the donor atom. The net unpaired spin in both cases can then be distributed according to a simple valence bond description.[4] A mechanism for spin transfer in other octahedral nickel complexes has been given elsewhere.[36]

Finally, we mention briefly the type B complexes. These species are highly insoluble in inert solvents such as chloroform or benzene, but dissolve readily upon the addition of a small amount of an aliphatic amine to give a greenish brown solution. Solubility is very probably effected by hydrogen bonding between the amine and the hydroxyl group. The insolubility of these complexes in nonhydrogen-bonding solvents appears to be due to intermolecular hydrogen bonding such as has been found in crystalline bis(N-2-hydroxyethylsalicylaldimine)copper(II).[37]

Acknowledgment.—Financial support by the National Science Foundation (Grant GP-590) and the Milton Fund of Harvard University is gratefully acknowledged.

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(36) R. S. Milner and L. Pratt, *Discussions Faraday Soc.*, **34**, 88 (1962).

(37) E. R. Boyko, Abstracts, Intern. Union of Crystallography, Sixth Intern. Congress, Rome, Italy, Sept. 1963.

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Semiempirical Molecular Orbital Theory for Transition Metal Complexes

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Although the modified Wolfsberg and Helmholz approach to molecular orbital theory for transition metal complexes has had apparent success in recent applications, evaluation of the technique indicates that not only are the results strongly dependent upon the initial assumptions but also agreement between theory and experiment obtained in previous calculations may not be valid. Specifically, consideration is given to the use of hybridized ligand orbitals for σ-bonding, estimation of H_{ij} terms in the secular determinant, and approximation of the ligand diagonal term, H_{jj}, by the hydride method with respect to the determination of the energy levels in TiF_6^{-3}. The results show that among other things appreciable covalent character and the importance of π-bonding are automatic consequences of rather arbitrary assumptions. In general the method can lead to erroneous values and interpretations and should not be accepted without strong reservations.

Introduction

In recent months there has been renewed interest in a semiempirical molecular orbital method for the determination of the electronic energy levels of transition metal complexes. The method, originally suggested by Wolfsberg and Helmholz[1] and modified by Ballhausen and Gray,[2] has been applied to the vanadyl,[2] hexafluorotitanate(III),[3] and permanganate[4,5] ions. However, closer examination of these and similar calculations brings to light certain ambiguities which tend to undermine one's trust in the validity of the method.

This discussion deals essentially with the estimation of electronic energy levels. Although not explicitly treated here, we also have reservations concerning the compatibility of the results with other experimental evidence such as n.m.r. hyperfine splittings. However, proponents of the method have never claimed the approach to be necessarily useful in this regard, its principal application being to the interpretation of absorption spectra. It will be shown that discrepancies arise even in this limited application. It is the purpose of this report to call attention to these discrepancies and to examine their causes.

Because of the simplicity of the system, particular attention will be given to the evaluation of the energy levels of the TiF_6^{-3} complex. In the original calculation for this complex by Bedon, Horner, and Tyree,[3] the excellent agreement between the theoretical and experimental value of $10Dq$ was cited as indicative of the usefulness of the semiempirical approach. It should be noted that neither the transition assignment, $^2T_{2g} \rightarrow {}^2E_g$, nor the $10Dq$ value of 17,500 cm.$^{-1}$ proposed by Bedon, *et al.*, is being questioned here. What is in doubt is that the agreement obtained between the calculated and experimental result substantiates the validity of the theoretical method.

The Method of Calculation

The secular determinant, $|H_{ij} - EG_{ij}| = 0$, which arises from the adoption of the LCAO approach to molecular orbital theory, is conveniently factored by application of group theory. In the secular determinant the G_{ij} are group overlap integrals which can be expressed in terms of two center overlap integrals multiplied by suitable coefficients.

In the modified method[2-5] the diagonal terms *for the central metal* orbitals, H_{ii}, are estimated as the negative of the valence state ionization energies (VSIE) of the atoms or ions. The VSIE values are dependent upon the assumed electron configuration of the valence state and the assumed charge on the metal. In general, the

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

(2) C. J. Ballhausen and H. B. Gray, *Inorg. Chem.*, **1**, 111 (1962).

(3) H. D. Bedon, S. M. Horner, and S. Y. Tyree, Jr., *ibid.*, **3**, 647 (1964).

(4) R. F. Fenske and C. C. Sweeney, *ibid.*, **3**, 1105 (1964).

(5) A. Viste and H. B. Gray, *ibid.*, **3**, 1113 (1964).

dependence of the VSIE on the latter is the more significant of the two.

For the *ligand* diagonal terms, H_{jj}, two methods have been employed. In the "free ion" method, the term is estimated from the VSIE in a manner analogous to that for the central ion and hence is charge dependent. In the "hydride ion" method, the value for H_{jj} is estimated by the experimental ionization energy of an electron in a hydride of the ligand. For example, for fluoride the lowest ionization energy of an HF electron is used; for oxides the ionization energy for an H_2O electron has been employed. In this approach the H_{jj} value is presumed to be independent of the charge on the ligand.

The off-diagonal terms, H_{ij}, are approximated by the relation $H_{ij} = -FG_{ij}\sqrt{H_{ii}H_{jj}}$, where F is generally set equal to 2.

In certain of the applications of the method,[2-4] it has been assumed that the ligand σ-bonding orbital can be reasonably approximated as a hybridized atomic orbital. For example, in TiF_6^{-3} the fluoride σ-bonding function would be a hybrid of the 2s and 2p functions.

$$\Psi(\text{hybrid}) = (\sin\theta)\Phi(2s) + (\cos\theta)\Phi(2p\sigma)$$

The corresponding H_{jj} value is then given by

$$H_{\sigma\sigma}(\text{hybrid}) = (\sin^2\theta)H(2s) + (\cos^2\theta)H(2p\sigma)$$

A restriction on the choices of the configuration and the charge on the central metal ion is achieved by the requirement that self-consistency exist between these choices and the configuration and charge calculated by means of Mulliken's electron population analysis.[6] Generally such self-consistency can be obtained after a few cyclic trial calculations in which the calculated charge and configuration are used as the starting values for the next cycle.

Exact details of the method of calculation have been carefully outlined by Bedon, *et al.*[3]

Evaluation of the Method

At the outset it should be emphasized that there is much that is commendable in the modified approach. Relatively speaking, it presents few computational difficulties and is quite simple to use. Several of the reported calculations were carried out by means of desk calculators and published overlap tables. However, simplicity is only one of the desired characteristics in a semiempirical approach. Above all, the results should conform as closely as possible to the actual physical situation (or to the results of more exact calculations) and should be obtained in an unambiguous manner. In the light of these criteria it is worthwhile to examine several of the proposed approximations and the results achieved by their use.

(1) **Hybridization of Ligand Orbitals.**—In the applications of the modified method for vanadyl[2] and hexafluorotitanate(III)[3] ions, the σ-bonding orbitals on the ligands were considered to be hybrids of the s and p orbitals, as previously described, and good results were achieved. In our calculations on permanganate,[4] it was shown that hybridization leads to alternative energy level assignments depending upon the amount of s-character in the hybrid orbital. The proposed criterion that the ratio VSIE $(\theta)/S(\theta)$ be a minimum was shown to be unsatisfactory since it not only gave excessively large transition energies but also gave the incorrect ordering of the energy levels as ascertained by e.s.r. measurements on MnO_4^{-2}. Simultaneously, Viste and Gray[5] showed that when the individual 2s and 2p oxygen levels were considered, the preferred order and more satisfactory values of the transition energies could be obtained. Together these results suggest that the use of hybrid orbitals is incorrect, despite the fact that their application to the TiF_6^{-3} complex gave the desired $10Dq$ value. Certainly if a method is to be useful its applications to all systems must be uniform.

In addition, a strong objection on theoretical grounds can be made to the use of hybrid ligand orbitals for the fluoride complex. The σ-bonding wave function is given as

$$\Psi_\sigma = \sqrt{0.13}\Phi(2s) + \sqrt{0.87}\Phi(2p)$$

and the overlap of this function with the $3d_\sigma$ orbital on the central metal is 0.180. However, there exists a function orthogonal to this, which in this approach is presumed to be the nonbonding orbital for the lone-pair electrons on the fluorine, of the form

$$\Psi_{L.P.} = \sqrt{0.87}\phi(2s) - \sqrt{0.13}\phi(2p)$$

This orbital has an overlap with the central metal $3d_\sigma$ orbital of 0.103, which is obviously inconsistent with the presumption of a nonbonding orbital. Certainly if the method is to be applied in a systematic manner, this interaction cannot be ignored.

Since the hybrid orbital method appears questionable on both pragmatic and theoretical grounds, it is worthwhile to examine the effect of the individual 2s and 2p orbitals on the energy levels of TiF_6^{-3}. In order that suitable comparisons can be made, wherever possible the studies presented here use the same values for various quantities employed in the original calculations.[3] These include the atomic wave functions, overlaps, method of H_{ij} estimation, etc. However, for the sake of completeness additional possibilities were considered: (1) Since the original work did not include ligand–ligand overlap, calculations were made with and without this consideration. (2) Results were obtained in which both the "free ion" and "hydride" method were used to estimate the ligand H_{jj} values. The data obtained from these calculations are summarized in Table I.

In their original study on TiF_6^{-3}, Bedon, *et al.*,[3] indicated the worth of their calculation by the excellent agreement between the theoretical and experimental values of $10Dq$, the separation between the e_g^* and t_{2g}^* orbitals. As indicated by the results given in Table I, this criterion is no longer satisfied when the individual 2s and 2p ligand orbital interactions are con-

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[6] R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833 (1955).

TABLE I

RESULTS ON TiF_6^{-3} BY VARIOUS COMPUTATIONAL METHODS

		Individual ligand orbital interaction		
			With ligand–ligand overlap	
	Hybrid orbital	Without ligand–ligand overlap	Hydride method	Free ion method
10*Dq* value, cm.$^{-1}$	17,500[a]	28,300[b]	30,600	25,700
Self-consistent charge on metal	+0.54	+0.54	+0.59	+0.51
Electron configuration of metal	$d^{2.75}s^{0.37}p^{0.34}$	$d^{2.77}s^{0.33}p^{0.36}$	$d^{2.84}s^{0.31}p^{0.26}$	$d^{2.94}s^{0.32}p^{0.23}$

[a] Results taken from ref. 3. [b] Hydride method.

sidered. Indeed, the theoretical value of 10*Dq* is almost twice the experimental result. Note that this change in 10*Dq* cannot be attributed to drastic alterations in charge distribution or electronic configuration on the central metal since these are very similar in all cases. Nor, in this case, does there seem to be any particular benefit in the use of the "hydride" method over the "free ion" method for ligand VSIE estimation. Both yield unsatisfactory results. Reasons for the increase in 10*Dq* are examined below.

(2) **The Estimation of H_{ij} Terms.**—A clue to the cause of the drastic increase in the 10*Dq* value is seen in the results of the calculations with and without ligand–ligand overlap. This overlap is quite small. For example, for adjacent fluorine atoms the value of $S(2s,2p_\sigma)$ is only 0.0125. Yet the value of 10*Dq* changes by 2300 cm.$^{-1}$ when the overlap and hence the off-diagonal term, H_{ij}, is taken into account.

A further illustration of the cause of the 10*Dq* increase can be made by considering a calculation involving a simple 2 × 2 determinant. When the absolute value of one diagonal term is much greater than the other, *e.g.*, $|H_{jj}| >> |H_{ii}|$, and the off-diagonal term is estimated by $H_{ij} = -2G_{ij}\sqrt{H_{ii}H_{jj}}$, the bonding level is only slightly different from H_{jj}, but the antibonding level is appreciably different from H_{ii}. That is, the *inclusion of low-lying energy levels in the calculations drastically affects the antibonding levels because of the inordinate importance given to the off-diagonal term by the above method.*

This fact is further demonstrated by the results in Table II which allow comparison of the calculated energy levels of the E_g orbitals in TiF_6^{-3} with and without consideration of the 3d–2s interaction. If one assumes, incorrectly, that no 3d–2s interaction exists, the calculated energy levels are as given in the $3d_\sigma$–$2p_\sigma$ column. The value of E_1 in that column is the energy of the 2s ligand orbital which was presumed to be nonbonding. This calculation represents the limiting case of $H(2s\text{–}3d) = 0$. The second column tabulates the energy levels obtained with complete interaction, including ligand–ligand overlap. Note that only the antibonding level, E_3, is appreciably affected. Admittedly, the group overlap for 3d–2s is greater than $3d_\sigma$–$2p_\sigma$ and this enhances this effect, but the major factor is the method for the estimation of H_{ij}. The larger the absolute value of H_{jj}, the greater will be the significance given to the off-diagonal term since the F factor in $H_{ij} = -FG_{ij}\cdot\sqrt{H_{ii}H_{jj}}$ is kept at a constant value of 2 regardless of the interaction involved. Thus H_{ij} for the $3d_\sigma$–$2p_\sigma$ interaction is approximately −52,600 cm.$^{-1}$, while the $3d_\sigma$–2s interaction is roughly −91,200 cm.$^{-1}$ or about 1.7 times as large. In their more rigorous approach to similar calculations for $KNiF_3$, Sugano and Shulman[7] calculated the ratio of H_{ij} values to be $H(3d\text{–}2s)/H(3d_\sigma\text{–}2p_\sigma) \sim 1.2$.

TABLE II

EFFECT OF 2S LEVEL ON THE CALCULATED $3d_\sigma$–$2p_\sigma$ ENERGY LEVELS

	$3d_\sigma$–$2p_\sigma$ interaction	$3d_\sigma$–2s–$2p_\sigma$ interaction
E_1, cm.$^{-1}$	(−272,200)[a]	−273,600
E_2, cm.$^{-1}$	−145,400	−144,000
E_3, cm.$^{-1}$	−78,500	−50,400
VSIE values:	$3d_\sigma = -99,200$ $2s = -272,200$	$2p_\sigma = -136,000$
Group overlaps:	$3d_\sigma\text{–}2p_\sigma = 0.225$	$3d_\sigma\text{–}2s = 0.277$

[a] The 2s level is listed here as the first energy level for comparison purposes. In the $3d_\sigma$–$2p_\sigma$ column, E_2 and E_3 are the results obtained from the solution of the 2 × 2 determinant.

It is thus obvious that it is the H_{ij} term for the 3d–2s interaction which is responsible for the change in the calculated value of 10*Dq*. The 2s orbitals on the ligands do not transform according to the irreducible representation T_{2g} but do belong to the E_g irreducible representation. Hence of the two only the E_g levels are affected by the 3d–2s interaction and the t_{2g}^*–e_g^* separation is increased.

(3) **The "Hydride" Method for H_{jj} Terms.**—The "hydride" method assumes that the ligand levels are insensitive to the charge on the ligand because of the presence of the positively charged central metal which is presumed to have a moderating effect on the VSIE. Two points are overlooked in such an argument. First, not only is a particular ligand close to the positive charge of the central metal but also it is reasonably close to the negative charges of the other ligands. Indeed, simple electrostatic calculations for TiF_6^{-3} show the cumulative effect of these negative charges to be more important than the positive charge on the central metal.

Second, if such an influence should be considered for the ligand levels, some similar adjustment should be made in the central metal levels for the influence of the negative ligands. This has not been done in previous applications of this method. As a consequence, the calculations always indicate strong covalency and appreciable π-bonding. Note from Table I that the charge on the titanium is never greater than +1. With the fixed values of the ligand energy levels any charge greater than one results in central metal VSIE below the

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

ligand levels. This gives the bonding orbitals such appreciable central metal character that the calculated charge on the central metal is much less than the assumed starting charge and self-consistency is not achieved. Therefore, *appreciable covalency is an automatic consequence of the assumptions of the method.* Whether this conforms to physical reality is highly debatable.

For the same reasons, the method will always indicate that π-bonding is significant; that is, the π-bonding orbitals will have appreciable central metal character. In terms of relative separations, the 3d metal orbitals are closer to the π-ligand orbitals than to the σ-orbitals. Hence the $3d_\pi$–π-bonding orbitals will be responsible for a large part of the charge reduction on the central metal necessary to achieve self-consistency.

Conclusion

It is apparent from the foregoing discussion that the semiempirical method presently employed for the determination of the electronic energy levels in transition metal complexes should not be accepted without strong reservations. It is to be hoped that continued investigations, both theoretical and experimental, will eventually result in an approach having a comparable simplicity without the uncertainty of the present method.

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Infrared Studies of Ligand–Ligand Interaction in Dihalogenodiammineplatinum(II) Complexes[1]

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The infrared spectra of *cis*- and *trans*-[Pt(NH$_3$)$_2$X$_2$] (X = Cl, Br, I) and [Pt(ND$_3$)$_2$Cl$_2$] have been measured from 4000 to 200 cm.$^{-1}$. It has been shown that the infrared spectra of these complexes can better be explained if ligand–ligand interaction through a filled d-orbital of the platinum atom is considered. The results of a normal coordinate analysis of *trans*-[Pt(NH$_3$)$_2$Cl$_2$] support the postulated ligand–ligand interaction. The influence of *cis–trans* isomerism and of halogen substitution on the spectra has also been discussed.

I. Introduction

Chatt and co-workers[2] were the first to postulate the existence of intramolecular interaction between the ammine hydrogen atoms and the nonbonding d-electrons of the metal in a platinum ammine complex. They based this assumption on infrared studies (the N–H stretching region) of compounds of the type *trans*-[Pt(am)LCl$_2$], where am is a primary or secondary amine and L is a varied series of ligands. It is reasonable to expect that such an intramolecular interaction may operate in other platinum complexes, and that in them the ligands around the metal may interact electronically through the d-electrons of the platinum atom. Even though this interaction is electronic in origin, its effects will be observed more clearly in the vibrational spectra than in the electronic spectra, because of the rather small magnitude of the interaction.

The main purpose of this investigation was to investigate the possible presence of ligand–ligand interaction by a careful experimental and theoretical analysis of the vibrational spectra of dihalogenodiammineplatinum(II) complexes. The second purpose was to study the influence of *cis–trans* isomerism and of halogen substitution on the infrared spectra of these compounds.

II. Experimental

The compounds *cis*- and *trans*-[Pt(NH$_3$)$_2$X$_2$] (X = Cl, Br, I) have long been known, but it is only rather recently that their infrared spectra have been determined. Babaeva and Evstaf'eva[3] have reported the spectra of all these compounds in the NaCl region. Powell and Sheppard[4] have also reported the spectrum of *trans*-[Pt(NH$_3$)$_2$Cl$_2$] and Powell[5] that of the corresponding *cis* isomer, both in the range 4000 to 450 cm.$^{-1}$. Barrow, Krueger, and Basolo[6] have measured the spectra of *cis*- and *trans*-[Pt(NH$_3$)$_2$Cl$_2$] and their deuterated analogs from 4000 to 300 cm.$^{-1}$. Mizushima, *et al.*,[7] have also reported the infrared spectra of *cis*- and *trans*-[Pt(NH$_3$)$_2$Cl$_2$] and their palladium analogs in the NaCl region. Finally, the far-infrared spectra (460–170 cm.$^{-1}$) of *cis*- and *trans*-[Pt(NH$_3$)$_2$X$_2$] (X = Cl, Br) have recently been

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[1] This work was partly supported by a research grant, GM-10072-01, from the National Institutes of Health, Public Health Service.

[2] (a) J. Chatt, L. Duncanson, and L. Venanzi, *J. Chem. Soc.*, 4461 (1955); L. Duncanson and L. Venanzi, *ibid.*, 3841 (1960); (b) J. Chatt, L. Duncanson, B. Shaw, and L. Venanzi, *Discussions Faraday Soc.*, **26**, 131 (1958); J. Chatt, L. Duncanson, and R. Guy, *Nature*, **184**, 526 (1959).

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