varying ΔH_r values for the same metal with different halide and solvent.

To the lines of $\Delta H_{c(oct)}$ and $\Delta H_{c(tet)}$ may be added the values of ΔH_{LFSE} estimated for each atomic number, to give values of ΔH_r against atomic number as the difference between the resulting lines, shown in Figure 6. From the trends in these values, it can be predicted that the ΔH_r values for the analogous Mn and Fe reactions will be large and positive, while the value for Zn will be large and negative. The accuracy of this diagrammatic representation is insufficient to predict a value for the Cu reaction.

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Molecular Orbital Theory for Square-Planar Metal Halide Complexes

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The electronic spectra of the square-planar chloride complexes are assigned using molecular orbital levels derived by the SCCC–MO method. The d-orbital ordering $x^2 - y^2 > xy > xz,yz > z^2$ is calculated for the planar tetrahalides, and values derived from observed spectral band energies are given for the ligand field parameters Δ_1, Δ_2, and Δ_3. The apparent decrease in Δ_1 values with increasing oxidation numbers is discussed in terms of the high covalent character of these complexes.

Introduction

The ordering of the metal d orbitals in the d^8 tetrahalide square-planar complexes (D_{4h} symmetry) of Pd(II), Pt(II), and Au(III) has been the subject of numerous papers.[1-9] Interest has been focused on the absorption spectrum of the $PtCl_4^{2-}$ ion, where attempts have been made to match the bands in the visible and near-ultraviolet regions of the spectrum to one-electron excitations from the occupied d-orbital MO's [$2b_{2g}$ (xy), $2e_g$ (xz, yz), and $3a_{1g}$ (z^2)] to the empty $3b_{1g}$ ($x^2 - y^2$). The spectrum has been assigned variously depending on the authors' choice of ordering for the occupied d-orbital MO's and whether a low-intensity band found at 20,300 cm^{-1} is considered a transition to a spin-singlet or spin-triplet excited state. However, the recent, elegant experimental studies by several investigators,[4,5,8-11] particularly those of Martin and co-workers,[4,8,9] have narrowed the assignment possibilities considerably, and it would seem an opportune moment to put forward a more quantitative molecular orbital model for the square-planar halides. In this paper we report SCCC–MO calculations[12,13] and compare them with detailed assignments for both the d → d and charge-transfer spectra of the $PtCl_4^{2-}$ and $PdCl_4^{2-}$ complexes.

Computational Details

Bond distances for $PtCl_4^{2-}$ and $PdCl_4^{2-}$ were taken from the literature[14] as 2.32 A. Analytic orbital functions for the valence nd, $(n + 1)$s, and $(n + 1)$p orbitals for second- and third-row metals have been published.[15] Initially, the orbital functions were taken for a charge of +1 on the metal. Subsequent SCCC–MO calculations revealed that the charges on the metals were all much closer to zero than +1. Wave functions for the d orbitals *only* were then recalculated for the neutral metal species[16] and the SCCC–MO calculations were repeated. Analytic functions for the valence s and p orbitals of Cl were taken from the tabulations of Clementi.[17]

VOIP's for Pd, Pt, and Au were taken as the respective *VOIP*'s of the corresponding first-row metal,[13,16] minus 10,000 cm^{-1}. Recall that the first *VOIP* curve is for ionization of a d electron from the configuration d^n. For Au, this configuration does not exist, and thus, the configuration d^9s^2 was substituted[16] and the requisite changes made in the programmed procedure for calculating the metal d *VOIP*'s. Ligand *VOIP*'s for the valence s and p orbitals of Cl,[12,13] ligand symmetry orbitals,[3] and relationships between group and diatomic overlaps[3] have been given previously.

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TABLE I

MOLECULAR ORBITALS FOR $PtCl_4^{2-}$ AND $PdCl_4^{2-}$

Levels for A. $PtCl_4^{2-}$	ε, cm⁻¹ × 10⁻³	MO coefficients[a]					
		5d	6s	6p	3s	$3p\sigma$	$3p\pi$
$1a_{1g}$	−209.68	0.1023	−0.1699	...	−0.9104	0.01208	...
$1b_{1g}$	−207.81	0.1921	...	...	0.9448	0.01141	...
$1e_u$	−204.79	...	...	0.07635	0.9692	−0.02143	0.01017
$2b_{1g}$	−134.23	−0.4566	...	...	0.2215	−0.7772	...
$2a_{1g}$	−133.91	−0.2621	0.2224	...	−0.2408	0.7938	...
$1b_{2g}$	−122.83	0.6576	...	...	...	...	0.6540
$2e_u$	−122.67	...	...	−0.1340	0.7214	−0.9291	0.01834
$1e_g$	−119.58	0.6721	...	...	...	...	0.6672
$1a_{2u}$	−110.78	...	...	0.07007	...	...	0.9805
$3e_u$	−110.50	...	...	0.02583	−0.01337	−0.05639	−0.9943
a_{2g}	−110.40	...	...	...	...	...	1.000
b_{2u}	−110.40	...	...	...	...	...	1.000
$3a_{1g}$	−106.81	0.9328	0.3021	...	0.02139	0.1703	...
$2e_g$	−98.98	−0.7495	...	...	...	...	0.7538
$2b_{2g}$	−93.31	−0.7712	...	...	...	...	0.7742
$3b_{1g}$	−64.65	0.9295	...	...	−0.3141	−0.6818	...
$2a_{2u}$	−28.72	...	...	−1.029	...	...	0.3207
$4e_u$	88.98	...	...	−1.286	0.5438	0.7215	−0.2479
$4a_{1g}$	120.08	−0.3320	1.259	...	−0.6162	−0.9420	...
Levels for B. $PdCl_4^{2-}$	ε, cm⁻¹ × 10⁻³	MO coefficients[b]					
		4d	5s	5p	3s	$3p\sigma$	$3p\pi$
$1a_{1g}$	−210.45	0.08359	−0.1874	...	−0.9051	0.00916	...
$1b_{1g}$	−206.71	0.1663	...	...	0.9611	0.01115	...
$1e_u$	−205.26	...	...	0.09131	0.9614	−0.02358	0.01351
$2a_{1g}$	−134.13	−0.2338	0.2350	...	−0.2445	0.7997	...
$2b_{1g}$	−133.30	−0.4737	...	...	0.1868	−0.7816	...
$2e_u$	−122.98	...	...	−0.1385	0.08189	−0.9274	0.00969
$1b_{2g}$	−119.11	0.6431	...	...	...	...	0.6881
$1e_g$	−116.61	0.6454	...	...	...	...	0.7078
$1a_{2u}$	−110.66	...	...	0.05776	...	...	0.9836
$3c_u$	−110.46	...	...	0.01975	−0.01115	−0.04611	−0.9956
a_{2g}	−110.40	...	...	...	...	...	1.000
b_{2u}	−110.40	...	...	...	...	...	1.000
$3a_{1g}$	−106.49	0.9504	0.2561	...	0.00301	0.1581	...
$2e_g$	−101.58	−0.7692	...	...	...	...	0.7122
$2b_{2g}$	−97.71	−0.7765	...	...	...	...	0.7370
$3b_{1g}$	−74.13	0.9053	...	...	−0.2558	−0.6609	...
$2a_{2u}$	−27.72	...	...	−1.033	...	...	0.3207
$4e_u$	103.41	...	...	−1.296	0.5779	0.7240	−0.2542
$4a_{1g}$	128.08	−0.2740	1.263	...	−0.6224	−0.9278	...

Group Overlap Integrals

C.	$G(M,L)$[c]	$PtCl_4^{2-}$	$PdCl_4^{2-}$		$G(M,L)$	$PtCl_4^{2-}$	$PdCl_4^{2-}$
a_{1g}	$G(5d,3p)$	−0.1440	−0.1219	a_{2u}	$G(6p,3p)$	0.2456	0.2564
	$G(5d,3s)$	−0.1101	−0.0863				
	$G(6s,3p)$	0.5298	0.5276	b_{2g}	$G(5d,3p)$	0.1626	0.1276
	$G(6s,3s)$	0.3676	0.3758				
				e_g	$G(5d,3p)$	0.1150	0.0902
b_{1g}	$G(5d,3p)$	0.2494	0.2111				
	$G(5d,3s)$	0.1907	0.1495	e_u	$G(6p,3p)_\sigma$	0.4805	0.4760
					$G(6p,3p)_\pi$	−0.1736	−0.1813
					$G(6p,3s)$	0.3785	0.3939

[a] For $F_\sigma = 1.98$, $F_\pi = 1.80$; $Pt(+0.24)5d^{8.614}6s^{0.658}6p^{0.401}$; L-L neglected. [b] For $F_\sigma = 2.04$, $F_\pi = 1.75$; $Pd(+0.22)4d^{8.624}5s^{0.636}5p^{0.521}$; L-L neglected. [c] n quantum numbers listed are for Pt.

Results

Calculations were carried out on $PtCl_4^{2-}$, initially, to determine the predicted ordering of the d-orbital MO's. This was found to be $z^2 < xz,yz < xy$ for wide variations in analytical orbital functions, *VOIP*'s, and *F* factors (F_σ and F_π),[12] with and without ligand–ligand overlap. F_σ was determined by fitting the first observed charge-transfer band to the $b_{2u} \rightarrow 3b_{1g}$ separation.[3] F_π was obtained by requiring that the d-symmetry level separation fit approximately the observed excitation energies of the spin-allowed d–d bands. The simultaneous fitting of both F_σ and F_π to the d → d spectra is very difficult since there is a wide range of *F* factors which give essentially the same fit. Thus fitting F_σ to the assumed $b_{2u} \rightarrow 3b_{1g}$ separation is just an arbitrary way of choosing among many sets of parameters giving approximately the same d-symmetry level separations.

The relevant molecular orbital data are presented in Table I. It should be noted that the *F* factor values are not the same as those found[12] for the corresponding first-row metal in an octahedral or tetrahedral geometry.

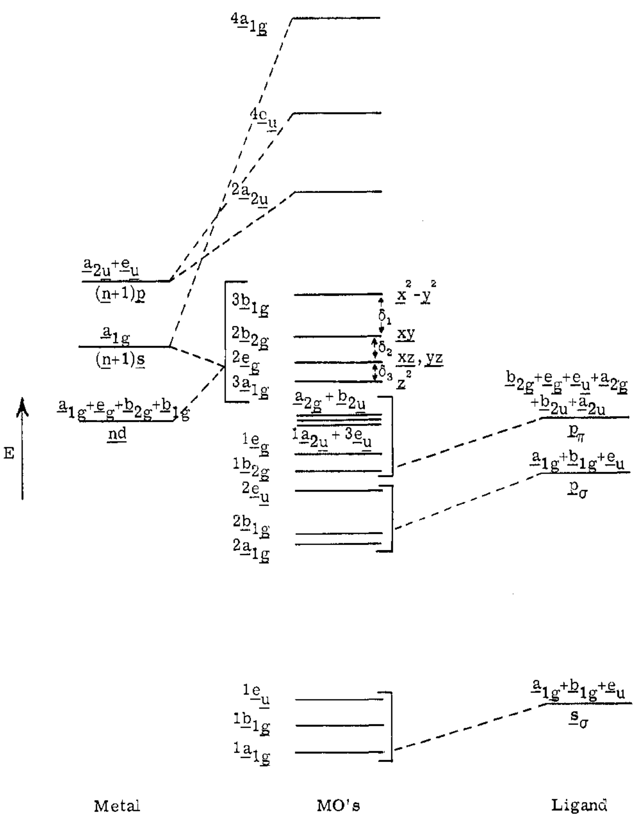

Figure 1.—Molecular orbital energy levels for square-planar MX_4^{n-} complexes.

The generalized MO energy level diagram representing these calculations is shown in Figure 1. For simplicity the MO's are connected to those atomic orbitals from which, by tradition, they are considered to be mainly derived. However, the similarity in energy of the metal d and ligand p levels shows that this partitioning is not strictly valid. The calculated separations between the antibonding d-symmetry MO levels are designated δ_1, δ_2, and δ_3, in order to emphasize that these quantities are in principle different from the ligand-field (LF) quantities Δ_1, Δ_2, and Δ_3. In the LF model, the d → d transition energies are defined by appropriate combinations of the Δ's and interelectronic-repulsion parameters.

TABLE II

ELECTRONIC SPECTRA OF $PtCl_4^{2-}$ AND $PdCl_4^{2-}$

(BAND MAXIMA IN $cm^{-1} \times 10^{-3}$; MOLAR EXTINCTION COEFFICIENTS IN PARENTHESES)

	$PtCl_4^{2-}$			$PdCl_4^{2-}$		
	Obsd[a]	Calcd		Obsd[j]		Calcd
Transition		MO	LF[i]		MO	LF[l]
$^1A_{1g} \to {}^3E_g$	17.0(<1)z, 18.0(2)xy, 19.0(<1)z		19.4	*d*		11.7
$^1A_{1g} \to {}^3A_{2g}$	20.9(9)xy, 20.6(10)z		19.2	*d*		12.8
$^1A_{1g} \to {}^3B_{1g}$	24.0(7)xy, 24.1(3)z		24.7	18.0(19)xy, 17.0(7)z		17.5
$^1A_{1g} \to {}^1A_{2g}$	26.3(28)xy	28.7[e]	26.2	20.0(67)xy	23.6[e]	20.0
$^1A_{1g} \to {}^1E_g$	29.2(37)xy, 29.8(55)z	34.3[f]	29.4	22.6(128)xy, 23.0(80)z	27.5[f]	22.3
$^1A_{1g} \to {}^1B_{1g}$	36.5[b]	42.2[g]	35.7	29.5(67)xy	32.4[g]	29.1
$^1A_{1g} \to {}^1A_{2u}, {}^1E_u(1)$	46.0(9580)[c]	*h*	...	36.0(12,000)[k]	*h*	...
$^1A_{1g} \to {}^1E_u(2)$	*d*	58.0	...	44.9(30,000)[k]	48.9	...

[a] Single-crystal absorption spectrum of K_2PtCl_4 at 15°K; from ref 8. [b] Reflectance spectrum of K_2PtCl_4; from ref 5. [c] Aqueous solution spectrum of K_2PtCl_4; from ref 3. [d] Not reported. [e] δ_1 value. [f] $\delta_1 + \delta_2$ value. [g] $\delta_1 + \delta_2 + \delta_3$ value. [h] Fitted. [i] For $\Delta_1 = 29{,}700$, $\Delta_2 = 4700$, $\Delta_3 = 6800$, $B = 500$, $C = 3500$ cm^{-1}. [j] Single-crystal absorption spectrum of K_2PdCl_4; from ref 5. [k] Aqueous solution spectrum of K_2PdCl_4 with excess KCl; from ref 3. [l] For $\Delta_1 = 23{,}600$, $\Delta_2 = 3900$, $\Delta_3 = 7400$, $B = 550$, $C = 3600$ cm^{-1}.

d → d Bands.—In Table II the assignments of the observed d → d spectral bands in the tetrahalides are compared with the computed differences in d-symmetry molecular orbital energy levels. In addition, the spectra have been calculated from a ligand-field model with Δ_1, Δ_2, Δ_3, B, and C values as given. The bands at 26,300 and 20,000 cm^{-1} in $PtCl_4^{2-}$ and $PdCl_4^{2-}$, respectively, are known to be x,y polarized.[4-6,8] Assuming the vibronic intensity mechanism, in D_{4h}, there is only one band which can be polarized exclusively in x,y: $xy \to x^2 - y^2$. This establishes the assignment of the above-mentioned bands as the spin-allowed transition, $^1A_{1g} \to {}^1A_{2g}$, in their respective complexes. Furthermore, with xy as the highest filled level, the 20,700 cm^{-1} band in $PtCl_4^{2-}$ must be an excitation to a primarily spin-triplet excited state. Also, magnetic circular dichroism has been observed[9] for the 29,500-cm^{-1} peak[8] (30,300 cm^{-1} in solution[3]) in $PtCl_4^{2-}$. This has been interpreted as due to a small Zeeman splitting of the ^1E_g excited state assigned to that transition. Thus, of the three primarily singlet transitions, the positions of two, $^1A_{1g} \to {}^1A_{2g}$ and $^1A_{1g} \to {}^1E_g$, are established. It is the position of the $^1A_{1g} \to {}^1B_{1g}$ ($z^2 \to x^2 - y^2$) transition that is ambiguous. Martin, Tucker, and Kassman (MTK) have recently suggested[8] two alternative placements of this transition. Alternative A assigns the $^1A_{1g} \to {}^1B_{1g}$ transition to the band observed[5] at 36,500 cm^{-1} in the reflectance spectrum of K_2PtCl_4. This leads to the ordering $x^2 - y^2 > xy > xz,yz > z^2$. Alternative B places the transition in the 29,000-cm^{-1} region and assumes that it gives rise to part of the absorption in that region. This latter assignment scheme brings us back to the d-level ordering[2,3] of $x^2 - y^2 > xy > z^2 > xz,yz$, although it is true that in this case the z^2 and xz,yz levels have about the same one-electron energy. The present calculation clearly favors the MTK alternative A, as is evident from the assignments given in Table II. An analogous assignment of the spectrum of $PdCl_4^{2-}$ is also presented and compared with the calculation. The band at 29,500 cm^{-1} in

$PdCl_4^{2-}$ is nicely accommodated by the $^1A_{1g} \rightarrow {}^1B_{1g}$ assignment and it would appear that the MTK alternative A is more consistent in dealing with both $PtCl_4^{2-}$ and $PdCl_4^{2-}$.

The calculated low-energy bands for $PdCl_4^{2-}$, representing transitions to triplet excited states, have not been observed experimentally. This must be due to their low intensity. Confirmation of the several spin-forbidden bands in $PtCl_4^{2-}$ was not forthcoming until low-temperature polarized spectra were taken.[8] Perhaps similar work on $PdCl_4^{2-}$ will reveal the missing d → d bands.

High-Intensity Bands.—The present molecular orbital model for the square-planar halides has been set up on the assumption that the first high-intensity band is a transition from a filled, predominantly halide level (b_{2u}) to the empty $3b_{1g}$ "metal" level. This type of transition is commonly referred to as L → M charge transfer. However, there is also the possibility that the lowest transitions are from the highest filled d-symmetry levels to the p_z-symmetry $2A_{2u}$ level (d → p bands). There should be three such transitions observable in a closely spaced band system, the fully allowed $^1A_{1g} \rightarrow {}^1E_u$ $[2e_g \rightarrow 2a_{2u}]$ and $^1A_{1g} \rightarrow {}^1A_{2u}$ $[3a_{1g} \rightarrow 2a_{2u}]$ bands and an orbitally forbidden $^1A_{1g} \rightarrow {}^1B_{1u}$ $[2b_{2g} \rightarrow 2a_u]$ band. Both known[3] energy shifts of high-intensity bands in the series MX_4^{n-} (M = Pd(II), Pt(II), Au(III); $X^- = Cl^-, Br^-$) and the calculated energy levels shown in Figure 1 support the L → M type assignments for the complexes under scrutiny here. Thus, the d → p bands in the planar halides are at higher energies than the L → M bands. However, in planar complexes where L → M charge-transfer transitions are of considerably higher energy than in the halide series, the d → p transitions should be responsible for the first group of high-intensity bands. Presumably, $Pt(NH_3)_4^{2+}$ and $Pd(NH_3)_4^{2+}$ are such cases.

Detailed assignments of the charge-transfer bands in $PtCl_4^{2-}$ and $PdCl_4^{2-}$ are given in Table II. The first broad band is expected to contain two allowed transitions, $^1A_{1g} \rightarrow {}^1A_{2u}$, $^1E_u(1)$ $[b_{2u}, 3e_u \rightarrow 3b_{1g}]$. Since interelectronic-repulsion effects are not considered in the calculated transition energies, the SCCC–MO model places these excitation energies very close together, with $^1A_{1g} \rightarrow {}^1A_{2u}$ being somewhat lower. The second high-intensity band, observed in the $PdCl_4^{2-}$ complex, is assigned $^1A_{1g} \rightarrow {}^1E_u$ (2) $[2e_u \rightarrow 3b_{1g}]$. In Table II the calculated and observed positions of this band are compared.

Discussion

In predominantly σ-bonded systems, with ligands such as H_2O and NH_3, and first-row metals, Δ_0 is known[18] to increase with an increase in metal oxidation number. With a large extrapolation, it has been argued that Δ_1 should not be larger in $PtCl_4^{2-}$ than the 25,100-cm^{-1} value observed for Δ_0 in $IrCl_6^{3-}$.[7] However, with either of the MTK assignments, it now seems firmly established that the first singlet band in a given square-planar Pd(II) or Pt(II) halide complex occurs at a *higher* wavenumber than the first singlet band in an analogous octahedral Rh(III) or Ir(III) halide. Credit should be given to Jørgensen for first suggesting[18] and defending[19] this particular trend.

We suggest here that an inverse dependence of Δ on oxidation number is not limited to the cases of changing geometry and d^n configuration (as in going from Ir(III) to Pt(II)), but rather will be found in many isoelectronic and isostructural complexes with extreme covalent character such as are formed with class B (or soft) transition metals. For example, molecular orbital calculations[16] of $AuCl_4^-$ with F factors in the same range as those used for the model $PtCl_4^{2-}$ give δ_1 values which are substantially *smaller* than the calculated δ_1 value for $PtCl_4^{2-}$. For the particular calculation of $AuCl_4^-$ which fits its charge-transfer spectrum, $F_\pi = 1.70$, $F_\sigma = 1.91$, and $\delta_1 = 20{,}800\ cm^{-1}$. A population analysis of the relevant levels in $PtCl_4^{2-}$ and $AuCl_4^-$ shows the following: $2b_{2g}$ (xy), 50% metal and $3b_{1g}$ $(x^2 - y^2)$, 65% metal in $PtCl_4^{2-}$; $2b_{2g}$ (xy), 42% metal and $3b_{1g}$ $(x^2 - y^2)$, 90% metal in $AuCl_4^-$. Recall that in the model used here, the metal diagonal elements decrease (become more negative) while those of the ligand stay approximately constant with increasing metal oxidation number. Presumably then, while the ligand π character of the $2b_{2g}$ (xy) increases, keeping the position of the $2b_{2g}$ (xy) approximately constant, the metal σ character of the $3b_{1g}$ $(x^2 - y^2)$ increases sharply in going from Pt(II) to Au(III), lowering the $3b_{1g}$ $(x^2 - y^2)$ level relative to the stationary $2b_{2g}$ (xy) and causing a net *decrease* in δ_1. This result from the molecular orbital model suggests that the ligand-field parameter Δ_1 will be larger for Pt(II) than for Au(III) in analogous halide complexes. In simple terms, the first ligand field band in these systems has considerable L → M charge-transfer character and thus it behaves accordingly.

Therefore, we expect an inverse Δ dependency on metal oxidation number in complexes in which the highest filled π ligand-field levels have an unusually large component of ligand orbitals. Of course, this analysis predicts that the first ligand-field band in an Au(III) square-planar chloride or bromide complex will fall at lower energy than in the corresponding Pt(II) complex. This is indeed the case in certain systems; for example, the first electronic band in $Au(dien)Cl^{2+}$ (33,100 cm^{-1}) falls lower than the first band in $Pt(dien)Cl^+$ (37,040 cm^{-1}).[20] Unfortunately, the spectra of the simple complexes in $AuCl_4^-$ and $AuBr_4^-$ have not been sufficiently resolved[21] to yield reliable values for Δ_1. However, another possibly related comparison may be found in the metal–mnt^{2-} (maleonitriledithiolate) complexes, where the highest filled ligand-

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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]

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

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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,

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