# Ab Initio Calculations of the Trigonal and Zero-Field Splittings in Trischelated Diketonato Complexes of Trivalent Chromium

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The ground and excited states of the neutral tris(1,3-propanedionato)chromium(III) $d^3$ complex are investigated with quantum chemical methods. Trigonal splittings are calculated and compared with experiment for the first two excited quartet states $^4T_{2g}$ and $^4T_{1g}$. The effect of spin−orbit coupling is also introduced, and a reassignment is proposed for three absorption bands in the doublet region. Trigonal symmetry-induced mixing between the $e_g$ and $t_{2g}$ shells is found to be responsible for the unusually large zero-field splitting of the $^4T_{2g}$ ground state. Orbitals pictures are presented which illustrate the role of the phase-coupling effect from the unsaturated ligands.

## 1. Introduction

The tris(acetylacetonato)chromium(III) complex, $Cr(acac)_3$, has been the subject of numerous spectroscopic, magnetooptical, and theoretical studies.[1] Especially the $\pi$ -bonding role of the conjugated bidentate chain and the possible occurrence of a *phase-coupling* effect have attracted attention.[2]

On the basis of a detailed analysis in the framework of the angular overlap model (AOM) Atanasov et al. concluded that the trigonal splitting of the first spin-allowed band, $^4T_{2g} \leftarrow {}^4A_{2g}$, by some 800 $cm^{-1}$ was indeed due to the phase-coupling effect.[3] In a further study[4] it was argued that the unusually large zero-field splitting (ZFS) of the ground state[5] by 1.2 $cm^{-1}$ could only be explained by assuming an anisotropic spin−orbit coupling mechanism. The low-temperature emission spectrum was assigned to phosphorescense from the $2\bar{A}(^3/_2)$ spin−orbit component of a trigonal $^2E$ state with predominant $^2E_g$ octahedral parentage.[1,4] The extremely large ZFS[6] and unusual **g** tensor[7,8] of the doublet state remained poorly understood.

Progress in correlated methods of computational chemistry currently allows us to perform electronic structure calculations that can throw a new light on these issues. In this paper we report the first investigation of a trischelated Cr(III) complex with the unsubstituted 1,3-propanedionato ligand, $PDO^-$, using the complete active space methods CASSCF and CASPT2. The conclusions corroborate the results by Atanasov et al. concerning the phase-coupling origin of the trigonal splitting.[3,4] In addition a new assignment for the doublet bands is suggested.

## 2. Computational Details

The calculations were performed with the MOLCAS program system,[9] and the effective symmetry was limited to the $C_2$ subgroup of the actual $D_3$ point group. Optimized orbitals were obtained with the CASSCF method for each state. The active space was restricted to the five d orbitals. It was noticed during optimization that the orbitals acquired some ligand character, but only to a minor extent. Orbitals of e, $a_1$, and $a_2$ type were prevented from mixing by using the supersymmetry option in the CASSCF program.

To introduce further correlation into the calculations a CASPT2[9,10] calculation was performed for each state, using the CASSCF wave function as reference. In the CASPT2 calculations all electrons, except 1s, 2s, and 2p on chromium and 1s on carbon and oxygen, were correlated (95 electrons). ANO type basis sets[11] were chosen as follows: Cr(17s12p9d4f/6s4p3d1f), O(10s6p/3s2p), C(10s6p/3s2p), and H(7s/2s).

The geometry of the $Cr(PDO)_3$ complex was determined in the following way. First we optimized the free $PDO^-$ ligand with the constraint that the O−O distance is 2.77 Å (see below). This produced a flat $C_{2v}$ geometry for the $PDO^-$ ligand. If the numbering of the carbons along PDO is $O-C_1-C_2-C_3-O$, the geometry is the following: distances (Å), O−O = 2.77, $O-C_1$ = 1.33, $C_1-C_2$ = 1.39, $C_1-H_1$ = 1.10, $C_2-H_2$ = 1.08; angles (deg), $O-C_1-C_2$ = 124.6, $O-C_1-H_1$ = 119.1, $C_1-C_2-H_2$ = 117.8. If the $PDO^-$ ligands are placed around the $Cr^{3+}$ ion so that the oxygens are in exact octahedral positions, an O−O distance of 2.77 Å corresponds to a Cr−O distance of $2.77/\sqrt{2}$ = 1.96 Å. For the closely related $Ga(acac)_3$ and $Cr(acac)_3$ complexes the geometry is available from X-ray diffraction data[12−14] and the coordination of the oxygens is very close to

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octahedral with Cr−O distances corresponding to the above value. For the calculations on $Cr(PDO)_3$ we used a geometry of the complex with oxygens in exact octahedral positions and all Cr−O distances at 1.96 Å.

In addition to the above calculations we also performed spin−orbit coupling calculations. This was done with an effective one-electron spin−orbit operator, where a parameter, the effective charge, is scaled so as to reproduce experimental excitation energies of the free Cr(III) ion. The state optimized in the CASSCF and compared with the experimental spectrum, was the $^4F$ state.[15] Further the orbitals were averaged (via the one electron density matrix) to get degenerate p and d shells. In this way the value of the effective charge was determined to 12 in atomic units of charge and, the corresponding one-electron orbital coupling matrix element between the ionic d orbitals to $\xi = 285\ cm^{-1}$.

The spin−orbit couplings between the different states in the complex were calculated according to the following procedure.[16] First, a set of orbitals was chosen from the CASSCF calculation of the $^2A_2$ state. These orbitals have the correct degeneracy and symmetry of the $D_3$ group. With these orbitals a configuration interaction (CI) calculation is then performed and the CI eigenvectors corresponding to different roots are saved. The Slater determinants were generated according to the restricted active space CI method. We constructed three different orbital subspaces, one with doubly occupied orbitals from which single and double excitations are performed, a second (active) space in which any number of excitations is allowed, and a third (virtual) space in which zero, one, or two electrons can be promoted from the other subspaces.

Next, the CI eigenvectors were used to calculate all spin−orbit couplings. According to the Wigner−Eckart theorem[17] we only need to calculate CI eigenvectors from the $M_s = {}^1/_2$ space. In this space components of both $S = {}^1/_2$ and $={}^3/_2$ are included. With the 3J coupling coefficients we can generate all the other components with $M_s = -{}^3/_2, -{}^1/_2, {}^1/_2, {}^3/_2$. For this purpose we decompose the spin−orbit operator into components with symmetry adaption to the rotational group

$$\hat{H}_{so} = 1/\sqrt{2}[i\,T^1_y - T^1_x + i\,T^{-1}_y + T^{-1}_x] + T^0_z$$

The spin−orbit tensor operators $T^m_a$ are defined as sums over one-electron operators: $a = \{x, y, z\}$, $m = \{1, 0, -1\}$, $s^+ = (s^x + i\,s^y)$, $s^- = (s^x - i\,s^y)$:

$$T^m_a = C(m)\frac{\alpha^2}{2}\sum_i \frac{Z_{\text{eff}}}{\hat{r}^3}\hat{l}^a_i\,\hat{s}^m_i$$

$$s^m_i = \{s^+_i, s^z_i, s^-_i\}$$

$$C(m) = \left\{-\frac{1}{\sqrt{2}}, 1, \frac{1}{\sqrt{2}}\right\}$$

The Cartesian coordinate orbital operator, $Z_{\text{eff}}\,\hat{r}^{-3}\,\hat{l}^a_i$, is computed, including the $\hat{r}^{-3}$ operator centered on Cr(III), over the atomic orbital basis set and later transformed to molecular orbital basis; since we have a one-center approximation, only the projections of the d type orbitals centered on Cr(III) are included.

It can be verified that the operators $T^m_a$ form a basis for the irreducible representation of order 1 of the rotational group R(3);[18] it is the case if

$$[S_z, T^m_a] = mT^m_a, \qquad [S_\pm, T^m_a] = \sqrt{2 - m(m\pm1)}\;T^{m\pm1}_a$$

Below we check one of the commutators, $[S_+, T^0_a]$, where $S_+ = \sum_i s_i^+$

$$S_+T^0_a - T^0_aS_+ = Z_{\text{eff}}\sum_{i,j}(s^+_i\,s^z_j - s^z_j\,s^+_i)\,\hat{l}^a_j\,\hat{r}^{-3}$$

$$= Z_{\text{eff}}\sum_i -s^+_i\hat{l}^a_i\,\hat{r}^{-3} = \sqrt{2}T^1_a$$

where we assumed that the products of the one-electron spin-operators commute if $i \neq j$. Since the transformation properties of the spin−orbit operators $T^m_a$ are irreducible, the Wigner−Eckart theorem can be used to achieve a relation between the matrix elements and a quantity known as the reduced matrix element.[17,18] The general expression for matrix elements in a basis (sums of Slater determinants) that are eigenfunctions to $S^2$ and $S_z$ is

$$\langle S,M_s,E|T^m_a|S',M'_s,E'\rangle = (-1)^{(S-M_s)}\begin{pmatrix} S & 1 & S' \\ -M_s & m & M'_s\end{pmatrix}\langle S,E||T_a||S',E'\rangle$$

where $\langle S,E||T_a||S',E'\rangle$ is the reduced matrix element without any dependence of the $M_s$. The matrix elements expressed in this form greatly simplify the calculations since the spin symmetry can be separated out from the problem and is contained in the 3J symbol.

We calculated only the matrix elements in the $M_s = {}^1/_2$ space with the spin−orbit operator $T^0_a$, $\langle S,{}^1/_2,E|T^0_a|S',{}^1/_2,E'\rangle$ and the related reduced matrix elements, $\langle S,E||T_a||S',E'\rangle$, from the Wigner−Eckart theorem. From the reduced matrix elements the Hermitian spin−orbit matrix is formed; with dimension equal to the total number of spin states, counting all different $M_s$ components. Since the spin−orbit operator is entirely complex (the angular momentum operator, $l$) and the CI basis real, the diagonal elements of the spin−orbit coupling are zero. Thus the diagonal elements in the Hermitian spin−orbit matrix are the real excitation energies for each state from the above CI calculation.

Finally, diagonalization of the above spin−orbit matrix gives spin−orbit coupled double group states. In the $D_3$ double group, spin−orbit coupled states for an odd number of electrons can be classified according to the symmetry species $2\bar{A}({}^3/_2)$ or $E({}^1/_2)$. The $^3/_2$ and $^1/_2$ denote the projection of the coupled angular momentum along the trigonal axis. For an odd number of electrons in absence of external magnetic field there will always be a degeneracy of at least two (Kramers degeneracy). The last step directly gives the spin−orbit splittings of the different states. In this step it is also possible to make use of the calculated CASPT2 energies to improve upon the correlation treatment in the spin−orbit coupling calculation. The diagonal values of the spin−orbit coupling matrix can be substituted with the more accurate CASPT2 energies before diagonalization. This

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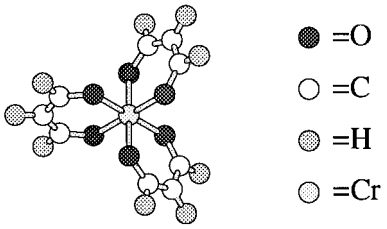


**Figure 1.** Geometry of the $Cr(PDO)_3$. complex viewed from the trigonal axis.

is justified by noting that the remaining correlation correction (going from the restricted full CI to the CASPT2) will not change the wavefunction to a large extent; only the diagonal elements will change.

In the calculations of the spin−orbit coupling we used a restricted full CI expansion of about half a million determinants in each symmetry and $M_s = {}^1/_2$. We included double excitations from the three highest occupied orbitals of ligand character, full CI of the 3d orbitals, and single and double excitations to 26 of the lowest virtual orbitals. The results without spin−orbit coupling of the CI calculation are presented in Figure 2 together with the CASSCF, CASPT2, and experimental values for $Cr(acac)_3$. The calculated spin−orbit levels originating from the lower doublet states are listed in Table 1. We have also included the improved (CASPT2 substitution) spin−orbit calculation.

### 3. Results

Fatta and Lintved[19] have measured the excitation energies for a number of different trischelated 1,3-diketonato Cr(III) compounds in solution. The effect of the solvent was rather small. The excitation energies for the lowest $^2E_g \leftarrow {}^4A_{2g}$ and $^4T_{2g} \leftarrow {}^4A_{2g}$ states show little variation in the series of diketonate complexes, with deviations from average not exceeding 250 $cm^{-1}$. In contrast, for the second spin-allowed band of $^4T_{1g} \leftarrow {}^4A_{2g}$ character and for the first ligand-to-metal charge transfer (LMCT) transition there are larger variations. Obviously the charge transfer is strongly affected by the substituents on the diketonate ligands. The $^4T_{1g} \leftarrow {}^4A_{2g}$ excitation is in most spectra obtained as a shoulder and it is probable that the variation is due to imprecise measurements; also interactions with the close lying LMCT state could add to this variation.

More precise measurements of the fine structure of some of the d−d transitions in the diketonato complexes have been made for $Cr(acac)_3$ doped into the host material $Al(acac)_3$.[3,4,7] Here both absorption and emission spectra have been measured in different polarizations. Of special interest are the trigonal splittings of the $^4T_{2g}$ and $^4T_{1g}$ states. For the lower $^4T_{2g}$ state the experimental splitting amounts to 800 $cm^{-1}$, with the $^4A_1$ component below the $^4E$ component. However for $^4T_{1g}$ the splitting is not observable due to the overlap with the intense LMCT absorption. Since the lowest excitation energies of $^2E_g \leftarrow {}^4A_{2g}$ and $^4T_{2g} \leftarrow {}^4A_{2g}$ are not much affected in going from 2,4-pentanedionate (acac) to 1,3-propanedionate (PDO) as ligand, it is likely that a relevant comparison can also be made between the calculated splitting for $Cr(PDO)_3$ and the experimental splitting for $Cr(acac)_3$.

We now turn to the results of the calculations. Figure 2 shows the calculated excitation energies at both the CASSCF and the CASPT2 level for the $Cr(PDO)_3$ compound. We have also included the experimental energies of the doped complex in $Al(acac)_3$ lattice. Going from CASSCF to CASPT2 the average of the quartet states is not much affected. However, the splittings of the $^4T$ states, and especially of the lower $^4T_{2g}$ state, increase considerably. We will return to this below. The position of the doublet states is also strongly affected by correlation. The difference between the calculated CASPT2 excitation energy for the lowest doublet state, and the measured phosphorescent level, is larger than for the lowest quartet state. The same observation has already been made in theoretical calculations of spectra of other Cr(III) compounds like $CrF_6^{3-}$ and $Cr(CN)_6^{3-}$.[20−22]

The trigonal splittings of the octahedral $^4T$ states are seen to increase at the CASPT2 level. The increase is somewhat larger for the $^4T_{2g}$ state than for the $^4T_{1g}$ state. The former state is split with $^4A_1$ below $^4E$. The CASPT2 calculations yield a splitting of 1300 versus 800 $cm^{-1}$ experimentally.[3] Both the absolute excitation energies and the trigonal splitting of these states compare well with experiment. For the next excited quartet state $^4T_{1g}$ an inverse splitting is calculated, with $^4E$ now below $^4A_2$; the magnitude is 1000 $cm^{-1}$. The absolute position of this state shows larger deviation from the measured position both for $Cr(acac)_3$ and $Cr(PDO)_3$.[19] This fact may be due to interaction with the lowest charge transfer state. Experimentally both for acac and PDO as ligand the charge transfer is at about 26 000 $cm^{-1}$, in near coincidence with the ligand field $^4T_{1g}$ state. The splitting of the second quartet band has not been determined in the absorption spectrum of $Cr(acac)_3$, since only the $^4E$ component could be observed.[3] Our calculations determine the $^4A_2$ component to be higher in energy, thus probably hidden in the charge-transfer band. In any case this transition is bound to be very weak since it is dipole forbidden.

Next we will discuss the spin−orbit coupling calculations. In Table 1 we present the calculated energies after spin−orbit coupling. Experimentally the $^4A_2$ ground state has a rather large ZFS of 1.2 $cm^{-1}$ with $2\bar{A}({}^3/_2)$ below $E({}^1/_2)$.[1,7] A simple ligand field analysis[2,23,24] reveals that this splitting cannot arise from isotropic interaction with the lowest quartet state through second-order perturbation—the trigonal splitting of the quartet state would have to be some 10 000 $cm^{-1}$ in order to induce a 1.2 $cm^{-1}$ ZFS of the ground state. However, it has been noted that a possible mechanism to induce large ZFS is configuration interaction within the d shell, with perturbation loops running over the trigonal ligand field.[24,25]

Our spin-orbit coupled CI calculation of the spin−orbit splitting of the ground state gives the values: 1.0 $cm^{-1}$ at the CI level and 1.2 $cm^{-1}$ with CASPT2 diagonal correction. The splitting is of the correct sign with $2\bar{A}({}^3/_2)$ below $E({}^1/_2)$, and in good agreement with experiment. The agreement with CASPT2 correction is a bit fortuitous since the lower doublet states are still off by a few thousand wavenumbers and further lowering would increase the ZFS. The ground state splitting seems to arise mainly from interaction of the ground state with the trigonal components of the $^4T_{2g}$ state and of the higher $^2T_{2g}$ state; they both contribute approximately to the same extent. The ZFS originates entirely from anisotropic spin−orbit coupling matrix elements with the excited states, the trigonal splitting of the excited states being unimportant (this was tested

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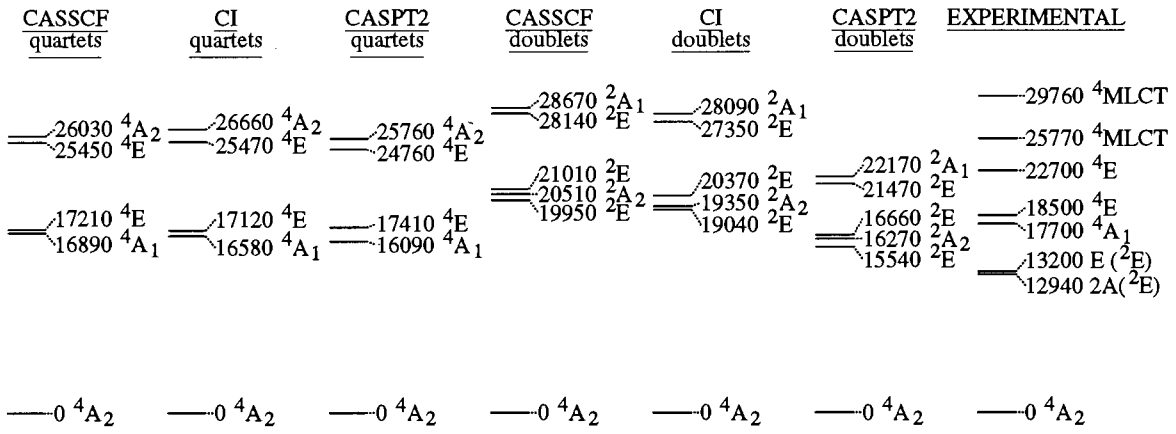


**Figure 2.** Calculated excitation energies for the quartet and doublet levels at three stages of calculation: CASSCF, CI, and CASPT2 (see text). For comparison experimental results from refs 3, 6, and 19.

**Table 1.** Calculated Energies of the Spin−Orbit States Belonging to Representations $E(^1/_2)$ and $2\bar{A}(^3/_2)$[a]

| | | $D_3$ | CI | | CASPT2 shifted | |
|---|---|---|---|---|---|---|
| | | double | energies | ZFS | energies | ZFS |
| $O_h$ | $D_3$ | group | $cm^{-1}$ | $cm^{-1}$ | $cm^{-1}$ | $cm^{-1}$ |
| $^2T_{1g}$ | $^2E$ | $E(^1/_2)$ | 20 420 | 110 | 16 672 | 75 |
| | | $2\bar{A}(^3/_2)$ | 20 310 | | 16 597 | |
| | $^2A_2$ | $E(^1/_2)$ | 19 358 | | 16 321 | |
| $^2E_g$ | $^2E$ | $E(^1/_2)$ | 19 070[b] | −12 | 15 476 | 53 |
| | | $2\bar{A}(^3/_2)$ | 19 082 | | 15 423[b] | |
| $^4A_{2g}$ | $^4A_2$ | $E(^1/_2)$ | −9.9 | 1.0 | −9.8 | 1.2 |
| | | $2\bar{A}(^3/_2)$ | −10.9 | | −11.0 | |

[a] The pattern of splitting is given going from $O_h$ to $D_3$ and further including spin−orbit coupling. Two calculations are presented: CI and a procedure where the diagonal elements corresponding to the lowest $^2E$, $^2A_2$, $^2E$, $^4A_1$, $2^4E$, and $^4A_2$ of the spin−orbit matrix were shifted according to CASPT2 before diagonalization. This changes the lowest doublet state from $E(^1/_2)$ to $2\bar{A}(^3/_2)$. [b] Lowest doublet component.

by artificially removing the trigonal splitting of the $^4T_{2g}$ state). We will come back to this point in the discussion.

The lowest excited doublet states are $^2T_{1g}$ ($^2A_2$ and $^2E$) and $^2E_g$ ($^2E$) with the latter lowest in energy. From absorption spectra, the ZFS of the lowest state in $Cr(acac)_3$ has been estimated to amount to 220−290 $cm^{-1}$ depending on the site in the host material.[4,6] The results in Table 1 clearly indicate that such a large ZFS cannot be reproduced by the present calculations. The lower state of $^2E_g$ parentage is split by only 53 $cm^{-1}$ with $2\bar{A}(^3/_2)$ below $E(^1/_2)$ at CASPT2 level. For the higher $^2E$ state of $^2T_{1g}$ parentage the calculated splitting amounts to 75 $cm^{-1}$, with $2\bar{A}(^3/_2)$ below $E(^1/_2)$. The parentages for these CASSCF wavefunctions could be assigned unambiguously from the principal determinants, which precisely match the trigonal combinations of reference 26. As we already noted, the energies of the lowest doublet states are substantially overestimated by the present calculations. To check if this discrepancy had any influence on the doublet ZFS we artificially lowered the doublet states. We shifted the diagonal elements of the $^2E_g(^2E)$ and $^2T_{1g}(^2E + {}^2A_2)$ further down than CASPT2, so that the lowest $^2E$ was at 13 000 $cm^{-1}$ now well below the $^4T$ states. The ZFS pattern did not change much; the ZFS of the lowest $^2E$ state decreased while for the higher $^2E$ it increased somewhat. There is a difference in the splitting pattern of the two $^2E$ states: the higher $^2E$ with $^2T_{1g}$ parentage, splits linearly with increasing spin−orbit coupling while the lower has a quadratic dependence. This could be concluded from a series of calculations with increasing spin−orbit coupling, and it explains the change of sign of the ZFS for the lower $^2E$ state that couples at second order with the lowest $^4T_{2g}$ state.

The lowest emitting state is believed to be of $2\bar{A}(^3/_2)$ character,[4,6] which coincides with the calculation with CASPT2 correction. On the basis of the calculated energy differences at the CASPT2 level and the spin−orbit splitting (see Figure 2 and Table 1), an alternative assignment may be suggested that would resolve the difficulty with the excited-state ZFS of the lowest $^2E$. In this alternative the three observed peaks at 12 940, 13 200, and 13 500 $cm^{-1}$ are attributed to spin−orbit components of the $^2E(^2E_g)$, $^2A_2(^2T_{1g})$, and $^2E(^2T_{1g})$ states, respectively. Remains however the difficulty to reconcile the $^2E$ assignment of the emitting state with the experimentally observed excited state **g** tensor.[7,8] Further investigation of this problem would require the ab initio calculation of the Zeeman effect.

## 4. Discussion

In this section we will be concerned with the origin of the trigonal splitting. The phase-coupling model[2,27−29] relates the trigonal splitting of the $t_{2g}$ shell in an orthoaxial trischelated complex to a difference in $\pi$-bonding between the in-phase and out-of-phase coupled ligator $\pi$-orbitals of the conjugated bidentates.

$$\Delta(t_{2g}) = E(e) - E(a_1) = {}^3/_2\,(e_\psi - e_\chi) \qquad (1)$$

Here $e_\psi$ and $e_\chi$ are bonding parameters for in-phase and out-of-phase interactions, respectively. From a spectral fit of the spin-allowed bands Atanasov et al.[3] deduced a $\Delta(t_{2g})$ value of approximately +2100 $cm^{-1}$. According to simple MO arguments the positive sign of the splitting is explained by a dominating $\pi$-donor interaction from the $\psi$-type ligand HOMO ($e_\psi > 0$).[2,28] Acceptor interactions with a $\chi$-type ligand LUMO ($e_\chi < 0$) may further contribute to the splitting. In the present calculation these orbital pathways can indeed be recognized in MO plots. The orbitals that diagonalize the density matrix for the active space are not very informative in this respect, since they are of almost pure 3d character. On the other hand pictures of the ligand frontier orbitals clearly reveal metal−ligand

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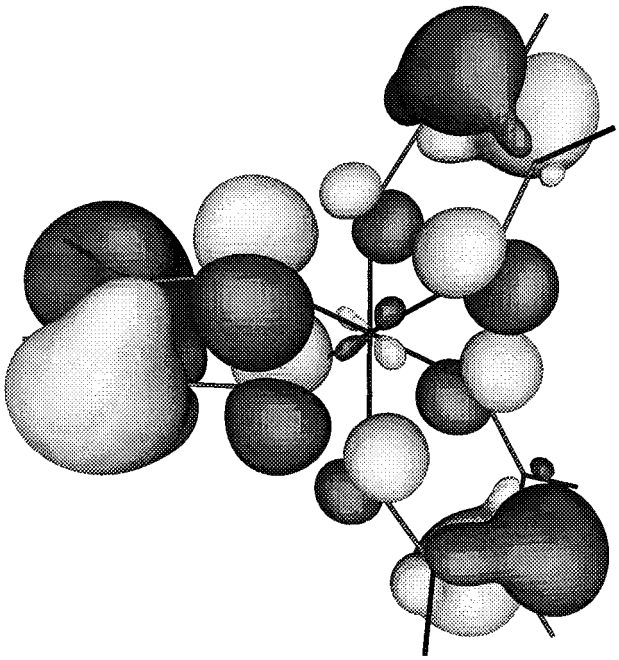

**Figure 3.** Contour plot of the highest occupied ligand $\psi$ type orbital with e symmetry. Note delocalization over an e($t_{2g}$) metal orbital.

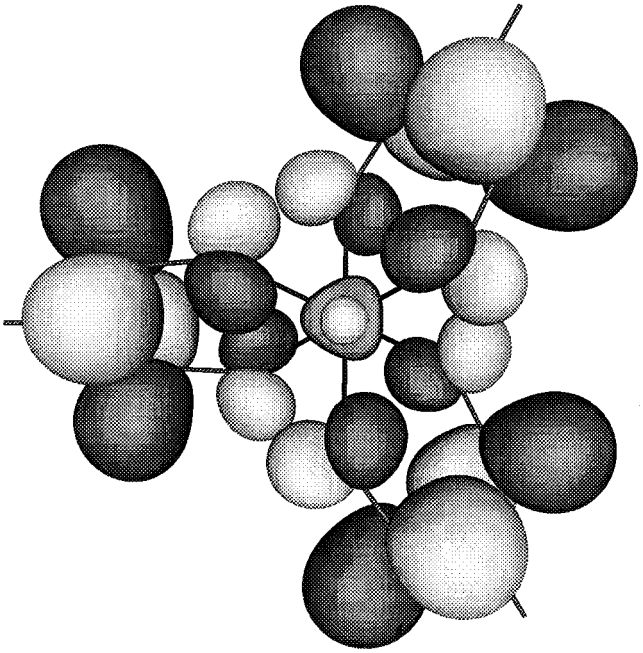

**Figure 4.** Contour plot of the lowest unoccupied ligand $\chi$ type orbital of $a_1$ symmetry. The metal orbital in the center is the $a_1(t_{2g})$ component.

$\pi$-conjugation. In Figure 3 we show the contour plot of an e combination of the ligand HOMO. Ligator orbital coupling is in-phase ($\psi$) and there is a bonding interaction with an e($t_{2g}$) component on the metal center. Figure 4 shows the $a_1$ combination of the ligand LUMO. Here ligator coupling is out-of-phase ($\chi$) and there is clear evidence for a $\pi$-acceptor interaction with the $a_1(t_{2g})$ component on the metal. The extent of ligand-to-metal delocalization is not very pronounced, as could be expected of moderate $\pi$-bonding.

The calculations do not support the alternative hypothesis that the trigonal splitting might originate from misdirected valency.[30] Note that Atanasov and Schönherr[3,4] already dismissed this hypothesis on the basis of its inability to predict the correct sign for $\Delta(t_{2g})$.

In the calculations of the ZFS of the $^4A_2$ ground-state we observed a sizable anisotropy in the spin−orbit coupling with the excited states $^2T_{1g}$ and $^4T_{1g}$. The source of this anisotropy can be traced mainly to two effects.[31] McGarvey has for different Cr(III) compounds investigated the effect of configurational interaction on the ZFS of the ground state.[25,32] He concluded[32] that a very small distortion of the charge distribution, compressing the trigonal axis, was sufficient to induce anisotropy in the spin−orbit coupling. The other mechanism is that of covalent anisotropy introduced by Stevens and Owen[33,34] to explain some features of the optical spectrum in transition metal complexes. Examples of recent applications to highly covalent transition metal complexes can be found in refs 35 and 36. As covalent bonds are formed between metal and ligand the metal d orbitals get diluted and as a result the spin−orbit coupling decreases. This mechanism was invoked previously by Atanasov and Schönherr[4] to explain the large ZFS in the $Cr(acac)_3$ complex.

The orbitals we used for the spin−orbit coupling calculation were optimized for the $^2A_2$ excited state and are therefore biased toward this state. To find out the reduction factors of the spin−orbit coupling from the free ion value we performed orthogonal transformations[37] on the d orbitals of e-type (in $D_3$) so that the angular parts became close to octahedral form with the $e_g$ and the $t_{2g}$ shell separated. With simultaneous $O_h$ and $D_3$ symmetry adaption the angular momentum operator within the d shell has a simple form. In this way we could determine effective parallel and perpendicular spin−orbit components:[31] $\xi_{||} = 251$ cm$^{-1}$ and $\xi_{\perp} = 254$ cm$^{-1}$. There is a total reduction of about 11% compared to the free ion value $\xi = 285$ cm$^{-1}$ but no pronounced anisotropy.

We conclude therefore that orbital mixing between the $t_{2g}$ and the $e_g$ shells is the source of the anisotropy of the spin−orbit coupling matrix elements between the $^4A_2$ ground state and the E and A components of the $^4T$ and $^2T$ states. This mixing is induced by the trigonal field of the ligands. The first orbital in Figure 3 is occupied and describes some of the excess negative charge on the PDO ligand that resides in the delocalized $\pi$-orbital. Clearly we see that a substantial fraction of the charge is located in the backbone and this indeed points toward a component of the ligand field with a trigonal compression. This coincides with the conclusion of McGarvey[25] for the $Cr(acac)_3$ complex.

## 5. Conclusions

We have performed ab initio calculations on $Cr(PDO)_3$ in an attempt to clarify some pending controversies concerning the

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(37) Under any orthogonal transformation within the active space, the restricted full CI wave function and energies are invariant. This means that we can apply orthogonal orbital rotations of the type $\psi_1' = \psi_1 \cos(\alpha) - \psi_2 \sin(\alpha)$, $\psi_2' = \psi_1 \sin(\alpha) + \psi_2 \cos(\alpha)$ to any pair of orbitals $\psi_1, \psi_2$ in the active space.

nature of the ligand field transitions in the closely related $Cr(acac)_3$. Three important conclusions could be reached.

(i) A significant trigonal splitting of the $^4T_{2g}$ parent state is reproduced with the correct sign for a perfectly octahedral first coordination sphere. The shape of the molecular orbitals indicates the presence of a phase-coupling effect from the unsaturated chelating bridge.

(ii) The unusually large ZFS of the ground state could be reproduced as well and can indeed be traced to an anisotropic spin−orbit mechanism. The source of this anisotropy is clearly identified as orbital mixing between the $t_{2g}$ and the $e_g$ shells. Due to the delocalized nature of the $\pi$-electrons we expect backflow of electrons from oxygen and a trigonal compression component of the ligand field.

(iii) The absolute positions of the doublet states were overestimated by about 2500 $cm^{-1}$. The spin−orbit coupled emitting doublet state is predicted to be $2\bar{A}(^3/_2)(^2E_g)$, which is in agreement with spectral assignment but in conflict with excited-state EPR experiments. The large ZFS of the $^2E_g$ level cannot be reproduced and may be based on a wrong assignment.

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