field level is suspected to be of predominantly ligand character.[22] It is interesting that the first spin-allowed band appears at 13,400 cm^{-1} for Au(mnt)$_2^-$ and at 18,500 cm^{-1} for Pt(mnt)$_2^{2-}$. This gives $\Delta_1 = 16{,}900$ cm^{-1} (using $C = 3500$ cm^{-1}) for Au(III) and $\Delta_1 = 22{,}000$ cm^{-1} for Pt(II) in the mnt^{2-} case, which nicely follows the predicted Δ trend.

Some comment is in order regarding the exceptionally low position of z^2 in the ligand-field levels of PtCl$_4^{2-}$. As MTK have pointed out, neither the $xz,yz > z^2$ nor the $xz,yz \approx z^2$ result is compatible with a point-charge crystal-field calculation,[2] which gives $x^2 - y^2 > xy > z^2 > xz,yz$. Fortunately, the molecular orbital model is compatible with the very low position of z^2 in PtCl$_4^{2-}$, probably as a result of very large participation of the 6s orbital in the σ bonding. Since the 6s and 5d$_{z^2}$ bond with the same ligand combination, the large participation of the 6s orbital in the Pt(II)–Cl bonds leaves 5d$_{z^2}$ at a relatively stable position.[23] We note that the limitation of a purely d orbital set and the neglect of overlap in the ionic model is unrealistic and can easily give an incorrect ordering of levels, particularly in cases where metal d orbitals are involved with the same ligand symmetry orbitals as are the metal s and p orbitals. However, it should be stated emphatically that the ordering $x^2 = y^2 > xy > xz,yz > z^2$ need not be correct for *all* square-planar complexes. In fact, the halides probably represent the case in which z^2 is at its lowest relative position in the ligand-field level scheme. We make this suggestion because of the low spectrochemical position of halide ligands, indicating good π-donor and poor ($\sigma \rightarrow$ d)-donor capabilities. With ligands of better π-acceptor or ($\sigma \rightarrow$ d)-donor potential (or both), the z^2 level in many cases should move significantly above the xz,yz orbitals. Simple O- and N-donor ligands would be in this category, as well as CN$^-$ and CO. We note that the best available experimental evidence[3,24] gives $z^2 > xz,yz$ in the case of Ni(CN)$_4^{2-}$.

A final observation of interest is that the calculated charge distributions (see Table I) in PtCl$_4^{2-}$ and PdCl$_4^{2-}$ are not significantly different. This result is in agreement with similar conclusions concerning the relative charge distributions in the two complexes deduced from measurements of their nuclear quadrupole resonance spectra.[25,26]

Acknowledgments.—We thank the National Science Foundation for support of this research. H. B. G. thanks the Alfred P. Sloan Foundation for a research fellowship.

---

[22] R. Williams, E. Billig, J. H. Waters, and H. B. Gray, *J. Am. Chem. Soc.*, **88**, 43 (1966).

[23] It is possible, if not probable, that overlap-included MO calculations using a strictly d-orbital metal basis will also yield the ordering $xz,yz > z^2$. We simply suggest here that decreasing degrees of antibondedness of the 3a$_{1g}$ level may best be correlated with increasing 6s participation in the σ bonding.

[24] C. J. Ballhausen, N. Bjerrum, R. Dingle, K. Eriks, and C. R. Hare, *Inorg. Chem.*, **4**, 514 (1965).

[25] K. Ito, D. Nakamura, Y. Kurita, K. Ito, and M. Kubo, *J. Am. Chem. Soc.*, **83**, 4526 (1961).

[26] E. P. Marram, E. J. McNiff, and J. L. Ragle, *J. Phys. Chem.*, **67**, 1719 (1963).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASSACHUSETTS 02139

Molecular Orbital Calculations for Complexes of Heavier Transition Elements. I. Study of Parameter Variations in the Case of Tetrachloroplatinate(II)[1]

BY F. A. COTTON AND C. B. HARRIS[2]

Received August 22, 1966

The electronic ground state of PtCl$_4^{2-}$ calculated by semiempirical molecular orbital theory of the extended Hückel type is a $^1A_{1g}$ with a Pt d orbital order and occupation of $(d_{z^2})^2(d_{xz},d_{yz})^4(d_{xy})^2(d_{x^2-y^2})^0$. This result was obtained over a wide range of variations in the Pt valence state ionization potentials, the Pt wave functions, and the Wolfsberg–Helmholz factor in both the Mulliken–Wolfsberg–Helmholz and the Ballhausen–Gray approximations. The numerical dependence of the Pt–Cl bond order and the one-electron molecular orbitals of PtCl$_4^{2-}$ have been examined as functions of variations in the Pt 6s, 6p, and 5d wave functions, the corresponding valence state ionization potentials, and the weight given to the off-diagonal terms in the Hamiltonian matrix. A method is outlined for computing Slater-type orbital (nodeless wave functions) overlap integrals that accurately approximate overlap integrals between self-consistent field wave functions. Using what appear to be optimum choices of parameters, results in excellent agreement with the nuclear quadrupole coupling constant for ^{35}Cl are obtained.

Introduction

Previous studies of the electronic structure of PtCl$_4^{2-}$ have led to several ambiguities concerning the splitting of the Pt 5d orbitals. Ballhausen and Gray[3] have proposed a Pt 5d orbital order of $(d_{xz};d_{yz})$, (d_{z^2}), (d_{xy}), $(d_{x^2-y^2})$. Fenske, Martin, and Ruedenberg[4] proposed the same order by considering the problem in terms of electrostatic crystal field theory. Chatt, Gamlen,

---

[1] This work was supported by the U. S. Atomic Energy Commission.

[2] N.I.H. Predoctoral Fellow, 1964–1966; A.E.C. Postdoctoral Fellow, 1966–1967.

[3] H. B. Gray and C. J. Ballhausen, *J. Am. Chem. Soc.*, **85**, 260 (1963).

[4] R. F. Fenske, D. S. Martin, and K. Ruedenberg, *Inorg. Chem.*, **1**, 441 (1962).

and Orgel[5] and more recently Martin[6,7] have proposed a (d_{z^2}), (d_{xz};d_{yz}), (d_{xy}), ($d_{x^2-y^2}$) orbital order. Unfortunately, the electronic spectrum of K_2PtCl_4 both in the solid state[7-10] and in various solvents[5] can be interpreted using either splitting scheme. In an attempt to resolve these ambiguities, Martin[6] has studied the vibrational fine structure of the polarized spectrum at low temperatures and has concluded that the latter orbital sequence is the more probable. Mortensen,[10] on the other hand, has briefly reported the polarized spectrum at 5°K and has stated, without detailed discussion, that the results (which closely resemble Martin's room-temperature results) are in agreement with Gray and Ballhausen's ordering of the levels.

For a number of reasons, we have wished to devise a practical even if crude scheme for carrying out extended Hückel-type molecular orbital calculations on complexes of the heavy transition elements (*e.g.*, those which form metal atom cluster compounds and their neighbors). In view of the facts that (1) the $PtCl_4^{2-}$ problem is inherently interesting and important, (2) there is a substantial possibility that experimental studies will, in due course, resolve the question of the d-level order and, (3) the square or nearly square MCl_4 grouping recurs often in heavy metal complexes (including metal atom cluster compounds[11] such as $Re_2Cl_8^{2-}$), the $PtCl_4^{2-}$ ion seemed to be a suitable example with which to explore the possibilities for devising a useful computational approach.

Method of Calculation

The LCAO–MO theory used in this case is a modification of the extended Hückel MO theory. The modification is a stringent but necessary restriction on the values of the "molecular" valence state ionization potentials,[12] H_{ii}, of the basis set orbitals. In every calculation all overlaps, S_{ij}, are evaluated. In our treatment no assumption is made as to the extent of hybridization of the ligand and/or metal wave functions. This ensures that the variational principle,[13] $\partial E/\partial c_i = 0$, where c_i is the MO coefficient and E is the MO eigenvalue, is satisfied for all atomic orbitals in the basis set. These conditions and the LCAO assumption,[14] *i.e.*, $\Psi^j = \sum_i c_i^j \phi_i$ where Ψ^j is the jth MO and ϕ_i is the ith atomic orbital, leads directly to the familiar condition for the secular determinant, *i.e.*

$$\det\left|H_{ij} - ES_{ij}\right| = 0 \tag{1}$$

where the H_{ij} are the usual Hamiltonian matrix elements between the ϕ_ith the ϕ_jth atomic orbitals and S_{ij} is the overlap integral between these atomic orbitals.

Choice of Atomic Orbitals and the Evaluation of Overlap Integrals.—A basis set of 25 orbitals, the Pt 6s, 6p, and 5d and the Cl 3s and 3p atomic orbitals, were used to construct the molecular orbitals. We assumed that the nonvalence electrons do not participate in bonding and these, together with the nuclei, form a core potential that is invariant to the interactions between the valence shell electrons.

The atomic orbitals were expressed as nodeless Slater-type[15] orbitals (STO) of the form

$$\Psi(n,l,m) = Nr^{n-1}\exp(-\alpha_i r)\,Y_l^m(\theta,\varphi) \tag{2}$$

where N is the normalization coefficient, α_i is the shielding parameter, and $Y_l^m(\theta,\varphi)$ is the usual spherical harmonic.

The shielding parameters, α_i, were chosen in the following fashion to best approximate overlaps between self-consistent field (SCF) wave functions. The Hartree–Fock wave functions of Watson and Freeman were used for Cl^0 and Cl^-.[16] Herman–Skillman wave functions[17] for the Pt^0 6s and 5d orbitals were used; the 6p wave function was approximated by assuming a slightly smaller α than for the 6s. First an interpolated numerical radial wave function for $Cl^{1/2-}$ was obtained from SCF wave functions of Cl^0 and Cl^-.[16] Numerical overlap integrals between the SCF wave functions for "*cis*" Cl 3s–3s, 3p–3p, and 3s–3p orbitals were then calculated. The α's in eq 2 were varied so that the overlap integrals between the STO wave functions differed insignificantly ($\leqslant 4\%$) from those obtained from SCF wave functions. In this way the Cl 3s and 3p shielding parameters were fixed. The same procedure was followed for Pt^0–$Cl^{1/2-}$ overlap integrals of the type 6s–3s, 6s–3p, 5d–3s, and 5d–3p; however, only the Pt^0 α_i's needed to be varied. The shielding parameters so obtained were: Cl(3s), 2.245; Cl(3p), 1.850; Pt(5d), 3.150; Pt(6s), 2.600; Pt(6p), 2.450. The overlap integrals obtained using these parameters[18] are on file with the American Documentation Institute, and Figure 1 shows the coordinate system used.

We have assumed that the overlap integrals do not change appreciably with variation of the charge distribution in the course of self-consistent charge refinement. The error inherent in such an assumption can be estimated if we assume that the Pt wave functions have a dependence on charge and configuration similar

---

(5) J. Chatt, G. A. Gamlen, and L. E. Orgel, *J. Chem. Soc.*, 486 (1958).

(6) D. S. Martin, M. A. Tucker, and A. J. Kassman, *Inorg. Chem.*, **4**, 1682 (1965).

(7) D. S. Martin and C. A. Lenhardt, *ibid.*, **3**, 1368 (1964).

(8) S. Yamada, *J. Am. Chem. Soc.*, **73**, 1182 (1951).

(9) P. Day, H. F. Orchard, H. F. Thompson, and R. J. R. Williams, *J. Chem. Phys.*, **42**, 1973 (1965).

(10) O. S. Mortensen, *Acta Chem. Scand.*, **19**, 1500 (1965).

(11) F. A. Cotton and C. B. Harris, *Inorg. Chem.*, **4**, 330 (1965); see also F. A. Cotton and T. E. Haas, *ibid.*, **3**, 10 (1964), for a general discussion of the structures of metal atom cluster compounds as aggregates of MX_4 units.

(12) The distinction between molecular valence state ionization potentials, H_{ii}, and atomic valence state ionization potentials, A_{ii}, is made in order to discuss the energy of the ith atomic orbital in a molecular and free ion field, respectively.

(13) R. Daudel, R. Lefebvre, and C. Moser, "Quantum Chemistry: Methods and Applications," Interscience Publishers, New York, N. Y., 1959.

(14) J. H. Van Vleck, *J. Chem. Phys.*, **2**, 22 (1934).

(15) J. C. Slater, *Phys. Rev.*, **36**, 57 (1930).

(16) R. E. Watson and A. J. Freeman, *ibid.*, **120**, 1125 (1960); **123**, 521 (1961).

(17) F. Herman and S. Skillman, "Atomic Structure Calculations," Prentice-Hall, Englewood Cliffs, N. J., 1963.

(18) A tabulation of overlap integrals and eigenvectors for the basis set given in Table V has been deposited as Document No. 9155 with the ADI Auxiliary Publications Project Photoduplication Service, Library of Congress, Washington, D. C. 20540. A copy may be secured by citing the document number and by an advanced remittance ($1.25 for photoprints or $1.25 for 35-mm microfilm) payable to: Chief, Photoduplication Service, Library of Congress.

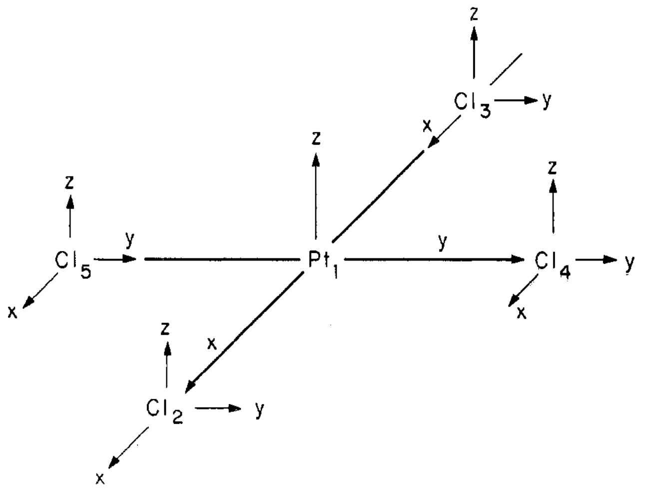

Figure 1.—$PtCl_4^{2-}$ molecular coordinate system used to calculate the overlap integrals. Subscript numbers correspond to the identifying numbers used in Table V.

to some other known wave functions. The wave functions of Pt are not available for configuration and charge states other than the Pt^0 state $5d^96s^1$. Ros[19] has already given simple diatomic overlap integrals for a limited number of charge distributions and configurations of $CuCl_4^{2-}$. Since the 3d to Cl overlaps were not listed for Cu $d^{10}s^1$ and $d^{10}p^1$ configurations, we restricted the comparison to Cu 4s and 4p to Cl overlap integrals. Table I lists the overlap integral ratios $Cu^0–Cl^{0.5-}:Cu^+–Cl^{0.75-}$ and $Cu^0–Cl^{0.5-}:Cu^{0.44}–Cl^{0.61-}$ for the orbitals and configurations listed. Since a Pt charge of +0.439 was obtained after full charge refinement, we concluded that although a 9% error is introduced in certain cases (6p–3s; 6s–3s) by neglecting to recalculate overlap integrals as a function of charge, the average error is only 5 to 6%.

TABLE I

Cu–Cl OVERLAP[a] INTEGRAL RATIOS OVER CHARGE AND CONFIGURATION

Configuration	ϕ_i–ϕ_j	$Cu^0–Cl^{0.50-}$: $Cu^+–Cl^{0.75-}$	$Cu^0–Cl^{0.50-}$: $Cu^{0.44}–Cl^{0.61-}$	%
$3d^44s^2$	4s–3s	1.16	1.09	9
	4s–$3p_\sigma$	0.96	0.98	2
$3d^94p^2$	4p–3s	1.07	1.04	4
	4p–$3p_\sigma$	0.83	0.91	9
	$4p_\pi$–$3p_\pi$	0.93	0.96	4

[a] All values calculated from ref 19.

Evaluation of the Diagonal Matrix Elements, H_{ii}.—H_{ii} is the energy of an electron in the ith atomic orbital moving in the field of the nuclei and other electrons in the molecule. In terms of the Hamiltonian operator and orthogonal wave functions, χ_i, these matrix elements can be expressed in the Dirac notation as

$$H_{ii} = \langle\chi_i|-{}^1/_2\nabla_i^2|\chi_i\rangle - \langle\chi_i|Z_\alpha/r_\alpha|\chi_i\rangle + \langle\chi_i|\sum_{i>i}\chi_j\chi_j/r_{ij}|\chi_i\rangle - \langle\chi_i|\sum_{\beta\neq\alpha}Z_\beta/r_\beta|\chi_i\rangle + \langle\chi_i|\sum_{\substack{k>i\\k\neq j}}\chi_k\chi_k/r_{ik}|\chi_i\rangle \tag{3}$$

where ${}^1/_2\nabla_i^2$ is the kinetic energy operator, Z_α/r_α is the nuclear attraction operation of the αth nucleus on which the ith atomic orbital is centered, and $\sum \chi_j\chi_j/r_{ij}$ are the electron repulsion operators where the jth atomic orbital is on the α nucleus. k designates atomic orbitals centered on the β nuclei.

If we define the free-ion contributions to H_{ii}, namely the first three terms in eq 3, as A_{ii} and the remaining terms as M_{ii} which are the contributions to H_{ii} from other atoms in the molecule, we can reexpress H_{ii} as

$$H_{ii} = A_{ii} + M_{ii} \tag{4}$$

For specific free-ion electron configurations the A_{ii}'s can be explicitly evaluated. They have, however, been traditionally estimated by the valence state ionization potentials ($VSIP_{ii}$).

The A_{ii}'s for the process $Cl^0 \rightarrow Cl^+ + e^-$ were estimated as the $VSIP$'s given by Hinze and Jaffé[20] for the 3s and 3p orbitals in the configurations $sp^2p^2p^2$ and $s^2p^2p^2p$, respectively.

The A_{ii}'s for the process $Pt^0 \rightarrow Pt^+ + e^-$ were estimated by averaging the spectral states and multiplicities given by Moore[21] for the configurations and processes listed in Table II. Since the spectral states of Pt^{2+} have not been recorded, we have estimated the A_{ii}'s for the process $Pt^+ \rightarrow Pt^{2+} + e^-$ according to the following considerations.

TABLE II

Pt STATES AND PROCESSES AVERAGED[a] TO OBTAIN A_{ii} FOR $Pt^0 \rightarrow Pt^+ + e^-$

i	Initial state		Final state + orbital	Pt^0 $\langle A_{ii}\rangle$, ev
6s	$5d^96s^1$	→	$5d^9$ + 6s	
	$5d^86s^2$	→	$5d^86s$ + 6s	−9.80
	$5d^86s6p$	→	$5d^86p$ + 6s	
6p	$5d^86s6p$	→	$5d^86s$ + 6p	−5.35
	$5d^96p$	→	$5d^9$ + 6p	
5d	$5d^{10}$	→	$5d^9$ + 5d	
	$5d^96s$	→	$5d^86s$ + 5d	−10.61
	$5d^86s^2$	→	$5d^76s^2$ + 5d	
	$5d^96p$	→	$5d^86p$ + 5d	

[a] All states were averaged over multiplicities and were obtained from ref 21.

Zerner and Gouterman[22] have obtained $VSIP$'s for many of the first-row transition metals, M. They found that the $VSIP$'s for M^+ were about 10 ev higher than for M^0 for 4s and 3d electrons and about 7 ev higher for 3p electrons. Since the ionization potentials[21] for Ni^+, Pd^+, and Pt^+ are 10.52, 11.09, and 9.56 ev higher than the ionization potentials for Ni^0, Pd^0, and Pt^0, we feel that it is reasonable to expect that the behavior of the $VSIP$'s of the Pt states is similar to the behavior of those for metals of the first row. Therefore, the approximation was made that the A_{ii}'s for Pt^+ were 10 ev higher than the A_{ii}'s of Pt^0 for the 6s and 5d atomic orbitals and 7 ev higher for the 6p atomic orbitals.

---

(19) P. Ros, Thesis (Chemistry), Eindhoven, Holland, 1964.

(20) J. Hinze and H. H. Jaffé, *J. Am. Chem. Soc.*, **84**, 540 (1962).

(21) C. E. Moore, "Atomic Energy Levels," U. S. National Bureau of Standards Circular 467, U. S. Government Printing Office, Washington, D. C., 1949 and 1952.

(22) M. Zerner and M. Gouterman, *Theoret. Chim. Acta*, **4**, 44 (1966).

In principle the multicenter integrals of M_{ii} can be calculated, but this would be a formidable undertaking requiring an unjustifiable amount of computer time. They can, however, in part be estimated by the point charge approximation[23]

$$M_{ii} \approx \sum_{\beta \neq \alpha} Z_{\text{eff}}/r_\beta \tag{5}$$

where Z_{eff} is the effective point charge of the β nucleus· The sum is over all nuclei except the nucleus (α) on which the ith atomic orbitals is centered. The internuclear distance between the α and β nuclei in Bohr radii is r_β.

Table III lists the values of A_{ii} and M_{ii} resulting from such an approximation for the Pt 6s, 6p, and 5d atomic orbitals. Δ_{ii}, defined in Table III, is significant in two respects: (1) it is larger for the more covalent Pt–Cl bonds (*i.e.*, Pt charge closer to zero); (2) it is larger for the more diffuse 6p orbitals. These results suggest that Δ_{ii} is in some way related to the penetration of the Pt wave function into the Cl inner core, an effect which is neglected in the point charge approximation of M_{ii}. The potential field around the Cl atom changes from negative to positive at some point approaching the Cl nucleus; therefore, the larger the amplitude of the Pt wave function, the greater will be the stabilization of the M_{ii} from the positive portion of the Cl potential field. Thus, the Pt 6p atomic orbital should be stabilized more by this effect than the 6s and 5d orbitals.

TABLE III

H_{ii}'S (IN EV) FOR PLATINUM AS A FUNCTION OF CHARGE

Pt charge ($\equiv q$)	0	0.5	1.0	1.5	2.0
Cl charge	−0.500	−0.625	−0.750	−0.875	−1.0
Point charge approx for M_{ii}	12.3	15.4	18.5	21.7	24.7
A_{ii}					
5d	−10.61	−15.61	−20.61	−25.61	−30.61
6p	−5.35	−10.35	−15.35	−20.35	−25.35
Δ_{ii}[a]					
5d	−12.3	−10.4	−8.5	−6.7	−4.7
6p	−15.3	−13.4	−11.5	−9.7	−7.7

[a] $\Delta_{ii} = A_{ii}(\text{Pt}^0) - A_{ii}(\text{Pt}^q) - M_{ii}$.

Rather than neglect this penetration correction, Δ_{ii} was assumed to be functionally related to it. The molecular terms H_{ii} corresponding to the Pt^+ states were therefore restricted to values 1 ev higher than values for the corresponding Pt^0 states. The Cl orbital energies were also assumed to change by 1 ev per unit change in Cl charge. All intermediate values were obtained by interpolation. This is a stringent constraint on the H_{ii}'s. However, in a later section of this paper it will be shown that the one-electron molecular orbitals can only be justified empirically if one does in fact impose such a constraint.

Evaluation of the Off-Diagonal Matrix Elements, H_{ij}.—The H_{ij}'s are the usual Hamiltonian matrix elements between the ith and jth atomic orbitals. They have been evaluated semiempirically by the Mulliken–Wolfsberg–Helmholtz (MWH) approximation,[24,25] eq 6. K is the Wolfsberg–Helmholtz[25] factor

$$H_{ij} \approx KS_{ij}(H_{ii} + H_{jj})/2 \tag{6}$$

and S_{ij} is the overlap integral between the ith and jth atomic orbitals.

This approximation was used for the main body of the calculations. However, the MWH approximation was compared to the Ballhausen–Gray[26] (BG) approximation (eq 7) for various values of K and K'. The

$$H_{ij} \approx -K'S_{ij}(H_{ii}H_{jj})^{1/2} \tag{7}$$

results of this variation are listed in Table IV for several molecular properties.

TABLE IV

MOLECULAR PROPERTIES CALCULATED EMPLOYING VARIOUS VALUES OF K AND K' (EQ 6 AND 7)

K	Pt charge	Pt–Cl bond order	$^1b_{2g}{}^* \rightarrow {}^1b_{1g}{}^*$ tran energy, ev
1.6	0.813	0.293	2.70
1.8	0.439	0.403	3.74
2.0	0.138	0.476	4.80
2.2	−0.116	0.529	5.90

K'	Pt charge	Pt–Cl bond order	$^1b_{2g}{}^* \rightarrow {}^1b_{1g}{}^*$ tran energy, ev
1.5	1.23	0.057	2.14
1.7	0.849	0.220	3.11
2.0	0.397	0.371	4.62
2.2	0.157	0.436	5.68

Computation Procedure.—Using the wave functions and the H_{ii} values listed in Table V the secular determinant (eq 1) was solved[27] for a full basis set of orbitals. The eigenvalues and eigenvectors were ob-

TABLE V

INPUT PARAMETERS

Orbital	Atom	Orbital type	Coordinates, A			Orbital exp	H_{ii}
			X	Y	Z		
1	1	6s	0	0	0	2.600	−9.80
2	1	$6p_z$	0	0	0	2.450	−5.35
3	1	$6p_x$	0	0	0	2.450	−5.35
4	1	$6p_y$	0	0	0	2.450	−5.35
5	1	$5d_{z^2}$	0	0	0	3.150	−10.61
6	1	$5d_{xz}$	0	0	0	3.150	−10.61
7	1	$5d_{x^2-y^2}$	0	0	0	3.150	−10.61
8	1	$5d_{xz}$	0	0	0	3.150	−10.61
9	1	$5d_{xy}$	0	0	0	3.150	−10.61
10	2	3s	2.33	0	0	2.245	−24.00
11	2	$3p_z$	2.33	0	0	1.850	−15.10
12	2	$3p_x$	2.33	0	0	1.850	−15.10
13	2	$3p_y$	2.33	0	0	1.850	−15.10
14	3	3s	−2.33	0	0	2.245	−24.00
15	3	$3p_z$	−2.33	0	0	1.850	−15.10
16	3	$3p_x$	−2.33	0	0	1.850	−15.10
17	3	$3p_y$	−2.33	0	0	1.850	−15.10
18	4	3s	0	2.33	0	2.245	−24.00
19	4	$3p_z$	0	2.33	0	1.850	−15.10
20	4	$3p_y$	0	2.33	0	1.850	−15.10
21	4	$3p_y$	0	2.33	0	1.850	−15.10
22	5	3s	0	−2.33	0	2.245	−24.00
23	5	$3p_z$	0	−2.33	0	1.850	−15.10
24	5	$3p_x$	0	−2.33	0	1.850	−15.10
25	5	$3p_y$	0	−2.33	0	1.850	−15.10

---

[23] J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953).

[24] R. Mulliken, *J. Chim. Phys.*, **46**, 497 (1949).

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

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

[27] A modified Fortran program written by Dr. R. Hoffmann was used. Orbital α_i values were calculated by a Mad Program "WAVWF" written by C. B. Harris.

tained, and a Mulliken population analysis of the eigenvectors yielded the reduced overlap populations (bond orders) and charge distributions. The calculations were cycled n times such that the differences between the Pt charge at the $(n-1)$th cycle was less than 0.001 charge unit from the nth cycle. All calculations were performed at the Massachusetts Institute of Technology Computation Center on the IBM 7094.

Results

K can be considered as a parameter that artificially controls the extent of charge flow from the ligand to the metal in the bonding region. Its value directly affects the calculated covalent character of the metal–ligand bond. Thus, the calculated molecular charge densities, bond orders, and electronic transition energies are very sensitive to the choice of K.

Table IV lists the metal charge, metal–ligand bond order, and ${}^1b_{2g}{}^* \rightarrow {}^1b_{1g}{}^*$ transition energy for various values of K in the MWH approximation and K' in the BG approximation. It is unlikely that Pt has a charge less than +0.1; therefore, an upper limit to $K = 2.0$ and $K' = 2.2$ can be assigned. The lower limits are more difficult to ascertain. If Pauling's electroneutrality principle[28] is qualitatively correct, the Pt charge should be lowered to at least +1.0. This would then place lower limits on K and K' at 1.5 and 1.6, respectively.

Figure 2 is a partial plot of the energy level diagram as a function of K. The dependence on K' is the same as on K except that energies are slightly shifted down (0.5 ev) for $K' = K$.

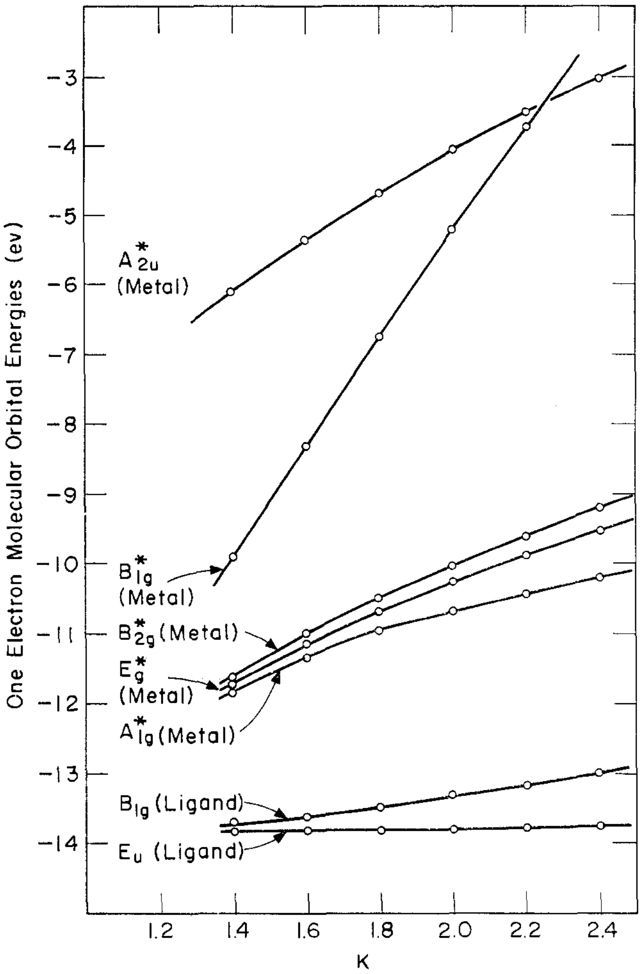

Figure 2.—Energies of the one-electron MO's *vs.* the Helmholz factor K.

Several features are apparent from this diagram. First, there is a strong K dependence of the energy of the first nonoccupied antibonding orbital ($b_{1g}{}^*$). The observed ${}^1b_{2g}{}^* \rightarrow {}^1b_{1g}{}^*$ transition energy,[5] however, falls nicely within the above limits of K at a value of about 1.7 to 1.8.

Secondly, there is no change in the order of the 5d orbitals over large ranges of K. Specifically, the $a_{1g}{}^*$ ($5d_{z^2}$) orbital is lower in energy than the $e_g{}^*(5d_\pi)$ orbital at all values of K from 1.4 to 2.8.

Finally, we find the first orbital above the $b_{1g}{}^*$ ($5d_\sigma$) is an $a_{2u}{}^*$ ($6p_\pi$) orbital. Gray and Ballhausen,[3] however, placed the $a_{1g}{}^*$ (6s) orbital in this position. Intuitively, one would expect the metal $6p_\pi$ orbital to be very nearly nonbonding; consequently, the energy of the $a_{2u}{}^*$ would be very near that of the atomic 6p orbitals. This is in fact clearly the case. The atomic 6s orbital mixes significantly with the ligand σ orbitals, resulting in a much higher energy for the molecular $a_{1g}{}^*$ orbital.

Since the metal 5d orbitals transform under different irreducible representations in D_{4h} symmetry, one could choose a different value of K for each orbital ($5d_\sigma$, $5d_\pi$, $5d_\delta$). This choice should, however, be governed by the π character of the overlap integrals (Pt–Cl)[29] such that the π interactions have larger K's than the σ interactions. This would result in a lowering of the $a_{1g}{}^*$ energy relative to the $e_g{}^*$. However, no inversion of the $e_g{}^*$ and $b_{2g}{}^*$ levels would occur. Figure 3 is a partial one-electron molecular orbital diagram in which $K(\sigma) = 1.75$ and $K(\pi) = 2.00$.

Variation of the Metal Shielding Parameters, α_i.—The Pt 5d, 6s, and 6p shielding parameters were varied over the ranges listed in Table VI. A plot of the total electronic energy of $PtCl_4{}^{2-}$ revealed an energy minimum extremely near the values of the shielding parameter determined by our method, as shown in Figure 4. Furthermore, this energy minimum corresponded to a maximum in the reduced overlap population (bond order) between Pt and Cl.

The 5d orbital splittings are extremely sensitive to the radial part of the Pt wave functions as shown in Figure 5. Note also that while there is no inversion of any of the occupied 5d-type molecular orbitals, the energy of the first nonoccupied antibonding molecular orbital ($b_{1g}{}^*$) is especially sensitive to the choice of the values of the α_i's.

Variation of the Pt Diagonal Matrix Elements, H_{ii}'s.—The hardest parameters to estimate are the diagonal

---

(28) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960.

(29) L. C. Cusachs, "Sur L'Approximation de Wolfsberg-Helmholz," Battelle Memorial Institute, Geneva, 1964.

TABLE VI

PT SHIELDING PARAMETER FOR POINTS IN FIGURE 5

α_i's	L2	L1	0	S1	S2	S3
6s	3.60	3.10	2.60	2.20	1.95	1.70
6p	3.45	2.95	2.45	2.05	1.80	1.55
5d	4.15	3.65	3.15	2.75	2.50	2.25

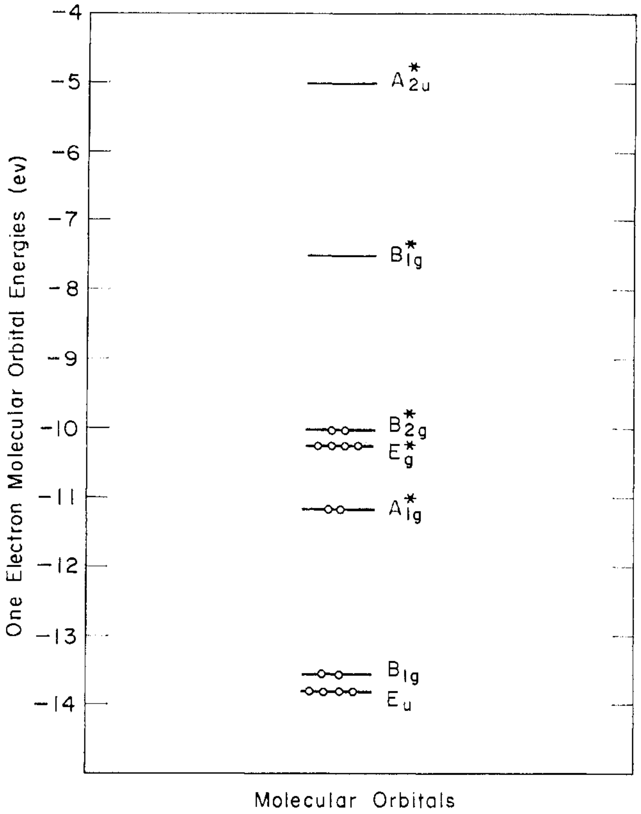

Figure 3.—Partial one-electron MO diagram of $PtCl_4^{2-}$: $K(\sigma) = 1.75$; $K(\pi) = 2.00$.

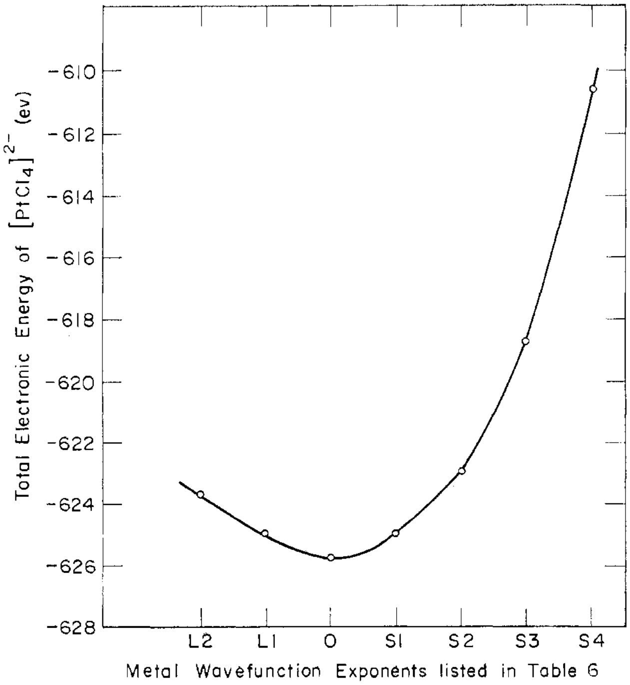

Figure 4.—Total electronic energy of $PtCl_4^{2-}$ vs. Pt orbital exponents.

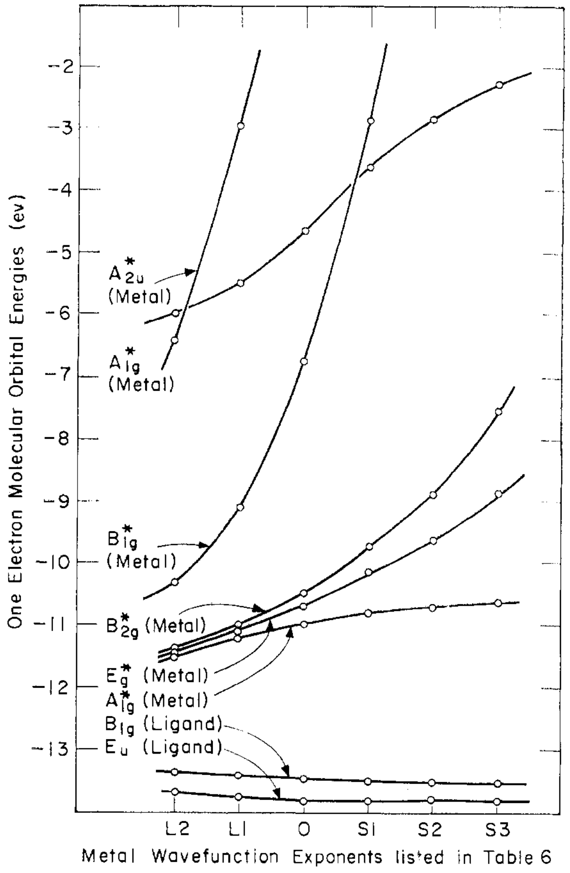

Figure 5.—One-electron MO's vs. Pt orbital exponents.

matrix elements, H_{ii}. In most first-row transition metals the free-ion contribution, A_{ii} (eq 4) to H_{ii} can be easily calculated from data given in Moore's tables[21] for integral charge distributions. Analytic calculation of the multicenter integrals, M_{ii} (eq 4), is a formidable problem requiring an unjustifiable amount of computer time. In lieu of any approximations, the H_{ii}'s of Pt were systematically varied in an attempt to arrive at a simple empirical method of estimating these terms.

Figure 6 is a partial plot of the one-electron molecular orbitals vs. assumed H_{ii}'s for Pt^0. The values, Q (0 through −15 ev), are added to the Pt^+ H_{ii}'s listed in Table V. If one were to assume that the Pt^+ H_{ii}'s were 10 ev higher than the corresponding matrix elements for Pt^0, then region I would be where the calculation is self-consistent in charge. The molecular orbital diagram is erroneous at this point for the following reasons: (1) the ${}^1b_{2g}{}^* \rightarrow {}^1b_{1g}{}^*$ transition energy is much too large. (2) The $a_{1u}{}^*$ molecular orbital has a lower energy than the $b_{2g}{}^*$ orbital. (3) The ligand b_{1g} molecular orbital is much too high in energy. (4) The energy difference between the $b_{2g}{}^*$ and $e_g{}^*$ molecular orbitals is too large. The above conclusions are substantiated by spectral studies.

A more reasonable interpretation of the spectra can be made in region II of Figure 6. This is, in fact, the region where we feel the H_{ii}'s would be most nearly correct based on our earlier arguments. In region II the Pt^+ H_{ii}'s are only 1–2 ev above the Pt^0 H_{ii}'s. This

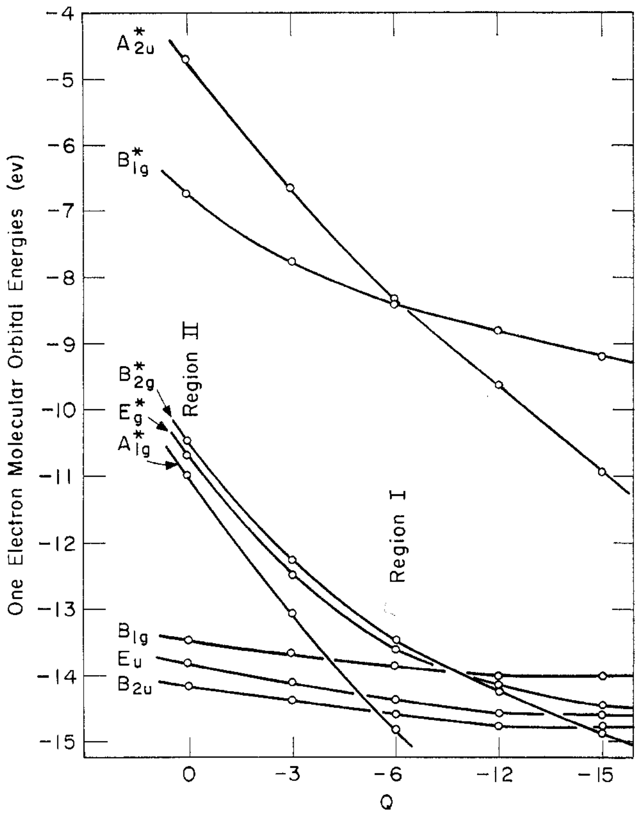

Figure 6.—One-electron MO's *vs.* the diagonal matrix elements (Table V) plus Q as a function of Q.

is consistent with the behavior of carbon and boron as pointed out by Lipscomb[30] and with that of copper as shown by Ros.[19]

Furthermore, the energy minimum in Figure 4 in effect says that the final H_{ii}'s, obtained after charge refinement, are the "best" values for the wave functions used.

Spectra.—We wish to emphasize that it is not the purpose of this study to attempt accurate *ab initio* computations of the positions of absorption bands in $PtCl_4^{2-}$, as we feel that the present status of semiempirical molecular orbital theory, especially when heavier metals are involved, does not lend itself well to this end. One can, however, obtain qualitative information from MO theory that may be of some assistance in spectral assignments. The calculated transition energies are listed in Table VII. These are calculated from Figure 3. The eigenvectors for $K = 1.80$ have been filed with the American Documentation Institute.[18] The eigenvalues ($K = 1.80$) and occupations are listed in Table VIII.

TABLE VII

CALCULATED TRANSITION ENERGIES FROM FIGURE 3

Transition	Energy, ev	Transition	Energy, ev
${}^1b_{1g}{}^* \rightarrow {}^1b_{2g}{}^*$	2.5	${}^1b_{2g}{}^* \rightarrow {}^1a_{2u}{}^*$	5.0
${}^1e_g{}^* \rightarrow {}^1b_{1g}{}^*$	2.7	${}^1e_g{}^* \rightarrow {}^1a_{2u}{}^*$	5.2
${}^1a_{1g}{}^* \rightarrow b_{1g}{}^*$	3.6	${}^1a_{1g}{}^* \rightarrow {}^1a_{2u}{}^*$	6.1

TABLE VIII

$PtCl_4^{2-}$ ONE-ELECTRON MO EIGENVALUES

MO	Energy, ev	Occupation	MO	Energy, ev	Occupation
1	8.51	0	14	−14.58	2
2	8.51	0	15	−14.58	2
3	4.24	0	16	−14.71	2
4	−4.70	0	17	−14.82	2
5	−6.76	0	18	−15.09	2
6	−10.49	2	19	−15.09	2
7	−10.68	2	20	−15.41	2
8	−10.68	2	21	−16.10	2
9	−10.98	2	22	−23.29	2
10	−13.49	2	23	−23.50	2
11	−13.83	2	24	−23.50	2
12	−13.83	2	25	−24.04	2
13	−14.18	2			

Sum = −625.73

The relative energies of the $e_g{}^*$ *vs.* $a_{1g}{}^*$ and $a_{1g}{}^*$ *vs.* $a_{2u}{}^*$ are opposite to those proposed by Gray and Ballhausen.[3] This is presumably a result of their method of obtaining hybrid orbitals *via* the minimization of the $VSIP/S_{ij}(\theta)$ of the atomic orbitals. The variational principle is not rigidly satisfied in their method for those orbitals that mix in the same irreducible representation. As a result, the energy of the $a_{1g}{}^*$ MO is higher in their MO diagram than in ours. All wave functions in our calculation at least rigidly satisfy the variational principle for all atomic orbitals in the basis set.

Nature of the Pt–Cl Bond.—The Pt–Cl bond is, classically, a two-center electron-pair bond. It is, however, more appropriate to discuss the ionicity or covalency of the Pt–Cl bond in the framework of MO theory. The amount of covalency or bond order, as defined by Mulliken,[31] can be calculated from the overlap integrals and the eigenvectors of the molecular orbitals. Table IX lists the various contributions to the Pt–Cl bond covalency. Several things are apparent from Table IX: (1) The main contributions to the Pt–Cl bond order are from the interaction of the Pt 6s, $6p_\sigma$, and $5d_\sigma$ with Cl $3p_\sigma$ atomic orbitals. (2) The interactions of 6s, $6p_\sigma$, and $5d_\sigma$ with Cl $3s_\sigma$ are approximately equal but only contribute one-third that of (1) to the covalency. (3) The interactions of Pt $5d_\pi$ and Pt $6p_\pi$ to Cl $3p_\pi$ atomic orbitals are slightly antibonding and constitute at best a weak π field.

TABLE IX

Pt–Cl BOND ORDER CONTRIBUTIONS

	Cl			
Pt	3s	3p(σ)	$3p_y$	$3p_z$
6s	0.023	0.112	...	...
6p(σ)	0.040	0.132	...	...
$6p_y$	...	...	−0.005	...
$6p_z$	...	...	...	0.022
$5d_{x^2-y^2}$	0.011	0.094	...	...
$5d_{z^2}$	0.002	0.008	...	...
$5d_{xz}$	...	...	...	−0.018
$5d_{xy}$	...	...	−0.017	...

---

(30) M. D. Newton, F. P. Boer, W. E. Palke, and W. N. Lipscomb, *Proc. Natl. Acad. Sci. U. S.*, **53**, 1089 (1965); W. N. Lipscomb, private communication.

(31) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1841 (1955); **23**, 1833 (1955).

By summing all the above contributions to the covalency, one obtains a total Pt–Cl bond order. This is 0.403 and is almost entirely σ in character. It should be emphasized, however, that the number 0.403 represents the covalency of the Pt–Cl bond. One minus this covalency is, then, the ionicity.

The covalency of the Pt–Cl bond in $PtCl_4^{2-}$ has been measured by nuclear quadrupole resonance (nqr).[32] Marrom, McNiff, and Ragle[33] estimated a covalency of 0.39 and a Pt charge of +0.44 using the usual Townes–Dailey treatment. We calculate a Pt charge of +0.439, using the input parameters of Table V and $K = 1.8$. The agreement is remarkably good, but perhaps open to question due to the assumptions inherent in the application of the Townes–Dailey equation to data.

However, we have recently derived an equation[34] which permits direct calculation of the quadrupole coupling constant and asymmetry parameter from the LCAO-MO eigenvectors and overlap integrals. Using our results for $PtCl_4^{2-}$ we obtain $eQq = 34$ Mc (for ^{35}Cl), compared to the experimental value of 36.1 Mc. Thus, insofar as the charge distribution–covalence criterion is concerned, the present treatment apparently gives very reliable results.

We predict the ^{35}Cl asymmetry parameter, η, equal to 0.072 with the **x** direction of the field gradient tensor perpendicular to the plane of the $PtCl_4^{2-}$ moiety.

---

[32] T. P. Das and E. L. Hann, "Nuclear Quadrupole Resonance Spectroscopy, Academic Press Inc., New York, N. Y., 1958.

[33] E. P. Marrom, E. J. McNiff, and J. L. Ragle, *J. Phys. Chem.*, **67**, 1719 (1963).

[34] F. A. Cotton and C. B. Harris, *Proc. Natl. Acad. Sci. U. S.*, **56**, 12 (1966).

Contribution from the Department of Chemistry,
Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Molecular Orbital Calculations for Complexes of Heavier Transition Elements. II. Hexachloro Complexes of Tetravalent Rhenium, Osmium, Iridium, and Platinum[1]

By F. A. Cotton and C. B. Harris[2]

Received August 22, 1966

Extended Hückel calculations, employing the Mulliken–Wolfsberg–Helmholz approximation for the off-diagonal elements of the Hamiltonian matrix, have been carried out for the $ReCl_6^{2-}$, $OsCl_6^{2-}$, $IrCl_6^{2-}$, and $PtCl_6^{2-}$ ions. One of the key features of the procedure was the use of orbital energies for the metal ions very close to those of the uncharged atoms and a very moderated dependence (1 ev/unit charge) of the metal d-orbital energies on effective charge of the metal atom instead of the large (~10 ev/unit charge) dependence which occurs for the free, gaseous metal ions. This moderated dependence is attributable to the molecular environment of the metal ion. A previously described procedure for fitting single Slater-type orbitals to give overlaps practically equal to those obtained with SCF orbital functions was also used. The results obtained are in generally satisfactory agreement with experiment in regard to d-orbital splittings, charge-transfer spectra, and, most particularly, charge distribution and metal–ligand covalence as implied by esr and nqr results. The good agreement in the latter respects is due primarily to the moderated dependence of orbital energy on charge and constitutes good evidence for the reasonableness of this part of the procedure.

Introduction

In the preceding paper[3] a molecular orbital method was developed and applied to the calculation of the molecular properties of $PtCl_4^{2-}$. A method for the interpretation of nuclear quadrupole resonance, based on the principles of molecular orbital theory, has been derived recently[4] and its applicability to the series MCl_6^{2-} (M = Re(IV), Os(IV), Ir(IV), and Pt(IV)) mentioned. This paper provides the details of the MO calculations for this series of complexes and of the application of these MO results to the verification and prediction of molecular properties associated with these molecules. This particular series of complexes was selected because of the opportunity thus provided to examine the effect of a steady increase in the atomic number of the metal ion in a homologous series of complexes for which quadrupole coupling constants are available.

Procedure

The metal 6s, 6p, and 5d atomic orbitals and the Cl 3s and 3p atomic orbitals, a total of 33 wave functions, were used to construct molecular orbitals in the LCAO-MO approximation.[5] All wave functions were expressed as Slater nodeless orbitals[6] using the same method described[3] for treatment of $PtCl_4^{2-}$ to determine the shielding parameters, α_i.

Herman–Skillman radial wave functions[7] were used for the metal 6s and 5d atomic orbitals. The radial portions of the 6p atomic orbitals were approximated

---

[1] Work supported by the U. S. Atomic Energy Commission.

[2] Predoctoral Fellow of the National Institutes of Health, 1964–1966; A.E.C. Postdoctoral Fellow, 1966–1967.

[3] F. A. Cotton and C. B. Harris, *Inorg. Chem.*, **6**, 369 (1967).

[4] F. A. Cotton and C. B. Harris, *Proc. Natl. Acad. Sci. U. S.*, **56**, 12 (1966).

[5] J. H. Van Vleck, *J. Chem. Phys.*, **3**, 22 (1934).

[6] J. C. Slater, *Phys. Rev.*, **36**, 57 (1930).

[7] F. Herman and S. Skillman, "Atomic Structure Calculations," Prentice-Hall, Englewood Cliffs, N. J., 1963.