The Electronic Structure of Zeise's Salt, $[PtCl_3C_2H_4]^-$

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A semiempirical SCF MO method including all the valence electrons in a molecule has been applied to Zeise's salt, which is one of the most simple metal-olefin π-complexes. The electron-repulsion integrals are included explicitly in the present method. The results agree well with the available experimental data, indicating that the C-C bond order is equal to 1.545 and that the ethylene is tightly bound to platinum. An attempt to assign the observed bands to particular electron transitions has been made on the basis of a calculation of the transition energies and transition moments. We identify the band at 40700 cm^{-1} as the charge-transfer band corresponding to the electronic transition from ethylene to platinum. Several properties of Zeise's salt are calculated, and much information on the bonding is obtained.

Since Zeise isolated the first olefin complex, $K^+[PtCl_3(C_2H_4)]^-\cdot H_2O$, known as Zeise's salt,[1,2] a very large number of olefin complexes of platinum and other metals have been reported. Many reviews of the research of metal-olefin complexes have been reported by many investigators.[3-6] Zeise's salt is one of the most simple metal-olefin π-complexes. The research into the structure and bonding mechanism is interesting and important. The X-ray structure determination has shown that the ethylene molecule forms an approximately symmetrical π-type bond with the platinum atom and that the C–C bond length is 1.44(3) Å.[7] Infrared studies of Zeise's salt have been reported by many investigators.[8-14] Recently, Raman and infrared spectra have been obtained by Hiraishi.[15] He identified the C–C stretching frequency as a strong, polarized Raman line at 1243 cm^{-1}, while the two Pt-C stretches were thought to be at 405 cm^{-1} (symmetric) and 493 cm^{-1} (antisymmetric). He concluded that the C_2H_4 group has many similarities to the C_2H_4 group in ethylene oxide and that the ethylene is tightly bound to the Pt(II) atom.

Various electronic structures have been proposed to explain the bonding scheme between the ethylene molecule and platinum, but that scheme was not satisfactorily explained until 1953. Chatt and Duncanson[8] then applied Dewar's description[16] of the bonding in silver-olefin complexes to Zeise's salt. The σ-type bond is formed by the overlap of a $5d6s6p^2$ hydrid orbital of the platinum atom with the filled π-orbital of the ethylene molecule. The π-type bond is formed by the overlap of a $5d6p$-hydrid orbital of the platinum atom with the vacant anti-bonding π-orbital of the ethylene molecule; this is referred to as "back-bonding." This interpretation of the bonding is now generally accepted for metal-olefin π-complexes.[5]

This paper will describe the results of a molecular orbital investigation of the electronic structure and bonding mechanism in Zeise's salt. The electronic spectra of Zeise's salt have been reported,[17-21] and three attempts have been made to assign the observed bands to particular transitions,[19-21] but in their molecular orbital treatment the electron repulsion integrals have not been considered explicitly. The electron-repulsion integrals are considered explicitly in the present semiempirical self-consistent molecular orbital calculation for all the valence electron systems. A new assignment based on the calculation of the excitation energies and on the calculation of the transition moments is proposed in this article. The C–C bond order, the dipole moments, and H-^{195}Pt coupling constant are also discussed.

Method of Calculation

A semiempirical LCAO-MO-SCF method including electron repulsion for all valence electrons is presented. The valence electrons are represented by LCAO molecular orbitals, as given by:

$$\Phi_i = \sum_\nu C_{i\nu}\chi_\nu \qquad (1)$$

where χ_ν's are valence atomic orbitals. We take as a χ_ν Slater-type AO (atomic orbital)[22] centered on each atom:

$$\chi_\nu(n, l, m) = Nr^{n-1}\exp(-\zeta r)\, Y_l^m(\theta, \varphi) \qquad (2)$$

where n is the principal quantum number. We use orbital exponents, ζ's which have been preferably

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determined by a variational procedure.[23] For a molecule with a closed-shell configuration, the variational treatment of the orbital coefficients, $C_{\nu i}$, leads to the Roothaan equations:[24]

$$\sum_{\nu} F_{\mu\nu}C_{i\nu} = E_i C_{i\mu}$$

where $F_{\mu\nu}$ are matrix elements of the Hartree-Fock Hamiltonian. The eigenvalues, E_i, are roots of the secular equation:

$$|F_{\mu\nu} - E\delta_{\mu\nu}| = 0$$

Using zero differential overlap approximation, we approximate the matrix elements, $F_{\mu\nu}$, as:

$$F_{\mu\mu} = H_{\mu\mu}^{\text{core}} - 1/2P_{\mu\mu}(\mu\mu|\mu\mu) + \sum_{\nu} P_{\nu\nu}(\mu\mu|\nu\nu), \quad (3)$$

$$F_{\mu\nu(\mu\neq\nu)} = H_{\mu\nu}^{\text{core}} - 1/2P_{\mu\nu}(\mu\mu|\nu\nu), \quad (4)$$

$$H_{\mu\mu}^{\text{core}} = -I_p(\mu) - (N_\mu - 1)(\mu\mu|\mu\mu) - \sum_{\nu(\neq\mu)} N_\nu(\mu\mu|\nu\nu), \quad (5)$$

$$H_{\mu\nu(\mu\neq\nu)}^{\text{core}} = 0.25S_{\mu\nu}[2(\mu\mu|\nu\nu) - (\mu\mu|\mu\mu) - (\nu\nu|\nu\nu) + (\mu|\nu\nu) + (\nu|\mu\mu) - (\mu|\mu\mu) - (\nu|\nu\nu)] \quad (6)$$

where I_p is the valence-state ionization potential, where N_μ is the number of valence electrons occupying χ_μ, where $S_{\mu\nu}$ is the overlap integral between χ_μ and χ_ν, and where $P_{\mu\nu}$ is the charge-density and bond-order matrix:

$$P_{\mu\nu} = 2\sum_{i}^{occ} C_{i\mu}C_{i\nu} \quad (7)$$

The one-center Coulomb repulsion integrals $(\mu\mu|\mu\mu)$ are semiempirically estimated by:

$$(\mu\mu|\mu\mu) = I_p(\mu) - E_A(\mu) \quad (8)$$

The valence-state electron affinities, E_A, are assumed to be equal to the experimental values, and the valence-state ionization potential, I_p, is assumed to be equal to the values of the valence orbital ionization potential (VOIP).[25,26] The required term energies and ionization potentials are taken from Moore's table.[27] The values of I_p and E_A are summarized in Table 1.

Table 1. Valence orbital ionization potential (I_p) and valence state electron affinity (E_A) of AO's

Atom	AO	I_p (eV)	E_A (eV)
H	1*s*	13.60	0.85
C	2*s*	21.01	8.91
	2*p*	11.27	0.34
Cl	3*s*	24.02	14.45
	3*p*	15.03	3.73
Pt	6*s*	8.74	0.1
	6*p*	4.59	0.1
	5*d*	8.61	0.1

The one-center and two-center Coulomb repulsion integrals are calculated by:[28]

$$(\mu\mu|\nu\nu) = \frac{14.3986}{R + a} \quad (9)$$

$$a = \frac{28.7972}{(\mu\mu|\mu\mu) + (\nu\nu|\nu\nu)} \quad (10)$$

where R is the distance between the centers, μ and ν, with R represented in Å units, and $(\mu\mu|\nu\nu)$, in eV's. The molecular integrals, $(\mu|\nu\nu)$, are evaluated by means of the product of the effective nuclear charge and $(\mu\mu|\nu\nu)$.

The calculated results obtained by this procedure do not vary with respect to an orthogonal transformation of the atomic orbital basis function. This can easily be proved by the invariance of the F-matrix under the unitary transformation.

The molecular dipole moments, μ_{total}, are obtained as a sum of two parts:[29]

(1) A contribution from the net atomic charge densities, Q_A,

$$\mu_{point}(\text{debyes}) = 4.803 \sum_{A}^{atom} Q_A r_A \quad (11)$$

(2) A contribution from atomic polarizations, μ_{atom}(debyes)

$$= 4.803 \sum_{A}^{atom} P_{ns(A),np(A)} \int \chi^A{}_{ns} \boldsymbol{r} \chi^A{}_{np} d\tau \quad (12)$$

where $\boldsymbol{r}$ is the vector of the appropriate cartesian coordinate in units of Å.

Calculations on the $[PtCl_3C_2H_4]^-$ Ion and Results

In order to apply this method of calculation, it is necessary to know the coordinates of the atoms in the molecule. The molecular structure of Zeise's salt in the crystal was determined by X-ray diffraction;[7] it was found that the deviations from ideal symmetry (C_{2v}) are small. The Raman and infrared spectra of an aqueous solution of $K^+[PtCl_3(C_2H_4)]^-$.

H_2O[15] were measured, and it was concluded that the $[PtCl_3C_2H_4]^-$ ion has C_{2v} symmetry, whether the C_2H_4 group is planar or whether the CH_2's are bent

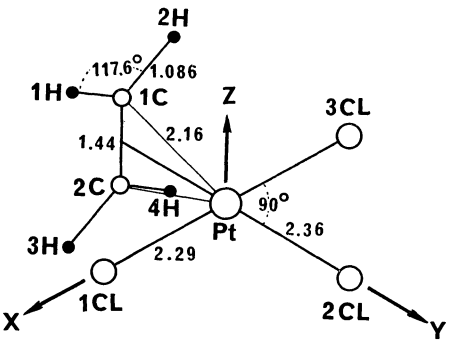

Fig. 1. A molecular orbital coordinate system and structure for $[PtCl_3C_2H_4]^-$ ion, and numbering convention.

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symmetrically toward or away from the Pt atom. The high-resolution proton magnetic resonance spectrum[10] of the $[PtCl_3C_2H_4]^-$ ion in deuterium oxide is in agreement with a symmetrically-co-ordinated ethylene molecule. On the basis of these results, it is reasonable to assume the C_{2v} symmetry for the $[PtCl_3C_2H_4]^-$ ion as the base of the molecular orbital calculations. The spatial arrangement is taken to be as is shown in Fig. 1. The C_2H_4 group is assumed to be planar, and the C–H bond distance and ∠HCH-bond angle are assumed to be equal to that of the free ethylene molecule.

The values of VOIP used in this calculation are as follows, in units of eV: 13.595 for $(1s)_H$, 23.384 for

TABLE 2. CALCULATED ORBITAL ENERGIES AND ORBITAL SYMMETRIES

	Molecular orbital	Symmetry representation	Orbital energy (in eV)		Molecular orbital	Symmetry representation	Orbital energy (in eV)
Occupied MO	Φ_1	a_1	−40.03		Φ_{18}	a_2	− 9.56
	Φ_2	b_2	−28.24		Φ_{19}	a_2	− 7.70
	Φ_3	a_1	−26.79		Φ_{20}	a_1	− 7.65
	Φ_4	b_1	−24.84		Φ_{21}	b_2	− 7.64
	Φ_5	a_1	−21.54		Φ_{22}	b_1	− 6.40
	Φ_6	b_2	−16.21	Vacant MO	Φ_{23}	b_1	− 0.33
	Φ_7	a_1	−13.53		Φ_{24}	b_2	1.08
	Φ_8	b_2	−13.43		Φ_{25}	a_1	1.29
	Φ_9	a_1	−13.33		Φ_{26}	b_1	2.23
	Φ_{10}	b_1	−13.27		Φ_{27}	a_1	3.34
	Φ_{11}	a_1	−12.15		Φ_{28}	b_1	4.22
	Φ_{12}	a_2	−10.98		Φ_{29}	a_1	5.74
	Φ_{13}	b_2	−10.59		Φ_{30}	a_2	7.52
	Φ_{14}	b_1	−10.02		Φ_{31}	b_1	8.07
	Φ_{15}	a_1	− 9.75		Φ_{32}	b_2	9.48
	Φ_{16}	b_2	− 9.67		Φ_{33}	a_1	10.90
	Φ_{17}	a_1	− 9.57				

TABLE 3a. MOLECULAR ORBITALS[a] FOR $[PtCl_3C_2H_4]^-$ ION: OCCUPIED MO

$\Phi_1 = -0.29s+0.39y-0.10(Cl_s^1+Cl_s^3)+0.05(Cl_y^1+Cl_y^3)+0.06Cl_s^2-0.50(C_s^1+C_s^2)-0.05(C_y^1+C_y^2)$
$+0.11(C_z^1-C_z^2)-0.21(H1+H2+H3+H4)$
$\Phi_2 = 0.54x+0.56(Cl_s^1-Cl_s^3)-0.10(Cl_x^1+Cl_x^3)+0.09Cl_x^2+0.10(C_x^1+C_x^2)$
$\Phi_3 = 0.37s+0.32y+0.35(Cl_s^1+Cl_s^3)-0.06(Cl_x^1-Cl_x^3)+0.06(Cl_y^1+Cl_y^3)+0.68Cl_s^2-0.13Cl_y^2$
$\Phi_4 = -0.44z+0.05yz-0.11(Cl_z^1+Cl_z^3)-0.08Cl_z^2-0.43(C_s^1-C_s^2)-0.24(C_z^1+C_z^2)-0.25(H1+H2-H3-H4)$
$\Phi_5 = 0.08y-0.54(Cl_s^1+Cl_s^3)+0.55Cl_s^2+0.16(C_s^1+C_s^2)-0.06(C_y^1+C_y^2)$
$\Phi_6 = 0.12xy+0.13(Cl_s^1-Cl_s^3)+0.11(Cl_x^1+Cl_x^3)+0.13(Cl_y^1-Cl_y^3)-0.52(C_x^1+C_x^2)-0.29(H1-H2+H3-H4)$
$\Phi_7 = -0.10s-0.33y+0.05zz+0.05(Cl_s^1+Cl_s^3)+0.11(Cl_x^1-Cl_x^3)-0.36(Cl_y^1+Cl_y^3)+0.33Cl_s^2$
$+0.54Cl_y^2-0.15(C_s^1+C_s^2)+0.24(C_y^1+C_y^2)+0.06(C_z^1-C_z^2)$
$\Phi_8 = -0.38x-0.60xy+0.29(Cl_s^1-Cl_s^3)+0.47(Cl_x^1+Cl_x^3)-0.09(Cl_y^1-Cl_y^3)-0.37Cl_x^2+0.11(H1-H2+H3-H4)$
$\Phi_9 = 0.28s-0.08zz-0.17(Cl_s^1+Cl_s^3)-0.36(Cl_x^1-Cl_x^3)-0.07(Cl_y^1+Cl_y^3)-0.12Cl_s^2-0.27Cl_y^2$
$-0.17(C_s^1+C_s^2)+0.38(C_y^1+C_y^2)+0.22(C_z^1-C_z^2)+0.08(H1+H2+H3+H4)$
$\Phi_{10} = 0.46z+0.45(Cl_z^1+Cl_z^3)+0.38Cl_z^2-0.26(C_s^1-C_s^2)+0.12(C_y^1-C_y^2)-0.08(C_z^1+C_z^2)-0.07(H1+H2-H3-H4)$
$\Phi_{11} = -0.13xxyy-0.21zz-0.07(Cl_x^1-Cl_x^3)-0.09Cl_y^2+0.25(C_y^1+C_y^2)-0.54(C_z^1-C_z^2)-0.21(H1+H2+H3+H4)$
$\Phi_{12} = -0.27xz-0.57(Cl_z^1-Cl_z^3)-0.22(C_x^1-C_x^2)-0.20(H1-H2-H3+H4)$
$\Phi_{13} = 0.08x-0.22xy-0.16(Cl_x^1+Cl_x^3)-0.59(Cl_y^1-Cl_y^3)-0.34Cl_x^2-0.12(C_x^1+C_x^2)-0.09(H1-H2+H3-H4)$
$\Phi_{14} = 0.06yz-0.37(Cl_z^1+Cl_z^3)+0.84Cl_z^2$
$\Phi_{15} = -0.05y-0.35xxyy+0.16zz+0.38(Cl_x^1-Cl_x^3)+0.35(Cl_y^1+Cl_y^3)+0.35(C_y^1+C_y^2)+0.08(C_z^1-C_z^2)$
$\Phi_{16} = -0.07x+0.22(Cl_x^1+Cl_x^3)-0.31(Cl_y^1-Cl_y^3)+0.82Cl_x^2$
$\Phi_{17} = -0.10y+0.26xxyy-0.27(Cl_x^1-Cl_x^3)+0.45(Cl_y^1+Cl_y^3)+0.59Cl_y^2$
$\Phi_{18} = -0.05xz-0.36(Cl_z^1-Cl_z^3)+0.37(C_x^1-C_x^2)+0.33(H1-H2-H3+H4)$
$\Phi_{19} = 0.96xz-0.18(Cl_z^1-Cl_z^3)$
$\Phi_{20} = 0.13s+0.94zz-0.10(C_x^1-Cl_x^3)-0.13(C_z^1-C_z^2)-0.05(H1+H2+H3+H4)$
$\Phi_{21} = 0.96xy-0.14(Cl_y^1-Cl_y^3)-0.12Cl_x^2$
$\Phi_{22} = 0.42z-0.49yz-0.31(Cl_z^1+Cl_z^3)-0.24Cl_z^2-0.19(C_s^1-C_s^2)+0.34(C_y^1-C_y^2)$

a) The contributions from the atomic orbitals whose AO coefficients are smaller than 0.05 are neglected in this table. s, x, y, z, xz, yz, xy, $xxyy$, and zz denote the atomic orbital 6s, 6p_x, 6p_y, 6p_z, 5d_{xz}, 5d_{yz}, 5d_{xy}, 5$d_{x^2-y^2}$, and 5d_{z^2} of platinum respectively. (Cl_s^i, Cl_x^i, Cl_y^i, Cl_z^i), (C_s^i, C_x^i, C_y^i, C_z^i), and Hi denote the atomic orbital (3s, 3p_x, 3p_y, 3p_z) of i-chlorine, (2s, 2p_x, 2p_y, 2p_z) of i-carbon, and 1s of iH proton respectively.

Table 3b. Molecular orbitals[a] for $[PtCl_3C_2H_4]^-$ ion: vacant MO

$\Phi_{23}=0.35z+0.81yz-0.16(Cl_z^1+Cl_z^3)-0.21Cl_z^2-0.19(C_s^1-C_s^2)+0.08(H1+H2-H3-H4)$
$\Phi_{24}=-0.47z-0.05xy+0.20(Cl_s^1-Cl_s^3)-0.36(Cl_x^1+Cl_y^3)+0.13Cl_x^2-0.28(C_x^1+C_x^2)+0.24(H1-H2+H3-H4)$
$\Phi_{25}=-0.06y+0.87xxyy-0.05(Cl_s^1+Cl_s^3)+0.23(Cl_x^1-Cl_x^3)+0.07Cl_s^2-0.23Cl_y^2+0.13(C_y^1+C_y^2)$
$\Phi_{26}=-0.30z-0.16yz+0.07(Cl_z^1+Cl_z^3)+0.09Cl_z^2-0.38(C_s^1-C_s^2)-0.08(C_y^1-C_y^2)+0.15(C_z^1+C_z^2)$
$+0.35(H1+H2-H3-H4)$
$\Phi_{27}=0.06s-0.22y+0.07(Cl_y^1+Cl_y^3)+0.06Cl_s^2-0.09Cl_y^2-0.39(C_s^1+C_s^2)-0.16(C_y^1+C_y^2)-0.29(C_z^1-C_z^2)$
$+0.30(H1+H2+H3+H4)$
$\Phi_{28}=0.42z-0.23yz-0.08(Cl_z^1+Cl_z^3)-0.08Cl_z^2-0.10(C_s^1-C_s^2)-0.59(C_y^1-C_y^2)$
$\Phi_{29}=0.37s+0.64y+0.05xxyy-0.07zz-0.09(Cl_s^1+Cl_s^3)+0.15(Cl_x^1-Cl_x^3)-0.11(Cl_y^1+Cl_y^3)$
$-0.28Cl_s^2+0.40Cl_y^2+0.07(C_y^1+C_y^2)-0.11(C_z^1-C_z^2)+0.11(H1+H2+H3+H4)$
$\Phi_{30}=-0.55(C_x^1-C_x^2)+0.31(H1-H2-H3+H4)$
$\Phi_{31}=0.09(C_s^1-C_s^2)-0.63(C_z^1+C_z^2)+0.20(H1+H2-H3-H4)$
$\Phi_{32}=0.55x-0.16(Cl_s^1-Cl_s^3)+0.18(Cl_x^1+Cl_x^3)-0.34(C_x^1+C_x^2)+0.28(H1-H2+H3-H4)$
$\Phi_{33}=0.71s-0.34y-0.06zz-0.12(Cl_s^1+Cl_s^3)+0.15(Cl_x^1-Cl_x^2)+0.06Cl_y^2-0.10(C_s^1+C_s^2)-0.20(C_y^1+C_y^2)$
$+0.09(C_z^1-C_z^2)-0.19(H1+H2+H3+H4)$

a) See references under Table 2a.

Table 4. Valence electron distributions of $[PtCl_3C_2H_4]^-$ ion

Atom	Orbital	Charge distribution	
		on AO	on atom
Pt	$6s$	0.684	10.558
	$6p_x$	0.927	
	$6p_y$	0.810	
	$6p_z$	1.204	
	$5d_{xz}$	2.000	
	$5d_{yz}$	0.511	
	$5d_{xy}$	1.993	
	$5d_{x^2-y^2}$	0.453	
	$5d_{z^2}$	1.976	
1Cl, 3Cl	$3s$	1.804	7.141
	$3p_x$	1.461	
	$3p_y$	1.956	
	$3p_z$	1.920	
2Cl	$3s$	1.814	7.171
	$3p_x$	1.952	
	$3p_y$	1.529	
	$3p_z$	1.876	
1C, 2C	2s	1.251	4.235
	$2p_x$	0.990	
	$2p_y$	1.083	
	$2p_z$	0.911	
1H, 2H 3H, 4H	$1s$	0.880	0.880

$(2s)_C$, 13.032 for $(2p)_C$, 25.272 for $(3s)_{Cl}$, 13.708 for $(3p)_{Cl}$, 8.619 for $(5d)_{Pt}$, 8.749 for $(6s)_{Pt}$, and 4.600 for $(6p)_{Pt}$.

The basic set of atomic orbitals used in this calculation is: platinum; $5d$, $6s$, and $6p$; chlorline; $3s$ and $3p$; carbon; $2s$ and $2p$, and hydrogen; $1s$. The initial electron configurations of the atoms in the $[PtCl_3C_2H_4]^-$ ion used in the calculation of the F-matrix are. $(5d)^9(6s)^1$ for platinum, $(3s)^2(3p)^5$ for chlorine, $(2s)^1(2p)^3$ for carbon, and $(1s)^1$ for hydrogen.

Table 5. Overlap integral and bond order between ethylene π-orbital and Pt atomic orbitals

Pt/C	Overlap integral		Bond order		
	$2p_y^{C1}$	$2p_y^{C2}$	$2p_y^{C1}$	$2p_y^{C2}$	
$6s$	0.184	0.184	0.253	0.253	σ-type bond
$6p_x$	0.0	0.0	0.0	0.0	
$6p_y$	−0.193	−0.193	−0.299	−0.299	
$6p_z$	0.137	−0.137	0.432	−0.432	π-type bond
$5d_{xz}$	0.0	0.0	0.0	0.0	
$5d_{yz}$	−0.060	0.060	−0.345	0.345	
$5d_{xy}$	0.0	0.0	0.0	0.0	σ-type bond
$5d_{x^2-y^2}$	−0.066	−0.066	−0.281	−0.281	
$5d_{z^2}$	−0.023	−0.023	−0.005	−0.005	
Overlap integral $(2p_y^{C1}2p_y^{C2})$	0.249		Bond order $(2p_y^{C1}2p_y^{C2})$	0.545	

The calculated orbital energies and the orbital symmetry representations in C_{2v} symmetry are given in Table 2, while the molecular orbitals are given in Table 3*a* and 3*b*.

We present, in Table 4, the valence electron distributions on each atomic orbital and on each atom in the $[PtCl_3C_2H_4]^-$ ion. In order to show the bonding mechanism between platinum and ethylene, we present in Table 5 the overlap integrals and the bond orders between the ethylene π-orbital and the Pt atomic orbitals, as well as those between the π-atomic orbital in 1C and that of in 2C.

Ultraviolet and visible spectra have been reported for the solution and the crystal of Zeise's salt,[17-20] and molecular orbital calculations have been carried out in an attempt to assign the observed bands to particular electronic transitions within the complex.[19-21] In our molecular orbital calculations, the excitation of an electron from the MO Φ_i to the MO Φ_j give rise to the excitation energies, δE_{i-j}, relative to the ground state. These energies are given by:

$$\delta E_{i-j}=\varepsilon_j-\varepsilon_i-J_{ij}+2K_{ij} \qquad (13)$$

where ε_i is the orbital energy of Φ_i, and the J_{ij} and K_{ij} are the Coulomb and exchange integrals respec-

TABLE 6. TRANSITION ENERGIES (δE) AND OSCILLATOR STRENGTHS (f)

Calcd. Transition	δE(cm^{-1})	$f\times10^2$	Polariz.	Exptl.[a] δE(cm^{-1})	$f\times10^2$
$\Phi_{22b_1}-\Phi_{23b_1}$	15198	0.11	y		
$\Phi_{22b_1}-\Phi_{25a_1}$	20385	0.12	z		
$\Phi_{20a_1}-\Phi_{24b_2}$	34784	0.70	x	34400	1.0
$\Phi_{21b_2}-\Phi_{24b_2}$	34994	0.37	y		
$\Phi_{22b_1}-\Phi_{26b_1}$	35018	3.83	y	37700	1.9
$\Phi_{22b_1}-\Phi_{27a_1}$	42101	0.60	z		
$\Phi_{18a_2}-\Phi_{23b_1}$	44448	6.99	x	41600	6.6
$\Phi_{19a_2}-\Phi_{26b_1}$	47022	0.68	x		

a) From Ref. 21.

tively. The calculated excitation energies and oscillator strengths are given in Table 6.

Calculation of H-^{195}Pt Nuclear Spin-spin Coupling Constant

The high-resolution proton magnetic resonance spectrum of the $[PtCl_3C_2H_4]^-$ ion in deuterium oxide[10] shows a strong singlet attributed to the ethylenic protons with a weak side band, 34 Hz apart, produced by the spin-spin coupling with ^{195}Pt.[30] The most important term giving nuclear spin-spin coupling is the term due to the Fermi contact interaction.[31,32] The Fermi contact coupling is also likely to be the principal contributor to the coupling constant between the hydrogen atom and ^{195}Pt in Zeise's salt, because the electrons on a hydrogen atom are represented by a 1s atomic orbital. By substituting the LCAO MO wave functions in the general Ramsey formulae, the following molecular orbital expression for the Fermi contact spin-spin coupling constant between a particular pair of nuclei, N and N', has been given by Pople and Santry:[33]

$$J_{NN'} = -\frac{64}{9}h\gamma_N\gamma_{N'}\beta^2\sum_i^{occ}\sum_j^{vac}({}^3\delta E_{i\to j})^{-1} \sum_{\lambda\mu\nu\sigma} C_{i\lambda}C_{j\mu}C_{j\nu}C_{i\sigma}\langle\chi_\lambda|\delta(\boldsymbol{r}_N)|\chi_\mu\rangle\langle\chi_\nu|\delta(\boldsymbol{r}_{N'})|\chi_\sigma\rangle \quad (14)$$

where γ_N and $\gamma_{N'}$ are the nuclear magnetic ratios, where β is the Bohr magneton, and where the other notations are in accordance with those in Ref. 32.

Using the results of the above MO calculations, we have calculated the H-^{195}Pt coupling constant on the basis of Eq. (14). The formula involves the value of the valence $(6s)_{Pt}$ atomic orbital at platinum: the magnitude at the center is important in the calculation of the H-^{195}Pt coupling constant. Accordingly, it is necessary to use a $(6s)_{Pt}$ atomic orbital accurate at the center of platinum in order properly to evaluate the molecular integrals, $\langle x_\nu|\delta(\boldsymbol{r}_N)|x_\mu\rangle$. The analytical wavefunctions accurate at the inner part have been calculated for a number of atoms.[34-36] However, so far these calculations have not been reported for platinum. Accordingly, we have employed an approximate analytical (6s) wavefunction for radon as (6s). The values of the atomic orbitals at platinum and at the proton (1H) are given in Table 7. It can easily be seen that the values of $\langle(1s)_H|\delta(\boldsymbol{r}_H)|(1s)_H\rangle$ and $\langle(6s)_{Pt}|\delta(\boldsymbol{r}_{Pt})|(6s)_{Pt}\rangle$ are dominant over the other molecular integrals, $\langle\chi_\lambda|\delta(\boldsymbol{r}_H)|\chi_\mu\rangle$ and $\langle\chi_\nu|\delta(\boldsymbol{r}_{Pt})|\chi_\sigma\rangle$ respectively. Thus, we have obtained -40.4 Hz as the calculated value of the H-^{195}Pt coupling constant; this indicates that the ethylene is firmly bound to

TABLE 7. VALUES OF THE ATOMIC ORBITALS AT PLATINUM AND PROTON (1H) (in atomic unit)

Atomic orbital	Values of radial part[a] of AO at proton (1H),	at platinum
$(5d)_{Pt}$	0.000	0.000
$(6s)_{Pt}$	0.081	(-7.344)[b]
$(6p)_{Pt}$	0.081	0.000
$(3s)_{1Cl}$	0.001	0.006
$(3p)_{1Cl}$	0.003	0.014
$(3s)_{2Cl}$	0.000	0.004
$(3p)_{2Cl}$	0.000	0.011
$(3s)_{3Cl}$	0.000	0.006
$(3p)_{3Cl}$	0.000	0.014
$(2s)_{1C}$	0.286	0.021
$(2p)_{1C}$	0.292	0.024
$(2s)_{2C}$	0.019	0.021
$(2p)_{2C}$	0.021	0.024
$(1s)_{1H}$	2.000	0.028
$(1s)_{2H}$	0.059	0.028
$(1s)_{3H}$	0.015	0.028
$(1s)_{4H}$	0.005	0.028

a) The radial part is $R_n(\zeta)=\frac{(2\zeta)^{\frac{2n+1}{2}}}{\sqrt{(2n)!}}r^{n-1}\exp(-\zeta r)$.

b) This is the value of $(6s)_{Rn}$-analytical wavefunction, see Ref. 36.

30) S. Maricic, C. R. Redpath, and J. A. S. Smith, *J. Chem. Soc.*, **1963**, 4905.

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platinum. This calculated value is in very good agreement with the observed value of 34 Hz. The sign of the experimental coupling constant is not known, but the theoretical calculation shows it to be negative.

Discussion

The signs and magnitudes of molecular orbital coefficients (Table 2*a* and 2*b*) indicate that the ethylene π^*(anti-bonding) orbital is included in the highest occupied orbital, Φ_{22}. This is consistent with the π-type bond which is referred to as "back-bonding." The ethylene π(bonding) orbital is included in the Φ_{15} and Φ_{19} orbitals. This is consistent with the σ-type bond.[8] The form of the molecular orbitals, Φ_{22} and Φ_{15}, are shown schematically in Figs. 2 and 3. These results show essentially the same bonding mechanism as when Chatt and Duncanson[8] applied Dewar's[16] description to Zeise's salt, but it should be pointed out that the mixing of the ligand chlorine atomic orbitals with these molecular orbitals is considerably large. It should also be pointed out that the ethylene π^* orbital is included in the vacant molecular orbital, Φ_{28}.

The importance of the *trans*-effect caused by ethylene should also be noted. A review[37] of the *trans*-effect favored the π-bonding mechanism for the *trans*-effect of olefins,[38] in which a ligand olefin which can form π-bonds will with draw some of the electron density of the d_{yz} orbital from the ligand in the *trans* position. Moreover, it was pointed out that this should weaken the Pt-X(*trans*) bond. Certainly it does (see Fig. 2) but we should also note that the σ-type bonding (see Fig. 3) strengthens the Pt-Cl(*cis*) bond, but not the Pt-Cl(*trans*) bond.

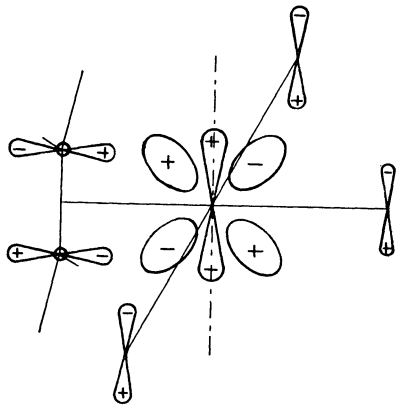

Fig. 2. Shematic scheme of MO Φ_{22}, illustrating the π-type bonding.

The ionization potential of a molecule should, according to Koopmans' theorem,[39] be approximately equal to the calculated orbital energy of the highest occupied orbital multiplied by -1. We can see in Table 1 that the calculated ionization potential of the $[PtCl_3C_2H_4]^-$ ion is equal to 6.40 eV. The experimental ionization potential of this salt has not been reported, but this calculated value seems to be reasonable with respect to the ionization potential of platinum. The orbital energy of the lowest vacant orbital, Φ_{23}, is slightly negative. Nevertheless, the over-all picture of orbital energies is very encouraging in comparison with the negative values of the vacant molecular orbitals in the calculation of many sorts of metallic compounds.[40-42]

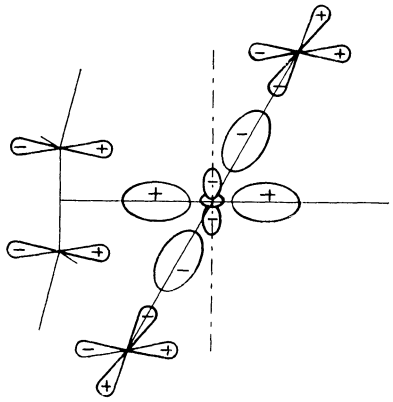

Fig. 3. Shematic scheme of MO Φ_{15}, illustrating the σ-type bonding.

Let us now consider the valence electron distributions obtained from the calculations (Table 3). The electrons of the protons in ethylene are redistributed to the carbons. The excess charge, (-e), is redistributed to platinum and chlorines. It should be noted that the electrons in the 5*d* orbitals in platinum are largely redistributed to the 6*p* orbitals. This redistribution can be considered to be due to the large contribution of 6*p* orbitals to the bonding of platinum with the ethylene molecule, as can easily be seen from the form of the molecular orbitals in Tables 2*a* and 2*b*. Our method predicts the dipole moment of $\mu_{total}=2.772$ debyes for the $[PtCl_3C_2H_4]^-$ ion, where $\mu_{point}=2.035$ debyes and $\mu_{atom}=0.737$ debyes. From the experimental dipole moments of compounds of the C_2H_4, amine, $PtCl_2$ type, Chatt and Duncanson[8] estimated that the dipole moment of the C_2H_4-Pt bond has a value of about 4 debyes. Our calculated result is in good agreement with their estimated value.

Let us next consider the data on the overlap integrals and bond orders between the ethylene π-orbital and platinum atomic orbitals (Table 4). From the signs and magnitudes of the overlap integrals and bond orders, we can understand the bonding mechanism due to the formation of the σ-type bond and the π-type bond. As can easily be seen, the total σ-type bond order is equal to 0.833, while the total π-type bond order is equal to 0.777. Accordingly, the bonding between ethylene and platinum is found to be through both the σ- and the π-type bonds. The calculated

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39) T. A. Koopmans, *Physica*, **1**, 104 (1933).
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ethylene π-bond order is reduced from 1.0 to 0.545 by forming a bond with $PtCl_3$. Thus, the C–C bond order is reduced from 2.0 to 1.5. This is consistent with the experimental results.

Let us now consider the assignment of the electronic spectra. We will not, in contrast to previous authors,[19,20] discuss the assignment on the basis only of the arrangement of the electronic energy levels (see Eq. (13)). Since the $[PtCl_3C_2H_4]$ ion is a molecule of low symmetry (C_{2v}), there are many group theoretically-allowed transitions. In spite of this fact, the number of probable transitions is reduced to a relatively small number by calculating the transition moments and neglecting the small ones. The transitions given in Table 5 are those which satisfy the following conditions: 1) the calculated oscillator strength (f) is larger than 10^{-3}, and

2) the excitation energy is smaller than 50000 cm^{-1}. Considering the intensities of the absorption spectrum and the calculated oscillator strengths, we can identify the band at 40700 cm^{-1} as $\Phi_{18a_1}-\Phi_{23b_1}$ ($^1A_1-^1B_1$), that is, the charge-transfer band corresponding to the transition from ethylene to platinum. The band at 37450 cm^{-1} may also be identified as $\Phi_{22b_1}-\Phi_{26b_1}$ ($^1A_1-^1A_1$) and the band at 33450 cm^{-1}, as $\Phi_{20a_2}-\Phi_{24b_1}$ ($^1A_1-^1B_1$). The calculated excitation energies for these transitions are 44448 cm^{-1}, 35018 cm^{-1}, and 34784 cm^{-1} respectively, showing good agreement with the experimental results. Previously, three attempts[19,20] have been made to assign the observed bands to particular electron transitions within the complex, but the three assignments are different. The present assignment is also different from previous ones and indicates that there is considerable mixing of the component atomic orbitals.

The magnitude of the spin-orbit interaction is given by ζ.[43] For the platinum $(5d)^9(6s)^1-^3D$ multiplet, the ζ-value is calculated to be [27] $\zeta=388$ cm^{-1}. In this molecular orbital treatment we do not consider the effect of spin-orbit coupling, although this effect is indefinably included through the evaluation of the VOIP's. However, this effect should be precisely considered if one wants to assign the small intensity bands of the polarized spectrum of crystal Zeise's salt.

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