculated  $H'_{ii}$ ,<sup>14,38,34-36</sup> and from charge-transfer spectra.<sup>37,38</sup>

The ligands investigated were F, Cl, Br, S, and O. Interatomic bond distances were either taken from the

TABLE II. VOIP curves for first-row transition metals<sup>a</sup> (in 1000 cm<sup>-1</sup>).

VOIP curve <sup>b</sup>	Ti	V	Cr	Mn	Fe	Co	Ni
A 1	17.15	15.8	14.75	14.1	13.8	13.85	14.2
2	18.45	14.0	9.75	5.5	13.8	13.85	14.2
3	18.45	14.0	9.75	5.5	13.8	13.85	14.2
4	9.3	8.55	8.05	7.6	7.35	7.25	7.35
5	9.3	8.55	8.05	7.6	7.35	7.25	7.35
6	9.3	8.55	8.05	7.6	7.35	7.25	7.35
7	7.8	7.45	7.25	7.2	7.3	7.55	7.95
8	7.8	7.45	7.25	7.2	7.3	7.55	7.95
9	7.8	7.45	7.25	7.2	7.3	7.55	7.95
B 1	60.85	68.0	74.75	80.8	86.2	91.15	95.5
2	77.85	87.0	95.95	105.0	101.5	106.25	110.7
3	76.75	87.3	96.95	106.0	101.9	105.55	108.2
4	50.4	54.15	57.55	60.9	63.85	66.65	69.05
5	58.5	62.95	66.85	70.3	73.05	75.25	77.05
6	55.0	57.55	60.45	63.8	67.35	71.35	75.65
7	35.6	45.45	47.55	49.3	50.8	51.95	52.85
8	48.9	50.85	52.85	55.2	57.8	60.65	63.75
9	48.9	50.85	52.85	55.2	57.8	60.65	63.75
C 1	27.4	31.4	35.1	38.6	41.9	44.8	47.6
2	44.6	51.4	57.9	64.1	70.0	75.6	80.9
3	55.4	61.4	67.7	74.3	81.2	88.4	95.9
4	48.6	51.0	53.2	55.3	57.3	59.1	60.8
5	57.2	60.4	63.3	65.9	68.3	70.5	72.3
6	66.0	70.6	74.7	78.3	81.4	84.0	86.0
7	26.9	27.7	28.4	29.2	29.9	30.7	31.4
8	35.9	36.8	37.8	38.8	39.7	40.7	41.6
9	34.4	36.4	38.1	39.4	40.3	40.8	40.9

<sup>a</sup> From Ref. 29.<sup>b</sup> The type of electron being ionized, and the configurations, are as follows for the nine VOIP curves: 1:  $d$ ,  $d^n$ ; 2:  $d$ ,  $d^{n-1}s$ ; 3:  $d$ ,  $d^{n-1}p$ ; 4:  $s$ ,  $d^{n-1}s$ ; 5:  $s$ ,  $d^{n-2}s$ ; 6:  $s$ ,  $d^{n-2}sp$ ; 7:  $p$ ,  $d^{n-1}p$ ; 8:  $p$ ,  $d^{n-2}p^2$ ; 9:  $p$ ,  $d^{n-2}sp$ . Successive points on a curve differ only in the number of  $d$  electrons.<sup>29</sup> S. Sugano and R. G. Shulman, Phys. Rev. **130**, 506, 512, 517 (1963).<sup>34</sup> R. E. Watson and A. J. Freeman, Phys. Rev. **134**, A1526 (1964).<sup>35</sup> H. Basch and H. B. Gray, unpublished calculations on  $\text{MnO}_4^-$ .<sup>36</sup> K. D. Carlson and R. K. Nesbet, J. Chem. Phys. **41**, 1051 (1964).<sup>37</sup> C. K. Jørgensen, *Absorption Spectra and Chemical Bonding in Complexes* (Addison-Wesley Publishing Company, Inc., Reading, Massachusetts, 1962).<sup>38</sup> C. J. Ballhausen and H. B. Gray, *Molecular Orbital Theory* (W. A. Benjamin, Inc., New York, 1964) Appendix 8.

literature<sup>39-49</sup> or estimated.<sup>50,51</sup> Day and Jørgensen<sup>52</sup> independently estimated the bond distances in  $\text{CoBr}_4^{2-}$  (2.43 Å),  $\text{MnCl}_4^{2-}$  (2.40 Å), and  $\text{FeCl}_4^{2-}$  (2.30 Å) which differ from ours (Tables IV and V) by +0.05, +0.07, and +0.03 Å, respectively. This gives a good indication of the accuracy of estimated bond distances. The parameter  $F_\pi$  was consistently taken to be 2.10 for all  $H_{ij}$  and  $F_\sigma$  was varied in order to fit the observed<sup>53-68</sup>  $\Delta$  exactly. All ligand-ligand correction factors<sup>68</sup> were calculated using  $F_m = 2.00$  for both  $\sigma$ - and  $\pi$ -type interactions. Wavefunctions for the ligands (neutral atom) were taken from Clementi<sup>69</sup> or (for Br) Watson *et al.*,<sup>70</sup> and for the metals from Richardson *et al.*<sup>71,72</sup> Neutral-atom functions were chosen for  $4s$  and  $4p$ , while the  $3d$  function was taken from the  $d^n$  configuration for  $M^+$ . The effect of choice of wave-

TABLE III. Ligand VOIPs<sup>a,b</sup> (in 1000  $\text{cm}^{-1}$ ).

Ligand	$s$	$p$
O	260.8	127.4
F	323.6	150.4
Cl	203.8	110.4
Br	193.8	99.6
S	166.7	93.4

<sup>a</sup> From Ref. 29.

<sup>b</sup> For configuration  $s^2p^n$ .

functions on the calculation was not investigated, but it is expected that the *trends* under consideration here are not altered for any consistent choice. Also, it has recently been claimed that the one-electron LCAO-MO model is relatively insensitive to such changes.<sup>73</sup>

Once the elements of the secular equations had been calculated as input, the secular equations were solved for eigenvalues and eigenvectors, and a Mulliken population analysis<sup>81</sup> was carried out. The output metal charge ( $q$ ),  $s$ , and  $p$  character were compared with the input  $q$ ,  $s$ , and  $p$  (the latter may be regarded as the independent variables of charge and configuration in the input). The input  $q$ ,  $s$ , and  $p$  populations were then adjusted by an iterative procedure until input and output  $q$ ,  $s$ , and  $p$  agreed to 0.005 at which point the calculation was considered self-consistent. The whole process was programmed in FORTRAN to iterate automatically, and run on an IBM 7094 computer. Input consists essentially of the total number of electrons, metal oxidation state, metal and ligand VOIP's, group overlap matrix,  $F$ -factor matrix, and initial guess values for  $q$ ,  $s$ , and  $p$ ; the program then iterates to a self-consistent charge and configuration (SCCC). Overlap integrals are evaluated by a separate machine program.

The results of the calculations on 16 octahedral and 16 tetrahedral one-atom-ligand transition-metal complexes are presented in Tables IV and V. Table VI summarizes the composition of the relevant secular determinants for both octahedral and tetrahedral geometries.

## DISCUSSION

The molecular orbital energy-level diagrams which represent these calculations of tetrahedral and octahedral complexes are shown schematically in Figs. 1 and 2. The MO's are connected to the atomic orbitals from which they are mainly derived and the MO schemes are most easily understood in terms of the ordering of the atomic energy levels. The brackets enclose levels of comparable energies derived from essentially the same atomic orbitals; in some cases there is a consistent ordering within a bracketed set (shown explicitly in the figures), in others not.

<sup>73</sup> R. G. Shulman, Bell Telephone Laboratories, Memorandum for File, Case 38140-13.

<sup>39</sup> A. F. Wells, *Structural Inorganic Chemistry* (Oxford University Press, London, 1962), Chap. 8.

<sup>40</sup> V. W. H. Baur, *Acta Cryst.* **11**, 488 (1958).

<sup>41</sup> C. K. Jørgensen, *Acta Chem. Scand.* **12**, 1539 (1958).

<sup>42</sup> H. W. Smith and M. Y. Colby, *Z. Krist.* **103**, 90 (1940).

<sup>43</sup> B. N. Figgis, M. Gerlock, and R. Mason, *Acta Cryst.* **17**, 506 (1964).

<sup>44</sup> M. Lister and L. E. Sutton, *Trans. Faraday Soc.* **37**, 393 (1941).

<sup>45</sup> W. N. Lipscomb and A. G. Whittaker, *J. Am. Chem. Soc.* **67**, 2019 (1945).

<sup>46</sup> B. Zaslav and R. E. Rundle, *J. Phys. Chem.* **61**, 490 (1957).

<sup>47</sup> P. Pauling, Ph.D. thesis, University College, London, 1960; quoted by A. B. Blake and F. A. Cotton, *Inorg. Chem.* **3**, 5 (1964).

<sup>48</sup> *Tables of Interatomic Distances and Configurations in Molecules and Ions*, Special Publication No. 11 (Chemical Society, London, 1958).

<sup>49</sup> R. W. G. Wyckoff, *Crystal Structures*, Interscience Publishers, Inc., New York, 1951, Vol. 1.

<sup>50</sup> M. J. Sienko and R. A. Plane, *Physical Inorganic Chemistry* (W. A. Benjamin, Inc., New York, 1963), p. 68.

<sup>51</sup> N. S. Hush and M. H. L. Pryce, *J. Chem. Phys.* **26**, 143 (1957).

<sup>52</sup> P. Day and C. K. Jørgensen, *J. Chem. Soc. Suppl.* **2**, 1964, 6226.

<sup>53</sup> C. J. Ballhausen and F. Winther, *Acta Chem. Scand.* **13**, 1729 (1959).

<sup>54</sup> V. O. Schmitz-DuMont, H. Brokopf, and K. Burkhardt, *Z. Anorg. Chem.* **295**, 7 (1958).

<sup>55</sup> C. K. Jørgensen, *Advan. Chem. Phys.* **5**, 62, 85 (1962).

<sup>56</sup> Reference 37, pp. 110-111 and pp. 284-289.

<sup>57</sup> Reference 37, p. 113.

<sup>58</sup> R. Englman, *Mol. Phys.* **3**, 48 (1960).

<sup>59</sup> W. Low, *Phys. Rev.* **109**, 247, 256 (1959).

<sup>60</sup> S. Siegel, *Acta Cryst.* **9**, 684 (1956).

<sup>61</sup> R. J. H. Clark, *J. Chem. Soc.* **1964**, 417.

<sup>62</sup> N. S. Gill and R. S. Nyholm, *J. Chem. Soc.* **1959**, 3997.

<sup>63</sup> C. J. Ballhausen, *Introduction to Ligand Field Theory* (McGraw-Hill Book Company, Inc., New York, 1962), Chaps. 4, 5, and 7.

<sup>64</sup> Reference 63, p. 228.

<sup>65</sup> F. A. Cotton, D. M. L. Goodgame, and M. Goodgame, *J. Am. Chem. Soc.* **84**, 167 (1962).

<sup>66</sup> C. Furlani, E. Cervone, and V. Valenti, *J. Inorg. Nucl. Chem.* **25**, 159 (1963).

<sup>67</sup> G. P. Smith, C. H. Liu, and T. R. Griffiths, *J. Am. Chem. Soc.* **86**, 4796 (1964).

<sup>68</sup> N. K. Hamer, *Mol. Phys.* **6**, 257 (1963).

<sup>69</sup> E. Clementi, *J. Chem. Phys.* **40**, 1944 (1964); IBM Research Paper RJ-256.

<sup>70</sup> R. E. Watson and A. J. Freeman, *Phys. Rev.* **124**, 1117 (1961).

<sup>71</sup> J. W. Richardson, W. C. Nieupoort, R. R. Powell, and W. F. Edgell, *J. Chem. Phys.* **36**, 1057 (1962).

<sup>72</sup> J. W. Richardson, R. R. Powell, and W. C. Nieupoort, *J. Chem. Phys.* **38**, 796 (1963).

TABLE IV. Results of SCC calculations of various octahedral complexes (all energies in 1000 cm<sup>-1</sup>).

	Complexes							
	TiF <sub>6</sub> <sup>3-</sup>	TiCl <sub>6</sub> <sup>3-</sup>	TiBr <sub>6</sub> <sup>3-</sup>	VF <sub>6</sub> <sup>3-</sup>	VCl <sub>6</sub> <sup>3-</sup>	VF <sub>6</sub> <sup>4-</sup>	CrF <sub>6</sub> <sup>3-</sup>	CrCl <sub>6</sub> <sup>3-</sup>
Bond distances, Å	1.97 <sup>a</sup>	2.45 <sup>b</sup>	2.56 <sup>c</sup>	1.94 <sup>d</sup>	2.39 <sup>e</sup>	2.15 <sup>e</sup>	1.93 <sup>e</sup>	2.38 <sup>e</sup>
3d VOIP	-120.3	-88.6	-84.0	-127.3	-94.5	-116.7	-134.1	-99.2
4s VOIP	-100.6	-78.9	-76.9	-101.6	-80.4	-95.3	-103.7	-81.4
4p VOIP	-55.7	-44.0	-41.2	-70.7	-50.6	-65.3	-70.4	-49.4
Metal charge	+1.12	+0.66	+0.68	+1.02	+0.59	+0.93	+0.97	+0.53
3d population	2.81	2.95	3.14	3.77	3.95	3.88	4.76	4.95
4s population	0.00	0.15	0.00	0.01	0.10	0.05	0.06	0.16
4p population	0.07	0.24	0.18	0.20	0.36	0.14	0.21	0.36
t <sub>2g</sub> eigenvalue	-149.4	-108.4	-96.0	-149.2	-107.9	-149.8	-149.2	-108.9
2t <sub>2g</sub> eigenvalue	-90.4	-71.4	-70.2	-100.8	-80.2	-104.8	-110.3	-87.1
3e <sub>g</sub> eigenvalue	-73.1	-58.0	-57.1	-84.8	-66.5	-92.7	-94.7	-73.5
2t <sub>2g</sub> occupation	1	1	1	2	2	3	3	3
3e <sub>g</sub> occupation	0	0	0	0	0	0	0	0
Δ	17.5 <sup>e</sup>	13.8 <sup>b</sup>	13.0 <sup>e,a</sup>	15.9 <sup>f</sup>	13.9 <sup>b</sup>	12.0 <sup>e,g</sup>	15.2 <sup>h</sup>	13.8 <sup>h</sup>
First allowed L→M charge transfer: calculated orbital energy <sup>i</sup>	59.0	37.0	25.8	48.4	27.7	45.0	38.9	21.8
Observed band	>50 <sup>e</sup>	≥38 <sup>e,i</sup>	<38 <sup>e,i</sup>	>40 <sup>e,i</sup>	≥40 <sup>e,i</sup>	≫40 <sup>e,i</sup>	>37 <sup>e,i</sup>	>37 <sup>e,i</sup>
F <sub>σ</sub> (±0.005)	1.53	1.60	1.51	1.55	1.57	1.59	1.60	1.61
	CrBr <sub>6</sub> <sup>3-</sup>	CrO <sub>6</sub> <sup>3-</sup>	MnF <sub>6</sub> <sup>3-</sup>	MnF <sub>6</sub> <sup>4-</sup>	FeF <sub>6</sub> <sup>3-</sup>	CoF <sub>6</sub> <sup>3-</sup>	CoO <sub>6</sub> <sup>4-</sup>	NiF <sub>6</sub> <sup>4-</sup>
Bond distances, Å	2.53 <sup>e</sup>	2.00 <sup>e</sup>	1.74 <sup>k</sup>	2.12 <sup>d</sup>	1.92 <sup>d</sup>	1.89 <sup>d</sup>	2.10 <sup>l</sup>	2.00 <sup>m</sup>
3d VOIP	-92.6	-114.7	-150.9	-129.6	-145.2	-153.4	-122.8	-153.4
4s VOIP	-79.0	-91.6	-112.4	-99.9	-108.2	-112.3	-93.5	-112.1
4p VOIP	-50.1	-59.3	-75.1	-65.0	-69.0	-69.7	-54.6	-67.4
Metal charge	+0.64	+0.75	+1.00	+0.85	+0.87	+0.84	+0.56	+0.78
3d population	5.26	4.91	5.65	5.89	6.76	7.72	7.96	8.79
4s population	0.10	0.08	0.06	0.10	0.14	0.17	0.22	0.20
4p population	0 <sup>n</sup>	0.26	0.29	0.16	0.24	0.26	0.26	0.23
t <sub>2g</sub> eigenvalue	-95.8	-125.5	-147.9	-149.7	-149.1	-148.9	-126.1	-149.4
2t <sub>2g</sub> eigenvalue	-83.0	-93.6	-111.0	-120.1	-125.6	-132.0	-112.5	-139.1
3e <sub>g</sub> eigenvalue	-69.7	-77.5	-89.1	-111.7	-111.9	-118.9	-103.0	-131.8
2t <sub>2g</sub> occupation	3	3	3	3	3	4	5	6
3e <sub>g</sub> occupation	0	0	0	2	2	2	2	2
Δ	13.2 <sup>e</sup>	16.2 <sup>e,p</sup>	21.8 <sup>q</sup>	8.4 <sup>r</sup>	14.0 <sup>r</sup>	13.1 <sup>e,r</sup>	9.6 <sup>p,h</sup>	7.3 <sup>s</sup>
First allowed L→M charge transfer: calculated orbital energy <sup>i</sup>	12.8	31.9	36.9	29.6	23.5	16.9	13.6	17.6
Observed energy	<37 <sup>e,i</sup>	≥37 <sup>e,i</sup>	>28 <sup>r</sup>	>43 <sup>e,i</sup>	>30 <sup>r</sup>		~60 <sup>e,i</sup>	>60 <sup>e,i</sup>
F <sub>σ</sub> (±0.005)	1.58	1.61	1.61	1.62	1.67	1.69	1.71	1.68

<sup>a</sup> From Ref. 60.<sup>b</sup> From Ref. 61.<sup>c</sup> Estimated value.<sup>d</sup> From Ref. 39.<sup>e</sup> From Ref. 6.<sup>f</sup> From Ref. 53.<sup>g</sup> From Ref. 56.<sup>h</sup> From Ref. 59.<sup>i</sup> Uncorrected for electronic repulsions.<sup>j</sup> The values quoted are for hydrated salts from Ref. 58.<sup>k</sup> From Ref. 48.<sup>l</sup> From Ref. 62.<sup>m</sup> From Ref. 40.<sup>n</sup> CrBr<sub>6</sub><sup>3-</sup> was calculated without the metal 4p since it was found that a t<sub>1u</sub> level interceded between the 2t<sub>2g</sub> and 3e<sub>g</sub> levels.<sup>o</sup> From Ref. 57.<sup>p</sup> In MgO.<sup>q</sup> From Ref. 41.<sup>r</sup> From Ref. 55.

Only a few of the levels appear to be important in discussing electronic transitions. For tetrahedral complexes of one-atom ligands, the most important levels are 3t<sub>2</sub>, t<sub>1</sub>, 2e, and 4t<sub>2</sub>. For these four levels, the schematic energy level diagram of Fig. 1 agrees with the conventional Ballhausen-Liehr ordering.<sup>74</sup> The 2e and 4t<sub>2</sub> levels

<sup>74</sup> C. J. Ballhausen and A. D. Liehr, J. Mol. Spectry, 2, 342 (1958).

roughly correspond to the d orbitals of crystal-field theory, though with an admixture of ligand orbitals. The t<sub>1</sub> is a strictly ligand π level while 3t<sub>2</sub> tends to be predominantly composed of ligand π functions.

For octahedral complexes, the most important levels are 3e<sub>g</sub> and 2t<sub>2g</sub> for the d-d spectra, and, in addition, the two highest levels of odd parity, the 3t<sub>1u</sub> and t<sub>2u</sub>, for the ligand-to-metal charge transfer. The t<sub>1g</sub>, although

TABLE V. Results of SCCC calculations of various tetrahedral complexes (all energies in 1000 cm<sup>-1</sup>).

	Complexes							
	TiCl <sub>4</sub>	TiBr <sub>4</sub>	VCl <sub>4</sub>	VCl <sub>4</sub> <sup>-</sup>	CrO <sub>4</sub> <sup>2-</sup>	MnO <sub>4</sub> <sup>-</sup>	MnO <sub>4</sub> <sup>2-</sup>	MnO <sub>4</sub> <sup>3-</sup>
Bond distance, Å	2.18 <sup>a</sup>	2.31 <sup>a</sup>	2.03 <sup>b</sup>	2.14 <sup>c</sup>	1.60 <sup>d</sup>	1.59 <sup>d</sup>	1.63 <sup>e</sup>	1.67 <sup>e</sup>
3d VOIP	-90.8	-82.2	-95.1	-88.7	-128.3	-143.4	-137.2	-130.6
4s VOIP	-79.5	-74.3	-80.6	-76.7	-97.5	-104.5	-101.5	-98.2
4p VOIP	-45.3	-41.2	-50.7	-47.1	-61.8	-65.2	-63.3	-61.0
Metal charge	+0.64	+0.52	+0.58	+0.51	+0.67	+0.68	+0.68	+0.67
3d population	2.84	2.93	3.92	3.98	4.45	5.35	5.50	5.63
4s population	0.19	0.15	0.13	0.13	0.29	0.34	0.28	0.24
4p population	0.33	0.41	0.37	0.39	0.58	0.63	0.54	0.47
t <sub>1</sub> eigenvalue	-106.1	-93.5	-103.8	-105.6	-121.0	-120.8	-121.6	-122.3
2e eigenvalue	-65.9	-61.5	-66.1	-68.6	-72.8	-84.5	-87.0	-88.6
4t <sub>2</sub> eigenvalue	-57.2	-54.0	-57.1	-63.0	-46.8	-58.8	-67.8	-73.8
2e occupation	0	0	1	2	0	0	1	2
4t <sub>2</sub> occupation	0	0	0	0	0	0	0	0
Δ	8.7 <sup>o</sup>	7.6 <sup>o</sup>	9.0 <sup>o</sup>	5.6 <sup>o</sup>	26.0 <sup>f</sup>	26.0 <sup>f</sup>	19.0 <sup>f</sup>	14.8 <sup>f</sup>
First allowed L→M charge transfer: calculated orbital energy <sup>g</sup>	40.2	32.0	37.7	37.0	48.2	36.3	34.6	33.7
Observed energy	34.8 <sup>h</sup>	29.0 <sup>h</sup>	24.2 <sup>h</sup>		26.8 <sup>f</sup>	18.3 <sup>f</sup>	22.9 <sup>f</sup>	30.8 <sup>f</sup>
F <sub>o</sub> (±0.005)	1.64	1.62	1.60	1.59	1.95	1.96	1.78	1.81
	MnCl <sub>4</sub> <sup>2-</sup>	FeCl <sub>4</sub> <sup>-</sup>	FeCl <sub>4</sub> <sup>2-</sup>	CoCl <sub>4</sub> <sup>2-</sup>	CoBr <sub>4</sub> <sup>2-</sup>	CoO <sub>4</sub> <sup>3-</sup>	CoS <sub>4</sub> <sup>3-</sup>	NiCl <sub>4</sub> <sup>2-</sup>
Bond distance, Å	2.33 <sup>o</sup>	2.19 <sup>i</sup>	2.27 <sup>o</sup>	2.25 <sup>i</sup>	2.38 <sup>o</sup>	1.95 <sup>k,l</sup>	2.52 <sup>m,n</sup>	2.27 <sup>i</sup>
3d VOIP	-94.3	-105.6	-98.2	-104.3	-95.4	-121.4	-89.3	-112.4
4s VOIP	-76.9	-83.2	-78.8	-81.3	-76.8	-92.5	-71.4	-85.0
4p VOIP	-43.4	-46.4	-43.1	-43.9	-40.6	-53.5	-35.5	-46.3
Metal charge	+0.37	+0.38	+0.33	+0.32	+0.30	+0.54	+0.13	+0.34
3d population	6.03	6.92	7.01	8.01	8.19	7.95	8.06	8.99
4s population	0.24	0.27	0.27	0.28	0.18	0.22	0.36	0.34
4p population	0.36	0.42	0.38	0.38	0.33	0.29	0.45	0.33
t <sub>1</sub> eigenvalue	-107.7	-106.3	-107.1	-106.9	-94.5	-125.4	-89.8	-107.1
2e eigenvalue	-86.2	-92.6	-89.9	-95.7	-88.2	-108.7	-84.5	-102.3
4t <sub>2</sub> eigenvalue	-82.6	-87.6	-85.8	-92.0	-85.1	-104.7	-81.3	-98.7
2e occupation	2	2	3	4	4	4	4	4
4t <sub>2</sub> occupation	3	3	3	3	3	3	3	4
Δ	3.6 <sup>o</sup>	5.0 <sup>p</sup>	4.0 <sup>q</sup>	3.7 <sup>p</sup>	3.1 <sup>r</sup>	3.8 <sup>p</sup>	3.2 <sup>p</sup>	3.5 <sup>q</sup>
First allowed L→M charge transfer: calculated orbital energy <sup>g</sup>	21.5	13.7	17.2	14.9	9.4	20.7	8.5	8.4
Observed energy	30 <sup>o</sup>	27.2 <sup>m</sup>		42.5 <sup>m</sup>	23.4 <sup>t</sup>			35.8 <sup>o</sup>
F <sub>o</sub> (±0.005)	1.65	1.66	1.68	1.66	1.56	1.71	1.72	1.68

<sup>a</sup> From Ref. 44.<sup>b</sup> From Ref. 45.<sup>c</sup> Estimated value.<sup>d</sup> From Ref. 42.<sup>e</sup> From Ref. 64.<sup>f</sup> From Ref. 7.<sup>g</sup> Uncorrected for electronic repulsions.<sup>h</sup> From C. Dijkgraaf, Spectrochim. Acta 21, 769 (1965).<sup>i</sup> From Ref. 46.<sup>j</sup> From Ref. 43.<sup>k</sup> ZnO lattice.<sup>l</sup> From Ref. 48.<sup>m</sup> ZnS lattice.<sup>n</sup> From Ref. 49.<sup>o</sup> From Ref. 65.<sup>p</sup> From Ref. 56.<sup>q</sup> From Ref. 66.<sup>r</sup> From Ref. 68.<sup>s</sup> From Ref. 67.<sup>t</sup> From Ref. 62.

a strictly ligand  $\pi$  level as is the  $t_{2u}$ , is relatively unimportant since both  $t_{1g} \rightarrow 2t_{2g}$  and  $t_{1g} \rightarrow 3e_g$  are parity-forbidden transitions. The  $3e_g$  and  $2t_{2g}$  roughly correspond to the orbitals  $e_g$  and  $t_{2g}$  of crystal-field theory. The  $3t_{1u}$  level is mainly composed of ligand  $\pi$  functions.

In calculations on the 16 octahedral complexes, permutations of levels occurred within some of the bracketed sets. Only one of these permutations is of

importance, that interchanging  $3t_{1u}$  and  $t_{2u}$ . Since they are both triply-degenerate orbitals of odd parity and of similar composition it is not likely that the correct order can be established in these cases. For consistency, the first L→M charge transfer was calculated from the  $t_{2u}$ .

However, with the possible exception of the  $t_{2u}$ - $3t_{1u}$  comparison, these calculations, for reasonable choices

TABLE VI. Metal and Ligand Orbital Contributions to the Secular Equations.<sup>a</sup>

Irreducible representation	Contribution		Dimension	Degeneracy
	Metal	Ligand		
<b>Octahedral</b>				
$a_{1g}$	$s$	$s, p_\sigma$	3	1
$e_g$	$d$	$s, p_\sigma$	3	2
$t_{1g}$	...	$p_\pi$	1	3
$t_{1u}$	$p$	$s, p_\sigma, p_\pi$	4	3
$t_{2g}$	$d$	$p_\pi$	1	3
$t_{2u}$	...	$p_\pi$	1	3
<b>Tetrahedral</b>				
$a_1$	$s$	$s, p_\sigma$	3	1
$e$	$d$	$p_\pi$	2	2
$t_1$	...	$p_\pi$	1	3
$t_2$	$p, d$	$s, p_\sigma, p_\pi$	5	3

<sup>a</sup> Coordinate systems, ligand basis sets, analytic expressions for normalizations, group overlaps, and  $H_{ii}'$  correction factors are given in Ref. 38 for octahedral and Ref. 7 for tetrahedral.

of the parameters, yield the expected relative orderings for the levels, which should be most important in the  $d-d$  and  $L \rightarrow M$  charge-transfer spectra of both tetrahedral and octahedral complexes. In particular,  $4t_2 > 2e$  in tetrahedral, and  $3e_g > 2t_{2g}$  in octahedral.

The significance that can be attached to the wavefunctions and energies calculated by the simple MO method has been the subject of considerable debate.<sup>11,12</sup>

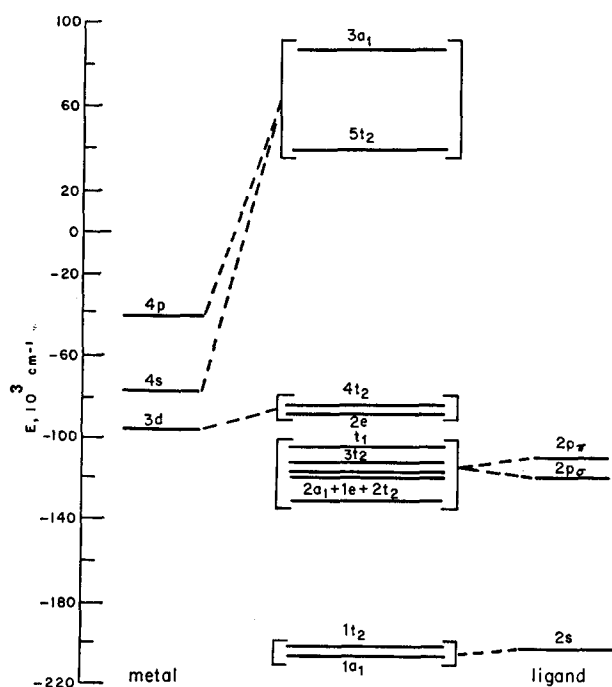


FIG. 1. Molecular orbital energy-level diagram for tetrahedral complexes. Drawn to scale for  $\text{FeCl}_4^{2-}$ .

Early investigators<sup>1,3</sup> placed great emphasis on the transition moments computed using the derived ground-state wavefunctions. In one case,<sup>1</sup> however, although the results compared satisfactorily with experimentally determined intensities, the band assignments subsequently have been shown to require revision.<sup>7</sup>

Direct experimental evidence of covalency in transition-metal complexes has come from magnetic resonance experiments which, under favorable conditions, can be interpreted to yield values for covalent mixing parameters.<sup>68</sup> In particular, one such work<sup>33</sup> reported the coefficients for the ligand  $2s$  and  $2p$  symmetry orbitals

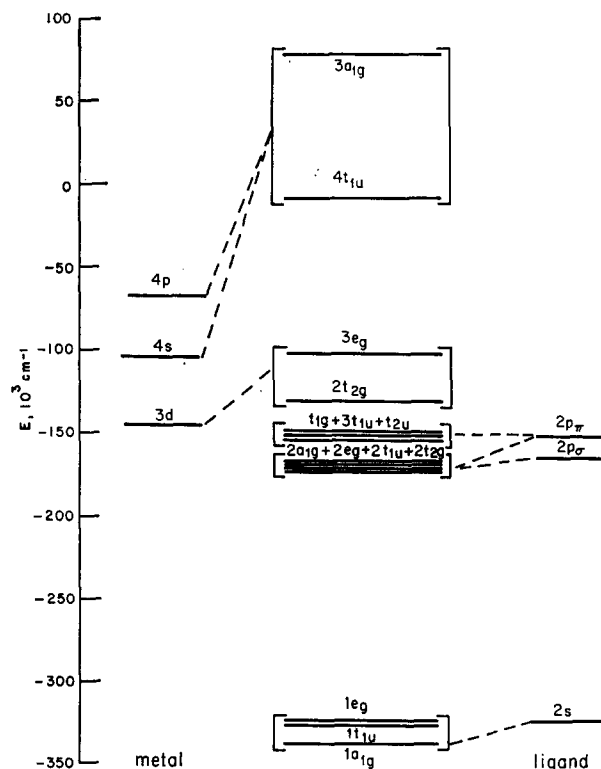


FIG. 2. Molecular orbital energy-level diagram for octahedral complexes. Drawn to scale for  $\text{FeF}_6^{3-}$ .

in  $3e_g$  as 0.116 and 0.337, respectively, in  $\text{KNiF}_3$ . This can be compared with 0.007 and 0.386 calculated here for  $\text{NiF}_6^{4-}$ . Unfortunately, the comparison is not quantitatively valid since the "experimentally" determined coefficients are actually derived from  $^{19}\text{F}$  hyperfine interactions using  $F^-$   $2s$  and  $2p_\sigma$  atomic wavefunctions which differ from the neutral atom  $F$  wavefunctions used in this investigation.

Of greater use and reliability are the calculated charge distributions partitioning the electrons in the MO's into localized contributions of the participating atoms. Although arbitrarily defined, these gross atomic populations and resultant bond orders and bond polarities have long been used successfully to predict and confirm the existence of chemically reactive sites

in complex organic molecules.<sup>75</sup> In addition, an examination of the dominating orbital contributions to a given calculated charge distribution has helped elucidate the factors governing the formation and properties of molecules. Of particular interest in the realm of transition-metal complexes are the relative magnitudes and trends in the derived charge distributions indicating degree and kind of covalency.

In the calculations reported here (Tables IV and V) the computed charge on the metal decreases and the occupation of the metal  $4s$  and  $4p$  orbitals increases with increasing atomic number ( $Z$ ). This increased participation of  $4s$  and  $4p$  in the bonding reflects the increased stability of these orbitals in going across the transition series. The lowering of charge is indicative of increased covalency (for a given ligand) with increasing  $Z$  and is in qualitative agreement with the orbital electronegativities calculated for these metals by Hinze and Jaffé.<sup>28</sup>

Additional evidence is supplied by an examination of the transition-metal radial wavefunctions of Richardson *et al.*<sup>71</sup> or Clementi and Raimondi.<sup>76</sup> They show that the radii of maximum radial charge density of the free atom and ion wavefunctions shrink by approximately  $0.04 \text{ \AA}$  on increasing  $Z$  by one unit. However, the computed ionic radii and observed bond distances in complexes (for a given oxidation state, ligand, and geometry) vary by a value somewhere between zero and  $0.03 \text{ \AA}$ . This can be interpreted by assuming that the reduced charge on the metal due to increased covalency compensates for most of the natural contraction of the  $3d$  radial function with increasing  $Z$ , yielding a slow net decrease in the observed bond distance. The calculations also reveal that, for a given ligand, the self-consistent charge changes slowly with increasing formal oxidation state. This is in qualitative agreement with a similar experimental observation made by Shulman and Sugano<sup>77</sup> for cyanide complexes, although their explanation may not be directly applicable here.

The variation of charge with ligand for a given metal is seen to follow  $F > O > Cl > Br > S$ , as is expected from the known trends in metal binding by these atoms. As outlined previously, transition-metal complexes are known to have substantial covalent character and this suggests that the ligand  $np$  ( $n=2, 3, 4$ )  $H'_{ii}$  are in the stability range of the metal  $3d$   $H'_{ii}$ . The actual choice of  $H'_{ii}$  wavefunctions, and  $F$  factors determines the degree of covalency for an isolated complex, and all three choices are somewhat arbitrary; although one set may be superior to another. The simple MO method, however, offers no unambiguous way of finding this set in an absolute sense. In addition,

since the numbers of interest to us here (electronic spectra) are of the same order of magnitude as the inherent error in the theory upon which the computations are based, significance can be attached only to consistent behavior within a group of molecules.

In both tetrahedral and octahedral geometries,  $\Delta$  measures the splitting of the  $d_{\pi}-d_{\sigma}$  (i.e.,  $\pi$  and  $\sigma$ , respectively, with regard to interactions with ligand orbitals) metal orbitals. For a given set of VOIP's and wavefunctions,  $\Delta$  is completely determined by the choice of  $F_{\sigma}$  and  $F_{\pi}$  [Eq. (7)]. Since  $F_{\pi}$  principally determines the position of the first  $L \rightarrow M$  charge-transfer band,  $F_{\pi}$  was fixed at 2.10 to approximately fit the  $L \rightarrow M$  band in the  $d^0$  and  $d^1$  cases, where the electronic repulsion corrections to the simple difference of the one-electron energy levels can be estimated [see later, Eq. (9)]. The results of fitting  $F_{\sigma}$  to reproduce the experimentally determined  $\Delta$ s are tabulated in Tables IV and V.

A detailed examination of  $F_{\sigma}$  values reveals the following:

(a) The  $F_{\sigma}$ 's belonging to the 16 octahedral complexes (Table IV) follow the equation,  $F_{\sigma}(n) = [0.027n + 1.546] \pm 0.02$ , where for Ti,  $n=0$ , for V,  $n=1$ ,  $\dots$  etc., independent of the metal oxidation state or combining ligand.

(b) Nine of the 16 tetrahedral complexes ( $VCl_4$ ,  $VCl_4^-$ ,  $MnCl_4^{2-}$ ,  $FeCl_4^-$ ,  $FeCl_4^{2-}$ ,  $CoCl_4^{2-}$ ,  $CoO_4^{6-}$ ,  $CoS_4^{6-}$ ,  $NiCl_4^{2-}$ ) in Table V follow the same equation with the same average deviation.

(c) For the high-oxidation-state (V, VI, VII) tetrahedral metal oxyanions ( $CrO_4^{2-}$ ,  $MnO_4^-$ ,  $MnO_4^{2-}$ ,  $MnO_4^{3-}$ ) the  $F_{\sigma}$ 's show a definite oxidation-state dependence and lie outside the range found for the other complexes.

We now proceed to a comparison of the calculated and observed variations in  $\Delta$  and  $L \rightarrow M$  charge transfer.

(1)  $\Delta$  with geometry. With the reservations specified above, it appears possible to transfer the  $F$  factor from octahedral to tetrahedral geometries quantitatively. It is important to note that this statement is limited to first-row transition metals containing one-atom ligands with a single  $\pi$  valence orbital. The inclusion of a second  $\pi$  valence orbital (as for example  $\pi^*$  in diatomic or complex unsaturated<sup>8</sup> ligands) could conceivably alter the whole character of this analysis. Extension to other geometries must be tested separately.

The variation of  $F_{\sigma}$  in the high-oxidation-state oxyanions seems to be a direct result of the unusually large  $\Delta$ s for these complexes.<sup>7,78</sup>

(2)  $\Delta$  with metal-ion oxidation number. For metal complexes, which do not have appreciable  $\pi$ -acceptor ability,  $\Delta$  is known to increase as the formal positive charge on the ion increases. For example, comparing

<sup>75</sup> C. A. Coulson, *Valence* (Oxford University Press, London, 1961), Chap. 9.

<sup>76</sup> E. Clementi and D. L. Raimondi, *J. Chem. Phys.* **38**, 2686 (1963).

<sup>77</sup> R. G. Shulman and S. Sugano, *J. Chem. Phys.* **42**, 39 (1965).

<sup>78</sup> A. Carrington and C. K. Jørgensen, *Mol. Phys.* **4**, 395 (1961).



experimental results for  $V(H_2O)_6^{2+} \rightarrow V(H_2O)_6^{3+}$ ,  $\Delta$  goes from 12 400 to 18 400  $cm^{-1}$ .<sup>56</sup> Similarly, comparing  $MnF_6^{4-} \rightarrow MnF_6^{2-}$ ,  $\Delta$  goes from 8400 to 21 800  $cm^{-1}$ ; such large changes in octahedral  $\Delta_s$  are accounted for by a nearly constant  $F_\sigma$ , as shown in Table IV.

(3)  $\Delta$  with ligand (the spectrochemical series). The spectrochemical series of the halide ligands is  $F > Cl > Br$ . A glance at the results for octahedral  $Ti(III)$  and  $Cr(III)$ , and tetrahedral  $Co(II)$  reveals a small scatter of  $F_\sigma$  values for the halide ligands in the calculations. This may be due to the inaccuracy of estimated bond distances for the complex or an ambiguity as to which value of  $\Delta$  (which varies slightly with state and solvent) is appropriate to these calculations. In any event, this result gives an indication of the accuracy that can be expected from these calculations.

(4) Charge transfer with metal oxidation number. In discussing charge-transfer spectra, we utilize an equation given by Jørgensen<sup>31</sup>

$$E = I(\pi) - I(3d) - (q-1)J(a, a) \\ + (q-k-1)J(a, b) + kJ(b, b) \quad (9)$$

approximately governing the energy ( $E$ ) of the transition,  $a^q b^k \rightarrow a^{q-1} b^{k+1}$ , from a nonbonding  $\pi$  MO level,  $a$ , with eigenvalue  $I(\pi)$  and occupation number  $q$ , to one of the "3d-orbital" MO levels,  $b$ , with eigenvalue  $I(3d)$  and initial occupation number  $k$ .  $J(a, b)$  is the two-electron integral  $[a, a/(r_{12})^{-1}/b, b]$  between MO's  $a$  and  $b$ . Exchange integrals are neglected. In these calculations  $q=6$  and  $k$  varies from 0 to 5. In an isoelectronic series of complexes with the same ligand, the first  $L \rightarrow M$  charge-transfer band is expected to move to lower energy as the formal oxidation state of the metal increases.<sup>31</sup> Presumably, as the oxidation state of the metal increases, the metal 3d orbitals become more stable, giving a smaller energy separation between the (fully occupied) nonbonding ligand  $\pi$  levels and the lowest empty "d orbital" ( $2e$  or  $4t_2$  in tetrahedral,  $2t_2$  or  $3e_g$  in octahedral).

In every case where an isoelectronic series can be compared (the interelectronic repulsion corrections to the simple differences of one-electron energy levels are approximately constant) these calculations give the expected trend. Thus we calculate  $CrO_4^{2-} > MnO_4^-$ ,  $MnCl_4^{2-} > FeCl_4^-$ ,  $VF_6^{4-} > CrF_6^{3-} > MnF_6^{2-}$ , and  $MnF_6^{4-} > FeF_6^{3-}$ .

As a rule of thumb, a similar movement of the first  $L \rightarrow M$  charge-transfer band to lower energy with increasing formal positive charge is also expected for complexes of a given ligand and different oxidation states of a single metal. Here the comparison is not an isoelectronic one and so the expectation is qualitatively less clear cut. The calculations predict that the orbital energy of the first  $L \rightarrow M$  transition is practically insensitive to oxidation number for such comparisons. However, the electronic repulsion correction factors

are expected to increase directly proportional to the number of electrons in the upper ("d-orbital") MO. This corresponds to increasing  $k$  in Eq. (9) and shifts the calculated trend in the expected direction.

(5) Charge transfer with metal  $Z$ . It has been established experimentally that the position of the first  $L \rightarrow M$  band in an analogous series of complexes shifts to lower energy in going from  $Ti$  to  $Co$ . For the series of octahedral fluorides and chlorides and tetrahedral chlorides, the calculated trend is as expected. The dominating factor seems to be the steady decrease in the metal 3d  $H'_{ii}$  with increasing  $Z$ , although the self-consistent charge on the metal decreases.

While the observed trend is generally followed by the calculated values, the magnitudes of the changes appear at first sight to be too large. It is probable that the VOIP curves exaggerate the increasing stability of the metal 3d  $H'_{ii}$  both with charge and with increasing  $Z$ .<sup>4</sup> This is not certain, however, since the interelectronic-repulsion corrections increase in a series from  $Ti$  to  $Co$ .

(6) Charge transfer with ligand. The energy of the first  $L \rightarrow M$  band for a metal in a given oxidation state is expected to parallel the instabilities of the various ligand  $p$  levels. In these calculations the VOIP order is  $S < Br < Cl < O < F$ . For octahedral  $Ti(III)$  and  $Cr(III)$ , and tetrahedral  $Co(II)$ , the first  $L \rightarrow M$  charge-transfer band follows the expected ordering,  $F > O > Cl > Br > S$ . The inclusion of electronic-repulsion terms in complexes with few  $d$  electrons is expected to reduce the calculated one-electron differences between adjacent ligands since, in terms of the quantities defined in Eq. (9),  $J(a, a)$  is expected to increase in the order  $S < Br < Cl < O < F$ .

## CONCLUSIONS

Two of the present results are particularly encouraging. First, for constant  $F_\pi$  and  $F_\sigma$  varied to obtain agreement with experimental values of  $\Delta$ , it has been found that the optimum value of  $F_\sigma$  varies only slowly in going across the first transition series. This general conclusion agrees with the findings of Cotton and Haas.<sup>13</sup> Further, a single value of  $F_\sigma$  appears adequate to account for variations of  $\Delta$  in the II through IV range of oxidation states for a given metal.

Secondly, a single value of  $F_\sigma$  is sufficient for both octahedral and tetrahedral complexes, with the same set of atomic orbitals. In previous calculations the transition from octahedral to tetrahedral has been particularly troublesome.<sup>12</sup> However, successful comparison seems to be limited to the II  $\rightarrow$  IV range in oxidation states thus far.

There are two interesting complications.  $F_\sigma$  does seem to depend significantly on oxidation state, if the V  $\rightarrow$  VII range in oxidation states is considered. Secondly, optimization of  $F_\sigma$  to bring agreement with  $\Delta$  may not necessarily give close agreement with the observed first  $L \rightarrow M$  charge-transfer band. However,

in most cases the interelectronic-repulsion correction to the calculated one-electron charge-transfer energy brings theory and experiment into closer agreement. We also get a qualitative correlation of L→M band energy with formal oxidation number, ligand, and metal  $Z$  for a single  $F_{\pi}$ .

Thus the over-all results are sufficiently promising that the semiempirical molecular orbital method may be recommended for additional study, in hope of further refinement.

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## Electronic Spectrum of (2, 2)Paracyclophane. II\*

ARZA RON AND O. SCHNEPP

*Department of Chemistry, Israel Institute of Technology, Haifa, Israel*

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The studies of the absorption and fluorescence spectra of single crystals of (2,2)paracyclophane in the region 3300–3100 Å reported in a previous paper have been extended. Well-characterized samples with the ( $h k 0$ ) developed crystal plane were used. In absorption two distinct spectra were obtained in the two polarization components. The fluorescence was strongly polarized in one direction (parallel to the fourfold  $c$  axis) and represents the mirror image of the equally polarized absorption component. It was concluded that the observations prove conclusively that the differently polarized spectral components represent transitions to two different electronic states, with an energy difference of 369  $\text{cm}^{-1}$ . The lowest-energy transition certainly contains the 0–0 line and all available evidence supports the conclusion that also the second transition has allowed character. The only interpretation consistent with all observed features of the spectra is as follows. The two observed states are the gerade dimer states ( $B_{2g}$  and  $B_{3g}$  in  $D_{2h}$ ) being the out-of-phase combinations of the  $B_{2u}$  and  $B_{1u}$  benzene moiety states. The transitions have allowed character due to a torsional distortion of the molecule in the excited state. The interpretation is fully consistent with theoretical energy calculations.

## INTRODUCTION

**I**N a previous paper<sup>1</sup> (hereinafter referred to as I) the electronic absorption spectrum of single crystals of (2,2)paracyclophane in polarized light was described. The transition studied in this work was assigned as the lower-energy and near-forbidden component of the dimer molecule arising from the  ${}^1B_{2u} \leftarrow {}^1A_{1g}$  benzene transition. Excitation exchange coupling was assumed to be the interaction mechanism between the moieties. This approach had previously been suggested on the basis of the solution spectra of the paracyclophanes.<sup>2</sup>

Several aspects of the spectrum remained unexplained in I. No reason for the extremely small intensity of the fluorescence could be given. It was a direct consequence of the low intensity that the assignment of the 0–0 frequency was not based on actual coincidence of absorption and fluorescence but rather relied on extrapolation to higher frequencies of the progression appearing

in emission. A further observation for which no satisfactory explanation was given was the small but definite difference between the principal progression forming frequencies in the two polarization components of the absorption spectrum (parallel and perpendicular to the fourfold  $c$  axis of the tetragonal crystal). Such a phenomenon is not to be expected for different vibronic progressions of the same electronic transition.

The (2,2)paracyclophane molecule represents an electronic system of particular interest. It seemed of special importance to investigate the nature and extent of the interaction between the two  $\pi$ -electron systems of the benzene rings which are rigidly held at a distance<sup>3</sup> smaller than the van der Waals distance between benzene rings observed in crystals. For this reason it was decided to extend and to complete the investigation begun in I, with the aim to record the absorption and emission spectra of a crystal plane such that the two oppositely polarized components would appear entirely

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<sup>1</sup> A. Ron and O. Schnepf, *J. Chem. Phys.* **37**, 2540 (1962).

<sup>2</sup> D. S. McClure, *Can. J. Chem.* **36**, 48 (1958).

<sup>3</sup> C. J. Brown, *J. Chem. Soc.* **1953**, 3265; K. Lonsdale, J. H. Milledge, and K. V. Krishna Rao, *Proc. Roy. Soc. (London)* **A255**, 82 (1960).