

Electronic Structure of Square-Planar Transition Metal Complexes. II. Zeise's Anion, $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]^{-1a}$

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Abstract: The self-consistent-field $X\alpha$ -scattered wave (SCF- $X\alpha$ -SW) method is used to calculate the electronic structure of Zeise's anion. The resultant description of the Pt-ethylene bonding is found to be somewhat more complex than the simple Dewar-Chat model. The σ -bonding components are found to be considerably more important than π back-bonding. Optical transitions have been calculated and found to be in agreement with the peak positions of the experimental spectrum. Some aspects of the photochemistry are also briefly discussed on the basis of the calculations presented.

In spite of the great fundamental and practical importance of transition metal olefin complexes,²⁻⁵ there have been very few attempts at a thorough quantum mechanical description due to the complexity of such systems. One of the chief theoretical interests in this class of compounds is in obtaining a detailed understanding of the metal-olefin bond, from which there is the hope that more insight into the role of transition metals as catalysts in olefin chemistry⁶⁻⁸ might evolve. The present work using the recently developed SCF- $X\alpha$ scattered wave method⁹⁻¹¹ provides the most thorough theoretical study to date for Zeise's anion, $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]^-$. This complex has been well-studied both experimentally and theoretically and is one of the simplest metal-olefin compounds; it is also representative of an important class of olefin π -complexes of platinum and palladium^{10,12} which are thought to be intermediates in catalytic processes.

The most widely accepted theoretical model for describing bonding between a transition metal atom and an olefin is that by Dewar¹³ and Chatt and Duncanson.¹⁴ This model describes the bonding by a two-way donor-acceptor mechanism, *i.e.*, a σ -donation from the bonding π -electrons of the olefin to empty d levels of the metal and a π back-donation from the metal to the empty π^* level of the ligand. Although this model has provided an explanation of the bonding

and the structure as well as other properties of such complexes in a qualitative manner, the quantitative contribution of the σ and π components is still a matter of considerable discussion.¹⁵⁻¹⁷

Previous Calculations of Metal-Olefin Complexes

For Zeise's anion, two semiempirical calculations have been reported, one using an iterative extended Hückel (IEH) method¹⁸ and the other a CNDO-type method.¹⁹ Both explained the optical spectrum of Zeise's salt very qualitatively, but their results concerning the relative importance of σ - and π -bonding differed. Extended Hückel calculations have also been carried out to gain some insight into the mechanism of Ziegler-Natta catalysts²⁰ and to explain the bonding of acetylene to platinum.²¹

It is only recently that more rigorous calculations of metal-olefin systems have become available. It was concluded from the results of the first such study, an *ab initio* calculation of the $\text{Ag}^+-\text{C}_2\text{H}_4$ complex,²² that σ -donation is significantly larger than π back-donation. Another calculation using the Hartree-Fock-Slater model implemented by the discrete variational method²³ investigated the interaction between ethylene and TiF_5 and NiF_5 clusters.²⁴ It was concluded there that π back-donation was extremely important in these two complexes.

In the present calculation, the SCF- $X\alpha$ -SW method is employed. This method has been used successfully to study the electronic structure of a wide variety of systems^{25,26} and in the present case provides the basis

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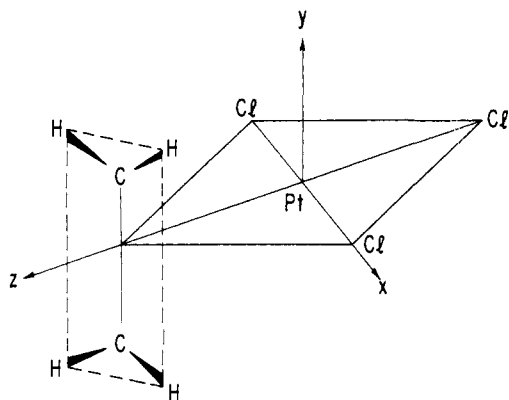


Figure 1. Coordinate system and geometry of Zeise's anion; the molecular orbitals are referred to this coordinate system.

for a discussion of the bonding and an interpretation of the optical spectrum.^{18,27-30}

Details of the Calculation

The SCF- $X\alpha$ -SW method is an all-electron first-principles method which employs the scattered-wave formalism¹¹ to solve the SCF- $X\alpha$ equations.⁹ It has been described in detail elsewhere.⁹⁻¹¹ For a short summary of the method see the preceding paper.³¹ The structure of Zeise's anion has been determined with high accuracy by a neutron diffraction study on Zeise's salt;³² this is the source of the experimental geometry used in the present calculation. The previous calculations on Zeise's anion^{18,19} were based on X-ray crystallographic data^{33,34} which show significant differences from the neutron diffraction results. The neutron study showed the C-C double bond to be at a right angle to the PtCl_3 plane and only slightly longer (1.354 Å) than the equivalent bond in ethylene (1.338 Å). The X-ray study³³ found, on the contrary, a marked bond lengthening (1.44 Å). The neutron diffraction study also confirmed the suggestion that the ethylene unit in Zeise's anion is not planar. The displacement of the carbon atoms toward the platinum—with respect to the plane defined by the four hydrogen atoms—amounts to 0.18 Å. The other bond lengths are: Pt-C, 2.14; Pt-Cl, 2.33; and C-H, 1.10 Å. The geometry and coordinate system used for the calculation are shown in Figure 1.

The radii for the muffin-tin spheres surrounding the various atoms are determined by symmetry and the requirement of touching spheres, once the radius of the Pt sphere is fixed. This is done by demanding that the ratio of the Pt radius to that of a cis Cl should be equal to the ratio of the corresponding Slater covalent radii.³⁵

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The radius of a carbon sphere is taken to be half the C-C bond length. The whole cluster of atomic spheres is surrounded by an outer sphere which touches the atomic sphere of the trans Cl. The various radii thus determined are (in bohr) $r_{\text{Pt}} = 2.526$, $r_{\text{Cl}(\text{trans})} = 1.943$, $r_{\text{Cl}(\text{cis})} = 1.868$, $r_c = 1.279$, $r_{\text{H}} = 0.789$, and $r_{\text{out}} = 6.412$. The Watson sphere radius is taken equal to the outer sphere radius and has a positive single charge on its surface, which provides an approximation to the stabilization effect arising from the crystalline environment.

The atomic exchange parameters for Slater's local statistical ($X\alpha$) approximation to the electron exchange correlation³⁶ are taken from the tabulation of Schwarz.³⁷ The α value for platinum has been extrapolated to be $\alpha_{\text{Pt}} = 0.7$.³¹ The α values for the interatomic and the extramolecular regions are set equal and taken as the weighted average over the atomic α values, where the ethylene subunit is given the same weight as the Cl ligands and the central atom.

As mentioned in the preceding paper,³¹ it can be shown that the mathematics of the scattered wave formalism are valid for overlapping spheres. It has been shown previously for the ethylene molecule that overlapping carbon spheres provide a more accurate potential which provides a very successful determination of the ionization potentials of this molecule.³⁸ As the C-C bond length³² in Zeise's anion indicates that the bond should be similar to the one in ethylene, we have also adopted the overlapping sphere parameterization³⁸ for the ethylene subunit as an alternative to the above procedure. In the previous ethylene calculation $r_c = 1.55$ bohr turned out to be a proper value to describe the C-C double bond. This leads to overlapping atomic potentials for C-C, C-Pt, and C-H. As in ref 38 we have used the exchange parameters for carbon and hydrogen which result from spin-polarized atomic calculations.³⁹ The results of both calculations are given below, and the meaning of the differences is discussed.

The core charges corresponding to the configurations C $1s^2$, Cl $1s^2 2s^2 2p^2$, and Pt up to $4d^{10}$ as determined from atomic calculations were included but kept fixed during the SCF cycles. This "frozen core" approximation⁹ has virtually no influence on the energies and the shapes of the one-electron molecular orbitals. The remaining 66 electrons were fully taken into account in the iterations to self-consistency. The SCF- $X\alpha$ procedure converged for Zeise's anion in about 30 iterations, requiring 9 min of computation time on an IBM 370/165 computer. To compute the optical excitations, Slater's "transition-state" procedure³⁶ was used. The singlet and triplet excitations were resolved by combining the results of non-spin-polarized and spin-polarized calculations, the latter yielding the triplet energies directly.³¹

Results of the Calculation

The results for the SCF- $X\alpha$ -SW ground-state orbital energies of Zeise's anion $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]^-$ are listed in Table I for the two parameter sets mentioned above.

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Table I. SCF- $X\alpha$ -SW Orbital Energies (in eV) of Zeise's Anion, Separated According to the Irreducible Representations of the C_{2v} Point Group^a

Orbital energies	Irreducible representation							
	a ₁		a ₂		b ₁		b ₂	
	A	B	A	B	A	B	A	B
	-2.83	-1.96					-2.67	-1.52
	-4.95	-3.97					-4.92	-3.29
	-8.27	-7.45	-8.19	-7.29	-7.92	-6.94	-8.16	-7.43
	-9.17	-8.24	-10.77	-9.06	-8.21	-7.34	-9.06	-8.24
	-9.76	-8.81	-12.19	-10.06	-8.95	-8.11	-10.91	-9.71
	-11.18	-10.28			-10.88	-9.68	-17.41	-16.10
	-11.80	-10.96			-14.55	-13.00		
	-14.23	-13.22			-21.03	-20.29		
	-20.26	-19.75						
	-21.19	-20.51						
	-21.62	-22.66						

^a Only valence-type orbitals and the lowest empty levels are shown. Levels below the dashed line are fully occupied in the ground state; those above the line are empty. ^b The levels calculated from the usual parameter set are given in column A; column B shows the results for the case of overlapping spheres and exchange parameters from spin-polarized atomic calculations. For details see text.

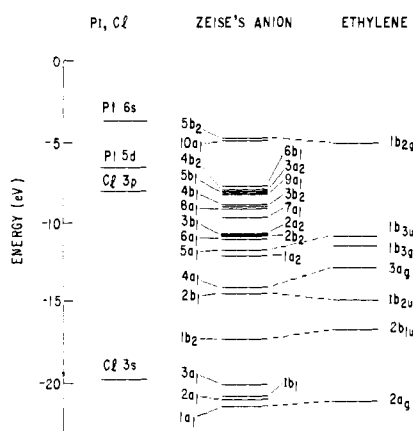


Figure 2. Ground state SCF- $X\alpha$ electronic energy levels of Zeise's anion—case A. The highest occupied orbital is $6b_1$.

Recall that case A is the standard parameter set and that case B uses overlapping carbon spheres, and α 's are determined by spin-polarized atomic calculations. The levels are labeled according to the irreducible representations of the C_{2v} point group. Only the lowest unoccupied levels and the valence-type orbitals are included in the table; orbitals which are completely localized within atomic "muffin-tin" spheres, such as the Pt $4f^{14}$ "frozen core" levels, are not listed. When labeling the various orbitals of the same representation, a sequential numbering is used starting with the lowest occupied orbitals listed in Table I. For example, we refer to the two lowest empty levels as $10a_1$ and $5b_2$, respectively. The levels of Table I, case A and case B, are also shown in Figures 2 and 3, respectively, and are compared with the SCF- $X\alpha$ atomic levels of Pt and Cl and the SCF- $X\alpha$ -SW orbital energies of ethylene.³⁸

Discussion

Bonding in Zeise's Anion. For discussing the bonding in Zeise's anion use has been made of contour plots of the individual orbitals as well as the orbital charge distribution as obtained from the SCF- $X\alpha$ -SW calculations. In the latter case, one determines for each orbital the fraction of charge in the various atomic spheres as well as in the interatomic and extramolecular

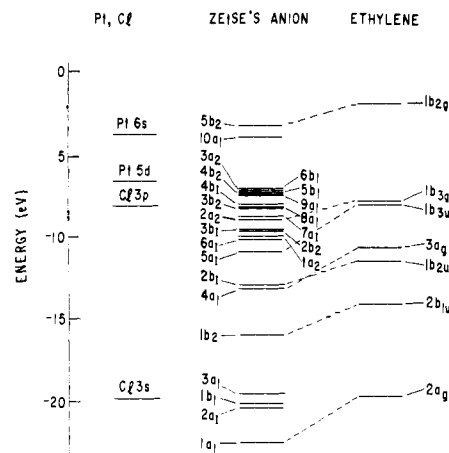


Figure 3. Ground state SCF- $X\alpha$ electronic energy levels of Zeise's anion—case B. The highest occupied orbital is $6b_1$.

regions. This procedure, based on the partitioning of space which is the basis of the scattered wave method, is analogous to a conventional population analysis. In the following we will discuss the bonding in Zeise's anion as deduced from the calculations using both parameter set A and parameter set B; a comparison of the results obtained will be provided. It should be mentioned at this stage, however, that this comparison shows only very small differences.

One of the most striking features in looking at the orbital contour plots and orbital charge distributions is the degree to which ethylene is preserved as a subunit in the molecule. This is of course consistent with much chemical^{3-5,12} and spectroscopic information.^{5,28} The ethylene levels,^{38,40} $2a_g$, $2b_{1u}$, $1b_{2u}$, $3a_g$, and $1b_{3g}$, can be identified in Zeise's anion as the $1a_1$, $1b_2$, $2b_1$, $4a_1$, and $1a_2$ orbitals, respectively, for case A; see Figure 2. For case B, the same identification can be made except that in this case the $1b_{3g}$ orbital of ethylene corresponds to the $2a_2$ orbital of Zeise's anion, see Figure 3. This identification is consistent with the Dewar-Chart scheme^{13,14} in which these orbitals are also not considered to contribute to the metal-olefin bonding. The b_{3u} orbital of ethylene, usually referred to as the π level

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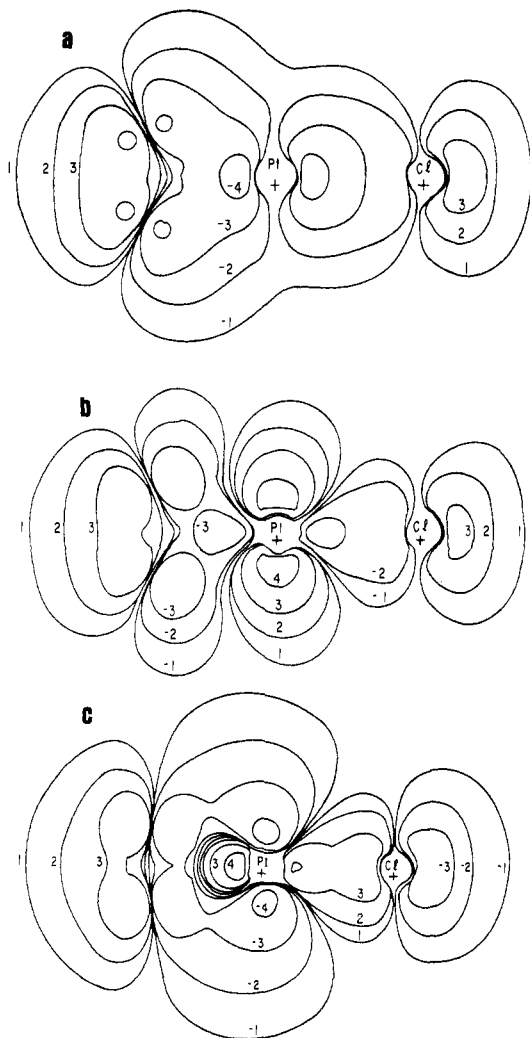


Figure 4. Contour plots of σ -like bonding orbitals of Zeise's anion. The contour values increase in absolute magnitude with increasing absolute values of the contour labels. The sign of the labels gives the sign of the orbital lobes. The set of contour values plotted is the same for each of the three orbitals. The interior nodes at the various atoms are not shown for clarity of presentation: (a) the $5a_1$ orbital, (b) the $6a_1$ orbital, and (c) the $7a_1$ orbital showing significant interaction between the ethylene π -orbital and the Pt $d_{z^2-y^2}$ orbital.

and thought of as being a basic component of the metal-olefin bond, undergoes very significant mixing with Pt orbitals and contributes nearly equally to the $5a_1$, $6a_1$, and $7a_1$ orbitals. Contour plots of these orbitals for case B are shown in Figure 4. Apparently the "classic" argument of σ -donation^{13, 14} from the ethylene π -orbital to the empty d_{z^2} orbital of Pt is somewhat too simplistic, as this description applies only to the $5a_1$ orbital of Figure 4a. The other two σ -orbitals involve the ethylene π -orbital with a combination of the Pt d_{z^2} and $d_{z^2-y^2}$ orbitals. These features can be clearly seen in Figure 4b and 4c.

Of particular note is the conclusion deduced from Figure 4c, that the $d_{z^2-y^2}$ orbital of Pt is important in describing the σ -bonding of ethylene in Zeise's anion. To our knowledge, this is the first suggestion that this orbital contributes significantly to σ -bonding in such complexes.

We also find that the π -bonding (back-bonding) into the π^* ethylene orbital is rather less important than the

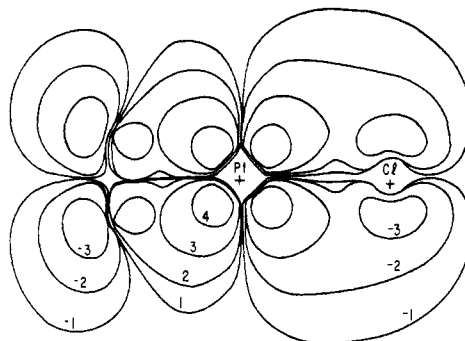


Figure 5. Contour plot of the π -like bonding orbital of Zeise's anion. The set of contour values are the same as those in Figure 4. This is the $2b_2$ orbital.

σ -bonding, amounting perhaps to at most 25% of the total bonding of ethylene to Pt. This π -orbital is the $2b_2$ orbital of Zeise's anion, and is shown for case B in Figure 5. Its importance in bonding can be roughly judged by comparing it to the σ -orbitals of Figure 4; all four orbital plots use the same contour values. Our results therefore seem to indicate a strong covalent bond formed between the metal and the olefin ligand mainly through a_1 orbitals. This is consistent with nuclear magnetic resonance studies which have indicated that the ethylene executes large amplitude rotational oscillations about the platinum-ethylene bond,⁴¹ thus suggesting that the π back-bonding cannot be very strong.

The findings of the present study disagree with those of both previous calculations on Zeise's anion.^{18, 19} In the extended Hückel-type calculation,¹⁸ π back-donation was calculated to be more important than σ donation. (Although it was concluded that the two effects were about equal, an examination of their results shows that the charge transfer due to σ donation should be 0.23 electron in contrast to the 0.33 electron claimed; this has the effect of increasing the importance of π donation.) One has to be careful, however, when trying to draw quantitative conclusions from EHT calculations, especially by the use of an LCAO population analysis. Mulliken and Löwdin analyses have been shown to give quite different results (e.g., atomic charges varying by >1.0 electron) for Pt-olefin complexes.⁴²

In the CNDO-type calculation,¹⁹ the σ - and π -bonding were found to be nearly equally important; however, one would hardly expect a charge of -0.558 on Pt as obtained from that calculation. In particular the Pt 6p population of 2.941 electrons seems to be almost completely an artifact of the basis functions chosen. It is therefore quite conceivable that the large amounts of π back-bonding found in these semiempirical LCAO calculations^{18, 19} are spurious and to a large extent caused by the basis set chosen. This is reminiscent of similar fallacious conclusions concerning the importance of d orbitals in molecules such as SO_1^{2-} .¹¹

The strong metal-olefin bond in Zeise's salt is accompanied by a weakening of the bond to the chlorine in the trans position to the ethylene; this results in a very marked trans effect.^{5, 28} In the present calcula-

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tions, this is reflected in the fact that the orbitals contributing most of the charge to the trans Cl sphere have mainly nonbonding character: $9a_1$, $6b_1$, and $4b_2$.

It is also instructive to compare the orbitals of Zeise's anion with those of PtCl_4^{2-} ,^{31,43} both calculated by the SCF-X α -SW method. In PtCl_4^{2-} the metal-ligand mixing was found to be stronger than usually assumed, resulting in significant d character for the bonding orbitals. Also the traditional d-like orbitals were found to be energetically close to the ligand orbitals. Compared to the 40–50% d character of the bonding orbitals in PtCl_4^{2-} , the low lying levels in Zeise's anion, $5a_1$, $6a_1$, $2b_2$, $3b_1$, and $2a_2$, show an even more pronounced Pt character (e.g., 50, 45, 75, 62, and 65%, respectively, for parameter set A). The levels from $8a_1$ upwards may be characterized as nonbonding or antibonding and the fraction of charge inside the platinum sphere never exceeds 21% compared to 44–59% for the antibonding orbitals in PtCl_4^{2-} .

This interpretation of the bonding in Zeise's anion based on the results of SCF-X α -SW calculations is essentially identical for both the parameter sets A and B. The set B gives a more satisfactory description for ethylene itself,³⁸ mainly through an upward shift of the orbital energies. In Zeise's anion we find also a corresponding shift of all levels upward by ~ 0.8 eV on the average (cf. Table I). The only exception to this general trend is the $1a_1$ orbital, corresponding to the $2a_g$ level of ethylene, thus indicating a slightly stronger interaction between platinum and ethylene.

Besides the four orbitals of Figures 4 and 5 which are essentially responsible for the bonding of ethylene to Pt, there are a few other orbitals which make rather smaller contributions to the bonding. These latter orbitals are the $3b_2$ and $4b_2$ orbitals which involve the π^* orbital of ethylene and the d_{yz} orbital of Pt and the $1a_2$ orbital which involves the interaction of p orbitals in the plane of the ethylene unit with the d_{xy} orbital of Pt in a δ -bonding fashion.

Optical Spectrum and Photochemistry. The results shown in Table I and Figures 2 and 3 were used as the starting point for carrying out transition-state calculations.^{7,31} The transition energies obtained are shown in Table II (case A) and Table III (case B) together with the experimental absorption energies^{18,28} and a rough characterization of the orbitals involved as derived from orbital contour plots and the calculated charge distributions of the orbitals. Ligand field transitions are denoted by d \rightarrow d, charge transfer from chlorine to platinum by L \rightarrow M, and charge transfer from platinum to ethylene by M \rightarrow ol.

As can be seen from Tables II and III the agreement between theory and experiment is quite good in the sense that, for each of the five absorption peaks determined experimentally, one or more calculated transitions can be assigned. However, as a consequence of the relaxed selection rules in $[\text{PtCl}_3(\text{C}_2\text{H}_4)]^-$, it is very difficult to make any unique assignments. We have not even calculated all the possible allowed transitions, since they lie quite close in energy to ones which have been calculated and included in Tables II and III.

There are some differences in the calculated transition

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Table II. Transition-State Energies, Case A

Transition	Symmetry	Type	Calcd transition state energy	Exptl transition energies (eV)
$6b_1 \rightarrow 10a_1$	3B_1	L \rightarrow M	3.0	2.9–3.3
$5b_1 \rightarrow 10a_1$	3B_1	L \rightarrow M	3.2	
$9a_1 \rightarrow 10a_1$	3A_1	L \rightarrow M	3.3	
$3a_2 \rightarrow 5b_2$	3B_1	M \rightarrow ol	3.5	3.3–3.8
$5b_1 \rightarrow 10a_1$	1B_1	L \rightarrow M	3.8	
$9a_1 \rightarrow 10a_1$	1A_1	L \rightarrow M	4.1	3.9–4.3
$8a_1 \rightarrow 10a_1$	3A_1	d \rightarrow d	4.2	
$3b_2 \rightarrow 10a_1$	3B_2	L \rightarrow M	4.2	
$3a_2 \rightarrow 5b_2$	1B_1	M \rightarrow ol	4.3	
$6b_1 \rightarrow 10a_1$	1B_1	L \rightarrow M	4.5	4.3–4.8
$8a_1 \rightarrow 10a_1$	1A_1	d \rightarrow d	4.7	
$7a_1 \rightarrow 5b_2$	3B_2	M \rightarrow ol	4.8	
$3b_2 \rightarrow 10a_1$	1B_2	L \rightarrow M	5.1	4.8–5.2
$7a_1 \rightarrow 5b_2$	1B_2	M \rightarrow ol	5.4	

Table III. Transition-State Energies, Case B

Transition	Symmetry	Type	Calcd transition state energy	Exptl transition energies (eV)
$6b_1 \rightarrow 10a_1$	3B_1	L \rightarrow M	3.1	2.9–3.3
$4b_2 \rightarrow 10a_1$	3B_2	L \rightarrow M	3.2	
$9a_1 \rightarrow 10a_1$	3A_1	L \rightarrow M	3.5	3.3–3.8
$5b_1 \rightarrow 10a_1$	3B_1	L \rightarrow M	3.6	
$6b_1 \rightarrow 10a_1$	1B_1	L \rightarrow M	4.0	3.9–4.3
$3a_2 \rightarrow 5b_2$	3B_1	M \rightarrow ol	4.2	
$5b_1 \rightarrow 10a_1$	1B_1	L \rightarrow M	4.2	
$8a_1 \rightarrow 10a_1$	3A_1	d \rightarrow d	4.2	
$9a_1 \rightarrow 10a_1$	1A_1	L \rightarrow M	4.3	
$3b_2 \rightarrow 10a_1$	3B_2	L \rightarrow M	4.5	
$8a_1 \rightarrow 10a_1$	1A_1	d \rightarrow d	4.7	4.3–4.8
$7a_1 \rightarrow 10a_1$	3A_1	d \rightarrow d	4.8	
$3a_2 \rightarrow 5b_2$	1B_1	M \rightarrow ol	5.0	4.8–5.2
$3b_2 \rightarrow 10a_1$	1B_2	L \rightarrow M	5.2	
$7a_1 \rightarrow 10a_1$	1A_1	d \rightarrow d	5.3	
$7a_1 \rightarrow 5b_2$	3B_2	M \rightarrow ol	5.5	

energies between the two parameters sets (A and B), but at low energy they both start with transitions to triplet states involving L \rightarrow M type transitions. This is consistent with the experimental fact that in the low energy region the extinction coefficient is smaller than at higher energies; this is of course the usual case. All of these lower energy transitions involve the $10a_1$ orbital as the final state; however, at somewhat higher energies, 3.5 eV for case A and 4.2 eV for case B, a transition to $5b_2$ becomes possible. The $5b_2$ orbital is essentially antibonding with respect to the Pt and ethylene. Thus the $3a_2 \rightarrow 5b_2$ transition would be expected to weaken the Pt-ethylene bond. In fact, Zeise's anion in solution undergoes a photoaquation reaction in which the ethylene is replaced by a water molecule. The onset of this reaction is at about 3.6 eV and reaches a maximum

quantum yield at about 4.2 eV.²⁹ Case A predicts two such transitions to the 5b₂ orbital, one at 3.5 eV and the other at 4.3 eV. Thus it is quite possible that it is these transitions to the 5b₂ orbital which weaken the Pt-ethylene bond and allow the aquation to take place. For case B, only one transition in this region is predicted, at 4.2 eV.

In summary, we believe that these results have provided not only new insight regarding the bonding in Zeise's anion but also a reasonable description of the optical spectrum and certain features of the photochemistry. Thus we are encouraged that the SCF-X α -SW method will provide useful information about other complex systems in the future.

Zinc(II) Catalysis of Oxalacetate Enolization and Decarboxylation

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Abstract: Detailed studies are reported for the Zn(II) catalyzed decarboxylation of oxalacetate. Two relaxations were observed, an initial absorbance increase being complete in about 30 sec and a subsequent absorbance decrease being complete after 15–30 min. Observation of these absorbance changes as functions of total metal ion, total acetate buffer, and hydrogen ion concentrations led to identification and characterization of the processes and of participant species. Use of high speed computational techniques allowed resolution of observed relaxation times into microscopic rate constants and definition of a number of formation constants for participant Zn(II)-oxalacetate complexes. The first relaxation arises from metal ion promoted keto-enol tautomerization and the second from catalyzed decarboxylation. The subsequent protonation of zinc pyruvate enolate product is rapid and unobservable.

Decarboxylation of β -keto acids is an important metabolic process in many biological systems. It is catalyzed by certain classes of enzymes that have a metal ion requirement and by metal ions alone, albeit at slower rates. Similarities in the enzymatic and chemical processes have stimulated interest in the single metal ion catalyzed reactions as models for the enzymatic systems.^{2–8} This interest has been focused mainly on the decarboxylation of oxalacetic acid (H₂oxac) and its derivatives.^{9–28}

When metal ion and oxalacetate solutions are mixed, an absorbance increase occurs which achieves a maximum value in a few seconds. It is followed by a slower absorbance decrease over a period of minutes. Steinberger and Westheimer⁹ observed similar behavior in the Cu(II) and Fe(III) catalyzed reactions of α,α -dimethyl oxalacetate, which can exist only in the keto form. These workers proposed the highly absorbing complexed pyruvate enolate, whose formation would give rise to the absorbance increase, as an intermediate.

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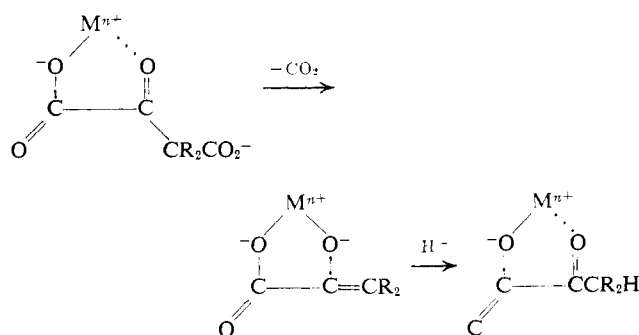
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Interpretation of the similar absorbance changes in the oxac systems is not as straightforward because oxac itself can exist in either keto or enol forms.

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