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The Electronic Structure of $K[Pt(C_2H_4)Cl_3]\cdot H_2O$

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A semi-empirical Self Consistent Charge and Configuration (SCCC) molecular orbital calculation has been carried out for Zeise's salt, $K[Pt(C_2H_4)Cl_3]\cdot H_2O$. The polarized crystal spectrum of this compound was measured at liquid nitrogen and liquid helium temperatures over the range 14 000 to 27 000 cm^{-1}. The calculated energy levels conform to the qualitative structure of the spectrum, but the calculated transition energies, especially for charge transfer, are smaller than the energies of the observed bands. A similar calculation for $PtCl_4^{2-}$ gives good agreement with the $d-d$ parity forbidden bands but also calculates the charge transfer levels at too low an energy. The Mulliken population analysis performed as part of the calculation provides an indication of the extent of back-bonding in the complex.

The history of theories of structure and bonding for metal-olefin complexes such as Zeise's salt, $K[Pt(C_2H_4)Cl_3]\cdot H_2O$, is a long and interesting one. From the time of its first preparation,[1] a large number of different structures and bonding schemes have been proposed[2] for Zeise's anion, culminating in the commonly accepted π-complex formulation due to Dewar.[3] The applicability of this formulation has been demonstrated by Chatt,[4] and evidence for the required structure has been derived from the infrared spectrum,[5] X-ray diffraction[6,7] and NMR[8] measurements.

The π-complex description explains the stability of metal-olefin complexes and their limitation to certain transition metals on the basis of "π-back-bonding" from filled d-orbitals on the metal to empty antibonding orbitals on the ligand. Since its introduction by Pauling[9] to explain the bond lengths in $Ni(CO)_4$, the concept of back bonding has been used to explain many other properties of transition metal complexes, such as the kinetic "*trans*-effect",[10] and the relative stabilities of M—SCN and M—NCS bonding in thiocyanate complexes.[11] Estimates of the extent of such dative π-bonding have varied greatly and thus it appeared to be useful to attempt a calculation which would give a quantitative measure of this effect. A calculation has been made

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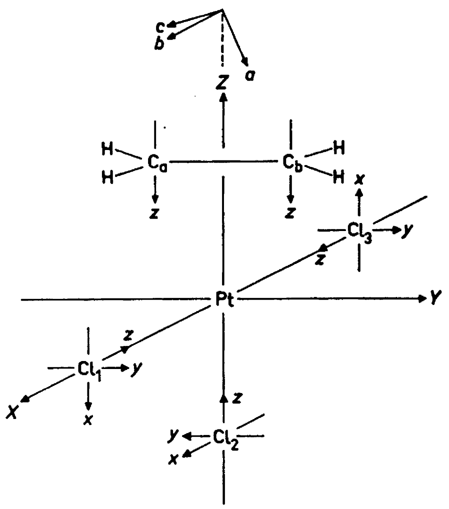

Fig. 1. Coordinate system for Zeise's salt. The plane of the ethylene molecule lies perpendicular to the Z axis with C—C parallel to Y. The b crystal axis is parallel to X while a and c lie in the YZ plane at angles of 23.2° and 73.8° from Z, respectively.

for a cyclopentadienyl complex[12] and Dyatkina[13] has discussed Zeise's anion qualitatively, but no quantitative study has been made.

This report describes a calculation of the one-electron energy levels of Zeise's anion using the semi-empirical molecular orbital treatment of Wolfsberg and Helmholz[14] as modified by Ballhausen and Gray.[15] The polarized crystal spectrum of the complex has been measured in order to provide an experimental basis for the calculations. The calculated energy levels are correlated with the observed spectrum and the electronic populations in various orbitals are used to discuss bonding in the complex.

MOLECULAR ORBITAL CALCULATIONS

Basis functions. The atomic orbitals used in the calculation are platinum $5d$, $6s$, and $6p$, chlorine $3s$ and $3p$, and carbon $2p$. The coordinate system used is shown in Fig. 1 and the orbital transformation scheme under C_{2v} symmetry appears in Table 1. As shown in Table 1, all linear combinations of ligand functions were normalized including ligand-ligand overlap.

Table 1. Orbital transformation scheme for C_{2v} symmetry.

Symmetry representation	Metal orbitals	Ligand σ orbitals	Ligand π orbitals
A_1	$6s$, $6p_z$ $5d_{z^2}$, $5d_{x^2-y^2}$	$(2+2S_{ab})^{-\frac{1}{2}}(p_a+p_b)$, p_2 s, $(2+2S_{13pz})^{-\frac{1}{2}}(p_{1z}+p_{3z})$ $(2+2S_{13s})^{-\frac{1}{2}}(s_1+s_3)$	$(2-2S_{13px})^{-\frac{1}{2}}(p_{3x}-p_{1x})$
A_2	$5d_{xy}$		$(2-2S_{13py})^{-\frac{1}{2}}(p_{1y}-p_{3y})$
B_1	$5d_{xz}$, $6p_x$	$(2-2S_{13pz})^{-\frac{1}{2}}(p_{1z}-p_{3z})$ $(2-2S_{13s})^{-\frac{1}{2}}(s_1-s_3)$	p_{2x} $(2+2S_{13px})^{-\frac{1}{2}}(p_{1x}+p_{3x})$
B_2	$5d_{yz}$, $6p_y$		p_{2y}, $(2-2S_{ab})^{-\frac{1}{2}}(p_b-p_a)$ $(2+2S_{13py})^{-\frac{1}{2}}(p_{1y}+p_{3y})$

Overlap integrals. Atomic overlaps were calculated on the GIER computer at the H. C. Ørsted Institute using an Algol program written by H. Johansen.[16] SCF functions were used for carbon [17] and chlorine.[18] The analytic functions used for the platinum $5d$ and $6s$ orbitals were obtained by fitting the numerical data of Herman and Skillman [19] using a linear combination of $2n$-$2l$-1 Slater type orbitals (n = orbital quantum number, l = azimuthal quantum number).[16] The $6p$ function is not given by Herman and Skillman and was approximated by a single STO, slightly more diffuse than the $6s$ SCF function, with orbital exponent of 1.2. The interatomic distances given by Wunderlich and Mellor [6] ware used. Group overlap integrals were calculated following Ballhausen and Gray.[15]

Coulomb and exchange integrals. The diagonal terms, H_{ii}, of the secular equation were estimated as the VSIE's of the various atoms. An estimate of VSIE as a function of charge for platinum was obtained from data in Moore's [20] tables and from Landolt-Börnstein.[21] Data for chlorine came from Moore [20] and for carbon from the work of Pilcher and Skinner.[22] The exchange integrals were approximated in the usual way as:

$$H_{ij} = -2G_{ij}\sqrt{H_{ii}H_{jj}}$$

and the secular equation

$$|H_{ij}-WG_{ij}| = 0$$

was solved for each irreducible representation of the group C_{2v}. The process was iterated using an Algol program written by H. Johansen [16] until the assumed and calculated charges on platinum, carbon, and chlorine agreed. The charge on the ethylene carbons was hard to determine, because the reduction of the carbon coulomb integral with increasing negative charge should allow a shift of the σ electron density toward the ethylene hydrogens. Since this shift in electron density is not included in the population analysis, the charge on each carbon atom was arbitrarily reduced by one-half before calculating the coulomb integral. This should introduce little error in any case, since the total (negative) charge per carbon atom never exceeded 0.07. The self-consistent charges and VSIE's calculated are given in Table 2.

Table 2. Self-consistent charge and VSIE data.

Atomic orbital	Electronic population Input	Electronic population Output	Coulomb energy (10^3 cm^{-1})
Pt $5d$	8.772	8.778	$-$ 90.7
$6s$	0.630	0.626	$-$ 85.2
$6p$	0.565	0.559	$-$ 43.2
Cl $3s$	1.92	1.92	$-$173.5
$3p$	5.36	5.35	$-$ 83.5
C_2H_4 π^b	1.79	1.77	$-$106.0
π^*	0.38	0.36	$-$ 52.8
Charge on Pt	+0.033	+0.036	–
Charge on Cl	$-$0.304	$-$0.303	–
Charge[a] on C	$-$0.042	$-$0.032	–

[a] Corrected as described in the text.

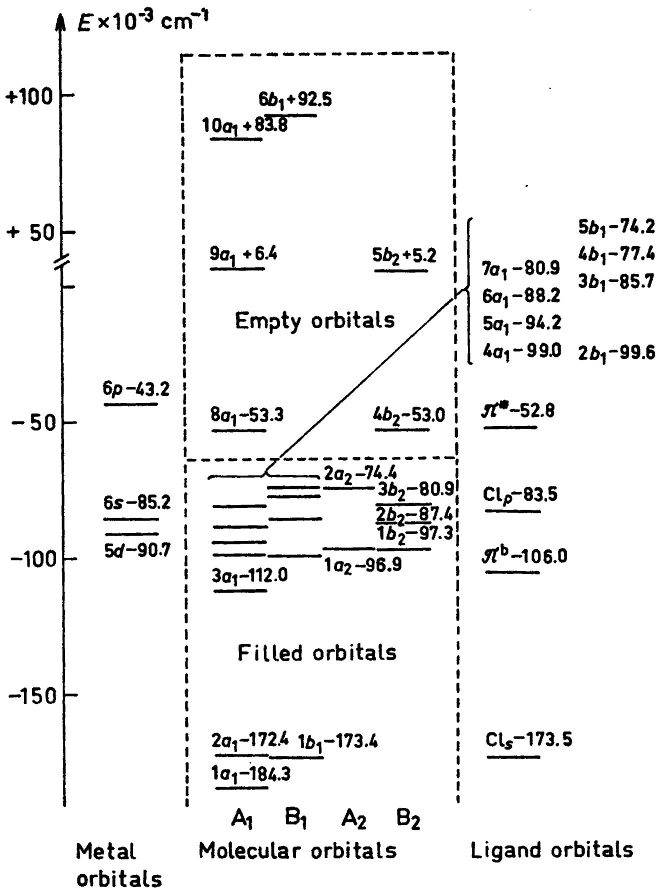

Fig. 2. One-electron energy levels for Zeise's salt. The usual connecting lines have been omitted for clarity and the levels are separated according to the irreducible representations of C_{2v} symmetry.

Energy levels. The calculated one-electron levels are shown in Fig. 2, drawn to the scale indicated in the figure. From these levels and their respective symmetry representations we can construct Table 3 which shows some of the predicted one-electron transitions together with their polarizations along the axes of Fig. 1. The energies listed in Table 3 are simply the differences between one-electron levels and have not been corrected for interelectronic repulsions or spin-orbit coupling.

EXPERIMENTAL

All spectra were measured using a Cary Model 14 recording spectrophotometer. A sample of Zeise's salt was kindly provided by Dr. P. Brandt, Chemical Laboratory A, Technical University of Denmark. The solution spectrum of this material corresponded to the ultraviolet-visible [23] and infrared [5] measurements made by previous workers.

Table 3. Polarization of expected transitions. Zeise's salt ground state is $^1A_1$.

Excited state	Transition	Polarization	Energy (cm^{-1})
$^{1,3}B_1$	$5b_1 \rightarrow 8a_1$	x	20 864
$^{1,3}A_2$	$2a_2 \rightarrow 8a_1$	forbidden	21 100
$^{1,3}A_2$	$5b_1 \rightarrow 4b_2$	forbidden	21 200
$^{1,3}B_1$	$2a_2 \rightarrow 4b_2$	x	21 370
$^{1,3}B_1$	$4b_1 \rightarrow 8a_1$	x	24 054
$^{1,3}A_2$	$4b_1 \rightarrow 4b_2$	forbidden	24 400
$^{1,3}A_1$	$7a_1 \rightarrow 8a_1$	z	27 550
$^{1,3}B_2$	$3b_2 \rightarrow 8a_1$	y	27 562
$^{1,3}B_2$	$7a_1 \rightarrow 4b_2$	y	27 854
$^{1,3}A_1$	$3b_2 \rightarrow 4b_2$	z	27 867
$^{1,3}B_1$	$3b_1 \rightarrow 8a_1$	x	32 337
$^{1,3}A_2$	$3b_1 \rightarrow 4b_2$	forbidden	32 641

Crystals were grown from dilute (5 %) hydrochloric acid solution and the best results were generally obtained by allowing a small quantity of solution to evaporate from a glass slide. Quite large crystals could also be grown by allowing a saturated solution to evaporate very slowly at about 5°C. Several of these crystals were polished carefully to a thickness of about 0.2 mm. Attempts to produce thinner crystals by polishing only resulted in cracking. For this reason it was not possible to measure the polarization of the more intense peaks in the spectrum and data are reported only for the first two inflections in the solution spectrum.

Measurements were made at room temperature, liquid nitrogen temperature, and liquid helium temperature, but there was very little change in the appearance of the first two peaks over this range. The peaks became somewhat sharper and the intensity of the first peak decreased to about 85 % of its former value when the crystal was cooled to liquid helium temperature. The intensities, transition energies (measured as the center of a Gaussian peak), and polarizations of the peaks are given in Table 4. The observed intensity *versus* wavelength data were fitted by a series of Gaussian (in wave number) curves using a least squares Gier program written by O. S. Mortensen.

Table 4. Solution and crystal spectra of Zeise's salt.

Spectrum	Polarization	$\tilde{\nu}$ (cm^{-1})	ε
Solution	—	23 900	40.1
	—	30 350	340
	—	33 450	605
	—	37 450	3100
	—	40 700	3260
Crystal	$\parallel$ *a* crystal axis	22 940	0.72[a]
	»	32 000[b]	25[b]
	$\parallel$ *b* crystal axis	21 828	0.04
	»	24 490	0.77
	»	29 000[b]	10[b]
	$\parallel$ *c* crystal axis	22 727	0.55
	»	32 000[b]	35[b]

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[a] Relative ε values consistent among all crystal spectra.

[b] Estimated from data up to 27 000 cm^{-1} (see text).

DISCUSSION OF ELECTRONIC SPECTRA

If we first consider the solution spectrum we can see that the general arrangement of the electronic energy levels predicted by the calculation is confirmed. That is, there are a number of strongly allowed, intense bands in the spectrum, as would be expected from the large number of filled levels just below the highest filled $5b_1$ level and the lenient selection rules under C_{2v} symmetry (see Table 3 and Fig. 2).

Also, we note that, so far as it has been measured, the spectrum parallel to *a* is very nearly the same as that parallel to *c*, but both differ from the spectrum with the electric vector of the light parallel to the *b* crystal axis. This is unexpected since in square planar complexes such as K_2PtCl_4 the spectrum parallel to the *Y* axis of Fig. 1 is unique while spectra parallel to *X* and *Z* of Fig. 1 are the same. This similarity along *a* and *c* may be coincidental since the full polarized spectrum has not been observed, but the calculated energy levels also predict that the *Y* and *Z* polarized spectra should be similar. The lowest unfilled levels in Fig. 2 are $8a_1$ and $4b_2$. The selection rules under C_{2v} symmetry allow transitions to $8a_1$ from filled a_1 and b_2 levels. These transitions should be polarized along the *Z* and *Y* directions, respectively. Transitions to $4b_2$ are also allowed from a_1 and b_2 levels, polarized along the *Y* and *Z* axes, respectively. Since the separation of $8a_1$ and $4b_2$ is calculated to be $\sim$ 300 cm^{-1} a one electron jump from, say, a filled a_1 level will have *Y* (to $4b_2$) and *Z* (to $8a_1$) polarized components separated by only 300 cm^{-1} and thus the spectra polarized along *a* and *c* should be similar.

When it comes to the observed transition energies the calculation does somewhat less well. The first three observed transitions in the solution spectrum are too weak in intensity to be assigned as fully allowed transitions, but the lowest calculated transition is fully allowed. However, there are two forbidden transitions calculated at nearly the same energy and the second and third solution bands may be assigned to these levels. The first solution band as well as the very weak band at 21 828 cm^{-1} in the *b* polarized crystal spectrum were assigned as triplet components of these transitions.

Further support for this assignment comes from the polarization data. From measurements up to about 27 000 cm^{-1} it appears that the third band in the *b* polarized spectrum occurs at lower energy than the second bands in the *a* and *c* polarized spectra. Thus, the band in the solution spectrum at 30 350 cm^{-1} probably is *b* polarized and the band at 33 450 cm^{-1} is polarized parallel to *a* and *c*. This was confirmed by the Gaussian analysis, which, although the maxima of peaks marked (*b*) in Table 4 were not observed, indicated the approximate location of the peaks as tabulated there. Since the first two transitions calculated for *b* polarization have nearly the same energy we would expect double the normal intensity and $\varepsilon = 340$ appears to be too small to correlate with two fully allowed transitions. The same argument applies to the *a* and *c* polarized spectra where there are calculated four allowed transitions at nearly the same energy.

Thus we assign the solution band at 37 450 cm^{-1} as ${}^1A_1 \rightarrow {}^1B_1(5b_1 \rightarrow 8a_1)$ and ${}^1A_1 \rightarrow {}^1B_1(2a_2 \rightarrow 4b_2)$ and the band at 40 700 cm^{-1} as ${}^1A_1 \rightarrow {}^1B_1(4b_1 \rightarrow 8a_1)$. The energies calculated for these transitions are about 21 000 cm^{-1} and

24 000 cm^{-1}, showing poor agreement with experiment. However, the agreement is better for the forbidden bands which are calculated at about 21 100 cm^{-1} and observed at 30 350 cm^{-1} and 33 450 cm^{-1}. Table 5 shows an assignment of the observed bands which is the best possible at this time.

It should be noted at this point that a calculation was also performed for K_2PtCl_4 following the same procedure used here. This gave quite good agreement with the observed *d—d* transitions but the calculated charge transfer levels were too low. For example, $^1A_{1g} \rightarrow {}^1A_{2g}$ was calculated at 24 000 cm^{-1}, observed at 25 500 cm^{-1}; $^1A_{1g} \rightarrow E_g$ calculated 26 800 cm^{-1}, observed 30 200 cm^{-1}; $^1A_{1g} \rightarrow {}^1B_{1g}$ calculated 37 300 cm^{-1}, observed 37 900 cm^{-1} but the first charge transfer was calculated at around 30 000 cm^{-1} and is observed at 46 000 cm^{-1}. Probably a large part of this error is due to the interelectronic repulsions, which are largely neglected in the calculation and would certainly be important in the charge transfer transitions. It is not surprising that the observed transition energies are not correctly calculated for Zeise's salt where all of the transitions involve some transfer of charge.

BONDING IN ZEISE'S SALT

We now consider the data on electron populations obtained from the calculation. Table 2 gives the gross electronic population of each type of orbital on each atom in the anion, where each overlap population is divided equally between the two basis functions involved.

The interesting fact is that in the final, self-consistent calculation a considerable amount of charge is found in the anti-bonding π^* orbital of the ethylene and there has been a depletion of the charge associated with the π^b orbital on ethylene. Thus there is π-back-bonding to the extent that the population of π^* increases from zero to 0.36, and the σ-bonding reduces the population of π^b by about 0.33. The net effect is that the ethylene stays very nearly neutral despite its contribution of electrons to platinum in forming the coordinate σ-bond. The calculation quantitatively confirms the qualitative formulation of bonding in Zeise's salt due to Chatt.[4]

We next consider the effect of the strong π-bonding ethylene ligand on the chlorine atom in the *trans*-position. Table 6 compares overlap populations calculated for the s, p_σ, and p_π orbitals on the two different chlorine atoms. We see immediately that the overlap populations associated with the s and p_σ orbitals are nearly independent of the position of the chlorine atom. But

Table 5. Assignment of spectrum.

Excited state	Transition	Obs. energy (cm^{-1})
$^3A_2$	$2a_2 \rightarrow 8a_1$	21 828
$^3A_2$	$5b_1 \rightarrow 4b_2$	23 900
$^1A_2$	$2a_2 \rightarrow 8a_1$	30 350
$^1A_2$	$5b_1 \rightarrow 4b_2$	33 450
$^1B_1$	$5b_1 \rightarrow 8a_1$ $2a_2 \rightarrow 4b_2$	37 450
$^1B_1$	$4b_1 \rightarrow 8a_1$	40 700

Table 6. Overlap populations of selected orbitals.

Orbital	Cl(2)	Cl(1 or 3)
$p\pi$	0.031	0.191
$p\sigma$	0.154	0.175
s	0.012	0.019

the Pop($p\pi$) is six times larger in the *cis*-position than in the *trans*-position. This shows that bond weakening in the position *trans*- to a π-bonding ligand will only be important when the *trans*-ligand is also a strong π-bonder, since only the π electron populations are affected. Also the region opposite a strongly π-bonding ligand will have greatly decreased electron density as required by the π-bonding theory of the *trans*-effect. Again the qualitative picture of the π-bonding effects is confirmed by the calculation.

CONCLUSION

In conclusion we note that, although the calculation has not been successful in giving a quantitative interpretation of the spectrum of Zeise's salt, the results are in partial agreement with experiment both for the olefin complex and for K_2PtCl_4. It appears that in both cases a fairly large correction ($\sim$ 15 000 cm^{-1}) must be made in order that the calculated charge transfer energies agree with experiment. However, the situation is much better in the case of forbidden transitions, especially for K_2PtCl_4, and the observed polarization of the crystal spectrum of Zeise's salt has been explained.

Perhaps the most interesting aspect of the calculation from the chemist's standpoint is the picture of bonding in Zeise's salt. The population analysis of the final molecular orbitals confirms the qualitative predictions made by Chatt and others regarding the effect of the π-bonding ethylene constituent on the electronic structure of this platinum complex.

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