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# Density Functional Calculations on Electronic Circular Dichroism Spectra of Chiral Transition Metal Complexes

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Time-dependent density functional theory (TD-DFT) has for the first time been applied to the computation of circular dichroism (CD) spectra of transition metal complexes, and a detailed comparison with experimental spectra has been made. Absorption spectra are also reported. Various Co$^{III}$ complexes as well as $[Rh(en)_3]^{3+}$ are studied in this work. The resulting simulated CD spectra are generally in good agreement with experimental spectra after corrections for systematic errors in a few of the lowest excitation energies are applied. This allows for an interpretation and assignment of the spectra for the whole experimentally accessible energy range (UV/vis). Solvent effects on the excitations are estimated via inclusion of a continuum solvent model. This significantly improves the computed excitation energies for charge-transfer bands for complexes of charge +3, but has only a small effect on those for neutral or singly charged complexes. The energies of the weak d-to-d transitions of the Co complexes are systematically overestimated due to deficiencies of the density functionals. These errors are much smaller for the 4d metal complex. Taking these systematic errors and the effect of a solvent into consideration, TD-DFT computations are demonstrated to be a reliable tool in order to assist with the assignment and interpretation of CD spectra of chiral transition metal complexes.

## 1. Introduction

Circular dichroism (CD) spectroscopy[1−4] is one of the major experimental tools employed in the characterization of chiral metal complexes and the investigation of their electronic and geometric structure. Theoretical methods[5−9] can help greatly in the assignment and interpretation of electronic CD spectra for these compounds. Much has been learned since the 1960s from theoretical approaches based on the ligand field model.[3,10−18] However, these methods are specifically developed in order to describe the d-to-d (or f-to-f) transitions at the metal center, while the nature of the charge-transfer ligand-to-d excitations cannot be addressed. Excitations within the ligands of chiral complexes have also

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been studied since the 1960s and 1970s (see refs 19−22 for examples). However, in both cases "the formidable complexity of these theories has restricted their usage and development to a limited number of specialists" (Kuroda and Saito[11]).

The size of even the smallest chiral transition metal systems and the computational difficulties related to an accurate description of their electronic structure have so far prevented first-principles theoretical investigations of their CD spectra. Accurate first-principles calculations of CD spectra of systems the size of a typical small chiral transition metal complex are only recently beginning to emerge and have so far been restricted to organic molecules.[23,24] To our knowledge no previous theoretical first-principles CD study has emerged for transition metal complexes. The present work intends to fill this gap, by investigating the whole experimentally accessible range of the CD spectra for a number of $Co^{III}$ complexes as well as $[Rh(en)_3]^{3+}$.

Because many highly accurate ab initio methods for the computation of electronic excitation energies are still prohibitively expensive for all but the smallest metal complexes, the present computations are based on time-dependent density functional (TD-DFT) response theory.[25−28] One of the great advantages of TD-DFT computations is that, once their accuracy for a certain class of compounds has been validated and the basis set and functional requirements are known, they can be applied in a "black box" manner by nonspecialists as well. Further, TD-DFT "combines moderate accuracy with low computational cost and provides a simple intuitive interpretation".[23] Regarding vibrational CD (VCD), the first density functional calculations on transition metal systems have been reported very recently.[29,30] The aim of this work is to investigate the applicability of TD-DFT for the calculation of electronic CD spectra of transition metal complexes and to determine the requisites for a computational model that is able to achieve reasonable accuracy.

On the basis of data for hydrocarbon benchmark molecules, it is now believed that TD-DFT is able to provide a reliable description of excitation energies and transition moments, at least for excitations well below the (Kohn−Sham) ionization limit.[31,32] Excitation energies for selected transition metal complexes ($MnO_4^-$, $Ni(CO)_4$, $M(CO)_6$, and others) have been treated successfully[33−39] as well. In particular for Rydberg excitations in small molecules it is important to use a Kohn−Sham potential that has the correct asymptotic behavior. Several such potentials that incorporate such corrections to improve the virtual orbitals have in the past been proposed and successfully applied.[40−43] For valence excitations in larger molecules these asymptotic corrections are not of such high importance, and standard gradient corrected functionals are expected to yield reasonably accurate excitation energies and intensities. This has been confirmed in the context of CD spectra in recent theoretical investigations of organic molecules by us[24] and others.[23] A recent study[44] on the absorption spectra of chiral $Ru^{II}$ complexes has validated that good agreement between TD-DFT and experimental absorption spectra can be achieved also for larger transition metal compounds[44] (i.e., the calculated absorption intensities are meaningful as well). In ref 44, the authors have employed the B3LYP hybrid functional. The present study addresses the applicability of "pure", i.e., nonhybrid, functionals to the calculation of excitation energies and the absorption and CD spectra of 3d transition metals.

The samples that are studied in this work are the $Co^{III}$ complexes $\Lambda$-$[Co(en)_3]^{3+}$, $\Delta$-$[Co(en)_2(acac)]^{2+}$, $\Lambda$-$[Co(acac)_3]$, *cis*-$\Delta$-$[Co(en)_2Cl_2]^+$, *cis*-$\Delta$-$[Co(en)_2(CN)_2]^+$, $\Delta$-$[Co(en)_2CO_3]^+$, $\Lambda$-$[Co(tn)_3]^{3+}$, and for comparison also $\Lambda$-$[Rh(en)_3]^{3+}$ (en = ethylenediamine, tn = trimethylenediamine, acac = pentane-2,4-dionato = acetylacetonato). Though all of their spectra share common features, they represent a chemically rather diverse test set due to the different nature of the ligands. This makes a computational study challenging because each set of ligands probes different aspects of the electronic structure that cannot all be treated at the same level of accuracy. Consequently, it is not possible to apply, e.g., uniform shifts to the excitation energies in order to bring all of the simulated spectra in agreement with experiment as it could be done in the aforementioned TD-DFT studies

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of helicene CD spectra.[23, 24] For instance deficiencies in the approximate density functional applied here have more severe consequences for 3d than for 4d or 5d metals. Accordingly, the accuracy for the excitation energies obtained here for the Co complexes is somewhat lower than that recently obtained for Ru$^{II}$ complexes in ref 44, whereas our results for the 4d metal complex $[Rh(en)_3]^{3+}$ are of comparable accuracy as in ref 44. This affects mostly the weak d-to-d transitions of the metal for which the error depends roughly on the strength of the covalent metal−ligand interaction. Another issue is the different charge of the complexes. This has, for example, severe consequences for their interaction with polar solvents. All complexes but $[Co(acac)_3]$ have been experimentally studied in aqueous solution. We have found that acceptable agreement with experimental spectra for the +3 charged complexes can only be achieved if the solvent is considered in the calculations. Solvent effects have in this work been estimated via a continuum solvation model being applied to the ground state. If one corrects for the systematic errors in the d-to-d excitation energies (that can be attributed to deficiencies in the density functionals), and considers solvent effects for highly charged species (thereby predominantly improving on the charge-transfer excitations), CD spectra can be obtained from TD-DFT computations that are in qualitative, sometimes quantitative, agreement with experiment and thus allow for their interpretation and assignment.

In section 2, we briefly summarize the details regarding the computations. In section 3, the results are interpreted and compared to experimental data. This section also contains a discussion of shortcomings of the present methodology. The findings are summarized in section 4.

## 2. Computational Details

The computations have been carried out with a modified version of the Amsterdam Density Functional (ADF) program package.[45−47] It incorporates our recently published methodology for the computation of optical rotations and CD spectra,[24,48,49] implemented into the previously developed TD-DFT code by van Gisbergen, Baerends, et al.[50−52] The program is currently restricted to closed-shell ground states. Typically, the 25 lowest allowed excitations have been calculated. From the computed singlet excitation energies, oscillator strengths, and rotatory strengths, spectra have been simulated as previously described in ref 24 in order to allow for an easier comparison with experimental data. Where necessary, a CD spectrum calculated for the optical antipode of the experimentally studied species has been inverted. We have confirmed that the configurations for which we report simulated spectra are in agreement with the experimentally reported configurations. The empirical recipe of Brown et al.[53] for the line widths has been employed which yields a reasonable overall agreement with experiments ($\Delta\tilde{\nu} = 7.5\sqrt{\tilde{\nu}}$, with $\tilde{\nu}$ in $cm^{-1}$). Numerical data for the experimental spectra have been extracted from graphical material accessible in the literature with the help of the "g3data" software.[54] The triple-ζ polarized "TZP" Slater basis (formerly "IV") from the ADF basis set database has been employed in all computations. Test calculations on $[Co(en)_3]^{3+}$ have not shown any significant[89] change regarding the simulated spectra (both absorption and CD) in case a larger basis set including diffuse functions and one more polarization function for Co, C, N, and H was used instead. Therefore, the TZP basis can be regarded as sufficiently flexible in the valence region in order to describe the d-to-d as well as the ligand-to-d charge-transfer excitations in our samples within the computational model without the need for additional polarization and/or diffuse basis functions. We have also confirmed for $[Co(en)_3]^{3+}$ that rotatory strengths calculated with the dipole-velocity form are in good agreement with those obtained from the dipole-length formula (deviations of less than 10% for the computed energy range). This is a further test of the suitability of the basis set for the computation of CD spectra. Since the dipole-velocity formula yields origin-independent rotatory strengths,[24] the results presented here obtained with the dipole-length formula can be regarded as sufficiently origin independent for all practical purposes. For the simulation of solvent effects, the "COnductor-like continuum Solvent MOdel" (COSMO)[55,56] has been applied in the calculations of the CD spectra. Details on the COSMO calculations are discussed in a separate paragraph in section 3. Further effects on the spectra, in particular due to molecular vibrations, are neglected in the present study.

As already indicated in the Introduction, the use of an asymptotically corrected Kohn−Sham potential (applied here in form of the "statistical average of orbital potentials" (SAOP)[42]) did not improve the results in comparison with experiment since the experimentally accessible range of the CD spectra is determined by valence excitations. Therefore, the data presented in the next section are based on the common Vosko−Wilk−Nusair[57] local density approximation (LDA) with Becke88−Perdew86 (BP) gradient corrections.[58,59] The use of other gradient-corrected functionals did not lead to an improvement over the BP functional for the spectra. As in our previous work we have used the adiabatic LDA (ALDA) kernel for the frequency-dependent linear response of the molecular potential. Deficiencies in these functionals that cause disagreement between the simulated and the experimental spectra are briefly discussed in section 3. All TD-DFT calculations have been carried out based on optimized geometries (VWN functional, TZP basis).

For each of the excitations $\lambda$, the ADF code reports the composition of a vector $\boldsymbol{F}_\lambda$, from which the transition dipole moments are computed,[24,48] in terms of contributions from pairs of occupied and virtual MOs. This provides a convenient and intuitive

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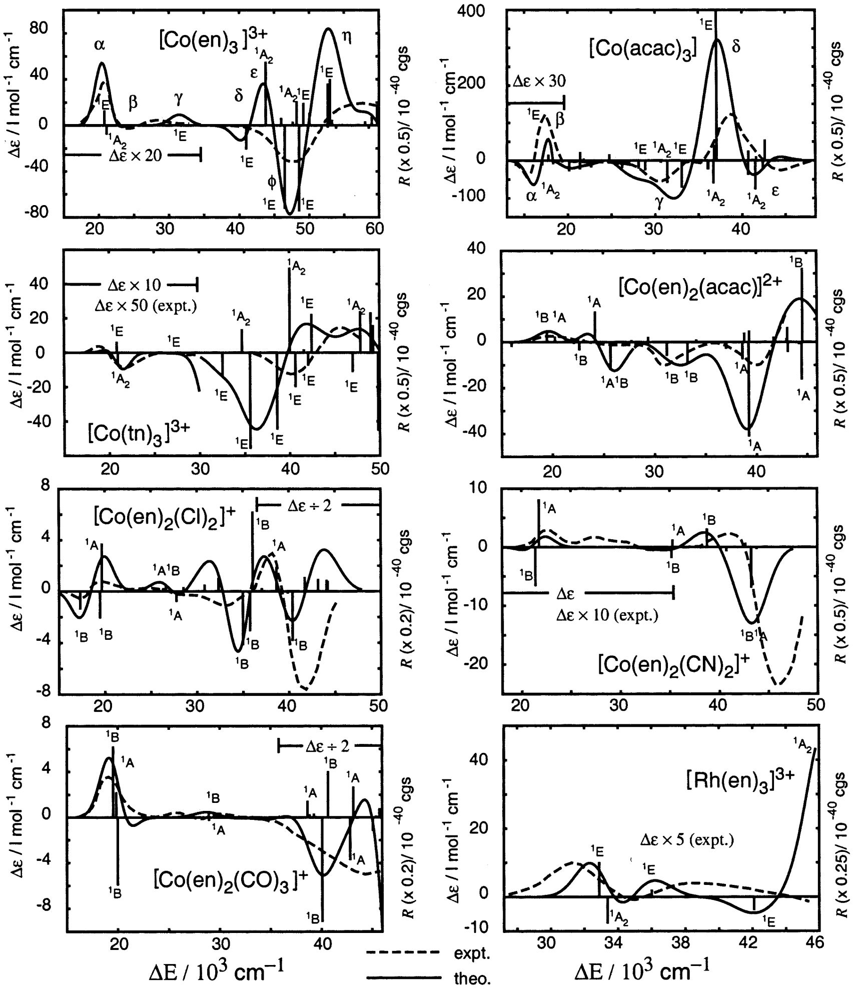

**Figure 1.** Experimental and simulated CD spectra for various $Co^{III}$ complexes and $[Rh(en)_3]^{3+}$. Calculated excitation energies and rotatory strengths are indicated in the form of line spectra (the numerical data are available in the Supporting Information). The COSMO model of solvation has been applied in the ground state calculations. The lowest d-to-d transitions are red-shifted as explained in the text by 6.0 × $10^3$ $cm^{-1}$ ($[Co(en)_3]^{3+}$), 4.0 × $10^3$ $cm^{-1}$ ($[Co(en)_2Cl_2]^+$), 8.1 × $10^3$ $cm^{-1}$ ($[Co(en)_2(CN)_2]^+$), 5.7 × $10^3$ $cm^{-1}$ ($[Co(en)_2CO_3]^+$), and 1.8 × $10^3$ $cm^{-1}$ ($[Co(tn)_3]^{3+}$). For $[Co(acac)_3]$ and $[Co(en)_2(acac)]^{2+}$, all calculated excitations have been red-shifted by 4.0 × $10^3$ $cm^{-1}$. $[Rh(en)_3]^{3+}$ is not shifted. Individual CD bands are labeled by Greek letters.

analysis of the TD-DFT results in terms of excitations from occupied to virtual Kohn−Sham orbitals. The energy gaps between occupied and unoccupied orbitals hereby serve as a zeroth order estimate for the excitation energies[25] (and are much better estimates for the excitation energies than, e.g., Hartree−Fock orbital energies). The transitions are calculated independently for each irreducible representation of the molecule's point group ($D_3$ or $C_2$ for our samples). $D_3$ symmetry has been employed for the complexes $[Co(en)_3]^{3+}$, $[Co(tn)_3]^{3+}$, $[Co(acac)_3]$, and $[Rh(en)_3]^{3+}$. The other complexes are of $C_2$ symmetry.

## 3. Results and Discussion

**Comparison of Simulated and Experimental Spectra.** In Figure 1 the computed excitation energies, rotatory strengths, and simulated CD spectra are displayed together with available experimental spectra. Experimental data for Δ-$[Co(en)_2(acac)]^{2+}$, *cis*-Δ-$[Co(en)_2(CN)_2]^+$, *cis*-Δ-$[Co(en)_2Cl_2]^+$, Δ-$[Co(en)_2CO_3]^+$ are taken from ref 60; Λ-$[Co(en)_3]^{3+}$ from ref 13; Δ-$[Co(tn)_3]^{3+}$ from ref 61; Λ-$[Co(acac)_3]$ from ref 11; and Λ-$[Rh(en)_3]^{3+}$ from ref 62. The respective absorption spectra are shown in Figure 2. Since they are much less specific in the charge-transfer region as compared to the CD spectra, we will not analyze them in detail. Figure 4 displays an orbital diagram for one of the $D_3$-symmetric complexes, $[Co(en)_3]^{3+}$. In the same diagram are also indicated the orbital levels of a hypothetical octahedral complex with similar orbital energies. The splitting of the degenerate levels in $O_h$ symmetry due to a trigonal distortion (leading to the symmetry $D_3$) is rather small. See also ref 63. This situation is similar for the other complexes of $D_3$ or $C_2$ symmetry as well.

**d-to-d Excitations.** It can be seen that for all of the $Co^{III}$ complexes the spectra afford a weak pair of CD transitions approximately in the range of (15−25 × $10^3$ $cm^{-1}$, resulting in a more or less unsymmetric pair of CD bands. $\log_{10} \epsilon$ typically ranges around 2 for these transitions in the absorption spectra. These CD signals are due to the d-to-d HOMO−LUMO singlet excitations at the metal center. They

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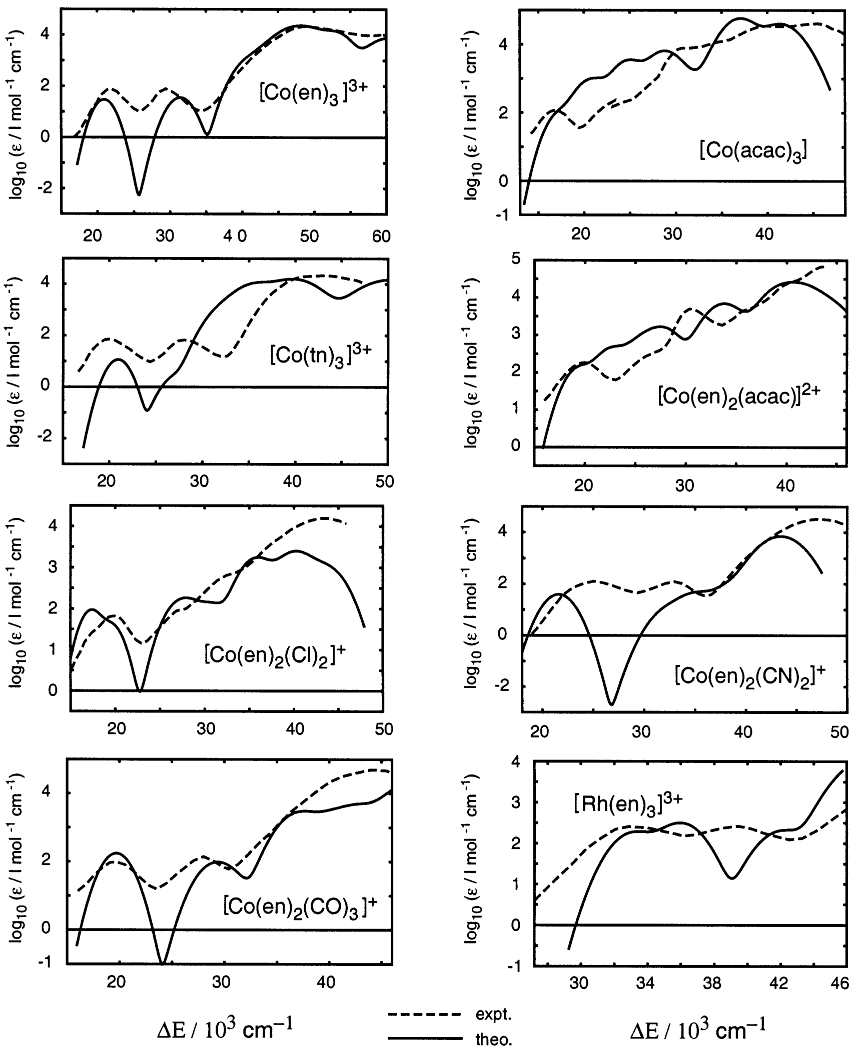

**Figure 2.** Experimental and theoretical absorption spectra for various $Co^{III}$ complexes and $[Rh(en)_3]^{3+}$. See also caption of Figure 1.

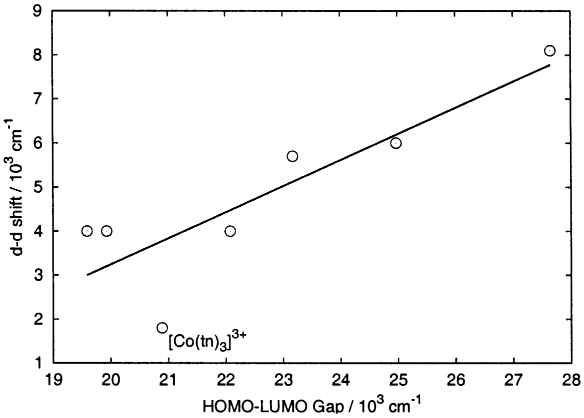

**Figure 3.** Applied correction to the d-to-d excitations (see caption of Figure 1) versus calculated HOMO−LUMO gap. The line represents a linear fit to the data points (slope = 0.592, *y*-intersection at $-8.60 \times 10^3$ cm$^{-1}$).

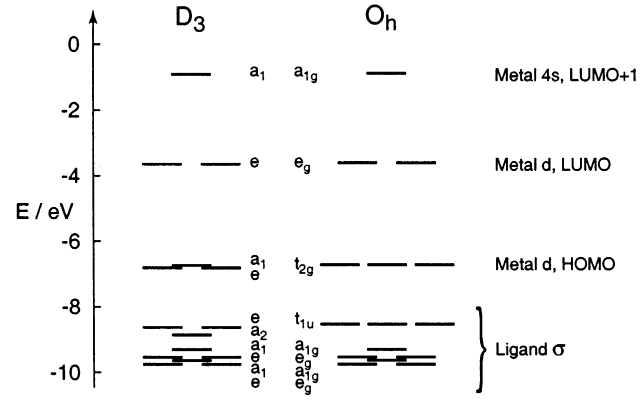

**Figure 4.** Orbital diagram of the *ob*$_3$ conformer of $[Co(en)_3]^{3+}$ ($D_3$ symmetry), from a DFT calculation employing a COSMO solvation model for water. The orbital levels of a related hypothetical $O_h$ complex (not calculated) are also shown.

correspond to the symmetry-forbidden $^1T_{1g}$ excitation in $O_h$ and are observed as a pair of $^1A_2$ and $^1E$ transitions in the $D_3$-symmetric distorted systems. See also Table 1 for symmetry classifications of selected transitions. For the $C_2$-symmetric complexes, the E ($D_3$) transition further splits into A and B components of opposite sign, and the $A_2$ ($D_3$) excitation is of B symmetry (note: for $[Co(en)_2(CN)_2]^+$ one of the lowest B transitions is very weak and therefore not explicitly labeled in Figure 1). The sign and energetic ordering of the $A_2$ and E (or A and B) components depend on the sign of the angular distortion around the 3-fold axis (in the $D_3$ case) and the magnitude of the distortion along this axis.[64] Due to the only small chiral perturbation of the metal d-orbitals the CD intensity of the d-to-d transitions is

**Table 1.** Selected Excitations from Metal or Ligand Orbitals into the Empty Metal d-Orbitals for a Complex with $O_h$ or $D_3$ Symmetry (See Figure 4), and Corresponding Excited Singlet States in $O_h$, $D_3$, and $C_2$ Symmetry

| transition between orbitals in $O_h$ system | excited $O_h$ singlet states (corresponding $D_3$ states) |
|---|---|
| $t_{2g} \leftrightarrow e_g$ | $T_{1g}$ ($A_2$, E), $T_{2g}$ ($A_1$, E) |
| $t_{1u} \leftrightarrow e_g$ | $T_{1u}$ ($A_2$, E), $T_{2u}$ ($A_1$, E) |
| $a_{1g} \leftrightarrow e_g$ | $E_g$ (E) |
| $e_g \leftrightarrow e_g$ | $A_{1g}$ ($A_1$), $A_{2g}$ ($A_2$), $E_g$ (E) |

| transition between orbitals in $D_3$ system | excited $D_3$ singlet states (corresponding $C_2$ states) |
|---|---|
| $a_1 \leftrightarrow e$ | E (A, B) |
| $a_2 \leftrightarrow e$ | E (A, B) |
| $e \leftrightarrow e$ | $A_1$ (A), $A_2$ (B), E (A, B) |

weak in all cases. In some experimental work, much weaker CD signals at even lower energy due to triplet d-to-d excitations could also be detected, for instance for $[\mathrm{Co(en)_3}]^{3+}$.[11] These excitations become more intense for increasing strength of the spin−orbit coupling, which can clearly be seen by comparison of the absorption and CD spectra for $[\mathrm{Co(en)_3}]^{3+}$ and $[\mathrm{Rh(en)_3}]^{3+}$. We have calculated the energy for the $^3T_{2g}$ ($O_h$) d-to-d excitation of $[\mathrm{Co(en)_3}]^{3+}$ to be approximately $4 \times 10^3$ cm$^{-1}$ below the lowest d-to-d singlet excitation, in good agreement with the experimental value quoted in ref 11. Since we cannot at the present time investigate the CD intensity of these very weak “spin-forbidden” transitions, we will in the following exclusively focus on the singlet excitations. In most of the CD spectra, there is another, usually very weak, CD band present between the lowest d-to-d transitions and the charge-transfer region. The symmetry is E for the $D_3$ systems, with an accompanying symmetry-forbidden $A_1$ excitation very close in energy. Therefore, this CD band represents the $^1A_{1g} \rightarrow {}^1T_{2g}$ d-to-d excitation in a system of $O_h$ symmetry. In the $C_2$-symmetric complexes, the E excitation splits into an A and a B component of opposite sign, perhaps most clearly visible in the spectra of $[\mathrm{Co(en)_2(CN)_2}]^+$ and $[\mathrm{Co(en)_2CO_3}]^+$.

All of the lowest d-to-d excitation energies are systematically overestimated in energy by the TD-DFT calculations for our samples. Upon closer inspection this error appears to be largest if ligands are present that cause a strong covalent interaction with the metal ($\mathrm{CN}^-$, $\mathrm{CO_3}^{2-}$), but is much smaller in the presence of the acac or $\mathrm{Cl}^-$ ligands. For easier comparison of the theoretical and the experimental spectra we have decided to red-shift the d-to-d excitations where necessary such that the peaks of the lowest CD bands match. For $[\mathrm{Co(acac)_3}]$ and $[\mathrm{Co(en)_2(acac)}]^{2+}$ better agreement with experiment is achieved if the whole CD spectrum is red-shifted by $4 \times 10^3$ cm$^{-1}$ (0.5 eV). We have previously noted that popular standard nonhybrid density functionals, mainly due to the self-interaction error, tend to overestimate the covalent interaction between the metal d-orbitals and the ligands (see ref 65 and references therein). This causes an overestimation of the HOMO−LUMO gap in 3d metal complexes and rationalizes why the TD-DFT computations tend to yield too high d-to-d excitation energies. The correlation of the value of the HOMO−LUMO gap with the overestimation is not perfect, but the trend is obvious as illustrated in Figure 3. This issue is further discussed below for the example $[\mathrm{Co(en)_3}]^{3+}$. If the errors in the d-to-d excitation energies are corrected for, good agreement between the calculated and the experimental CD spectra is obtained in the low-energy range since the shapes of the simulated spectra are predicted correctly. The absorption spectra in Figure 2 are also improved by red-shifting only the lowest d-to-d transitions.

**Charge-Transfer Excitations.** In addition to the weak d-to-d transitions, most of the spectra exhibit one or several pairs of intense CD bands at energies $>25 \times 10^3$ cm$^{-1}$, with $\log_{10} \epsilon$ values in the absorption spectra of typically 4. They are generally attributed to ligand-to-d charge-transfer excitations. $[\mathrm{Co(acac)_3}]$ and $[\mathrm{Co(en)_2(acac)}]^{2+}$ are exceptions because in these systems also excitations into low-lying empty ligand orbitals play a very important role for the transitions in this energy range. This is discussed in more detail below for $[\mathrm{Co(acac)_3}]$.

As can be seen from the line spectra, each charge-transfer CD band is generally caused by more than a single excitation, along with cancellation of large rotatory strengths of opposite sign, and thus difficult to reproduce correctly. Nevertheless, agreement of sign, and in most cases the order of magnitude, of $\Delta\epsilon$ between the TD-DFT calculations and experimental data is obtained, thereby reproducing the most important features of the experimental spectra. In some cases the positions of the charge-transfer bands are not exactly reproduced, which can be attributed to approximations in both the density functional and the treatment of solvent effects. These approximations are discussed separately below. Generally, however, the accuracy in the charge-transfer region is similar to that in previous TD-DFT calculations of CD spectra of helicenes and other organic molecules,[23,24] thereby allowing for a semiquantitative reproduction of the excitation energies as well as the absorption and CD intensities for each complex from a single computation.

Figure 4 shows the computed orbital diagram for $[\mathrm{Co(en)_3}]^{3+}$ together with the corresponding orbital levels of an $O_h$-symmetric complex. Note that the computed energetic ordering of the ligand $\sigma$-orbitals differs from textbook generalizations (e.g., in ref 66) in the sense that the ligand $e_g$ ($O_h$) level is below the $t_{1u}$ and $a_{1g}$ levels instead of above. We will use the diagram in Figure 4 as an example here in order to illustrate the nature of the charge-transfer transitions for complexes with $\sigma$-bonded ligands. All the CD spectra of the Co complexes share common features not only in the d-to-d region but also in the charge-transfer region of the spectra that can be interpreted with the help of Figure 4.

The experimentally reported range of the CD spectrum of $[\mathrm{Co(en)_3}]^{3+}$ and other Co complexes with a similar electronic structure can be assigned by considering transitions from the occupied metal and a small number of ligand orbitals within

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the energy range displayed in Figure 4, into the empty metal d-orbitals (LUMO). Only at the high-energy end of the spectrum (60 × $10^3$ $cm^{-1}$ and above for $[Co(en)_3]^{3+}$) do excitations into higher lying empty orbitals occur. Table 1 lists the symmetries of the corresponding singlet excitations into the $e_g$ LUMO for a complex of $O_h$ parent symmetry as well as the excitations and symmetry designations for a respective distorted $D_3$- or $C_2$-symmetric complex. Lowest in energy of the charge-transfer excitations can be expected those from the $t_{1u}$ ($O_h$) ligand $\sigma$-orbitals, according to Figure 4. In the $D_3$-symmetric complexes the $^1T_{1u}$ excitations manifest as a pair of $^1A_2$ and $^1E$ excitations with opposite rotatory strengths, which are clearly visible, e.g., for $[Co(en)_3]^{3+}$ and $[Co(tn)_3]^{3+}$ in Figure 1. The $^1T_{2u}$ corresponds to a single $^1E$ excitation (plus a symmetry-forbidden $^1A_1$ component within the same energy range). For the $C_2$-symmetric complexes, the $^1T_{1u}$ excitation splits into a $^1A^1B^1B$ triplet (e.g., clearly visible in the $[Co(en)_2CO_3]^+$ CD spectrum around 40 × $10^3$ $cm^{-1}$). The next higher charge-transfer excitations can be assigned to the $a_{1g} \rightarrow e_g$ and $e_g \rightarrow e_g$ ($O_h$) transitions. Since all these excitations are close in energy, and since the energy gaps between the orbitals are in the TD-DFT approach only a zeroth-order approximation to the excitation energies, a clean separation of the charge-transfer CD bands of the simulated spectra into pure transitions between the ligand orbitals and the LUMO is not possible at the experimental resolution. The analysis of the computational results also generally yields a strong mixing of different orbital transitions for all but the lowest charge-transfer excitations. We conclude that the lower range of the charge-transfer region is due to the excitations of $^1T_{1u}$ ($O_h$) parentage, but the final pattern of CD bands in the charge-transfer region of the spectrum is for all samples caused by a complex interplay between a larger number of transitions involving the range of ligand orbitals displayed in Figure 4.

**Solvent Effects.** The conductor-like screening continuum solvent model COSMO[55,56] has been applied to the ground state calculations since all experimental CD spectra have been recorded in solution. Similar to other continuum solvation models,[67,68] in the COSMO method point charges on a surface surrounding the molecule are determined self-consistently such as to mimic the interaction between the solvent and the solute. We have found that this significantly improves agreement between theory and experiment for the charge-transfer CD bands of the highest charged species $[Co(en)_3]^{3+}$ and $[Co(tn)_3]^{3+}$ by leading to a blue-shift of the respective calculated transitions. At the same time the simulated spectra for the neutral or singly charged species are not strongly altered. As expected, the d-to-d transitions are much less affected by the solvation. All but the $[Co(acac)_3]$ (ethanol) spectrum have experimentally been obtained from aqueous solution. For such a polar solvent, it is fair to expect a significant effect on the excitation energies already from a treatment of the solvation of the ground state alone. This will be the case in particular for highly charged species. It has recently been argued that inclusion of the counterion in the computational model is of less importance.[69] It has further been noted by various authors that for the computation of vertical excitation energies the "slow" contribution of the interaction between the solvent and the solute, being a function of the solvent's dielectric constant $\epsilon$ (approximately 80 for water), must be the same for the ground and the excited state.[67,68,70] The reason is that this interaction is due to the orientation of the polar solvent molecules, which cannot respond to the excitation within its time scale. Since the COSMO surface charges are not explicitly considered in the TD-DFT procedure other than through their influence on the ground state density, this effectively amounts to (correctly) using the ground state COSMO surface charges for both the ground and the excited state as a first approximation to the simulation of solvent effect on the vertical excitation energies. The high-frequency component of the solvent's electric susceptibility, accounting for changes of the electronic structure of the solvent upon electronic excitations within the solute, is not considered in this approach. It can be expected to yield a nonnegligible solvent effect on the excitation energies as well through a respective linear response of the portion of the molecular potential that is caused by the surface charges.[68,70,71] This response will be a function of $n^2$ (approximately 1.7 for water), with $n$ being the optical refractive index of the solvent, and should yield further improvement of the simulated spectra. We note in passing that a continuum solvent model has recently been developed for the density functional calulation of optical rotations.[72] Its application to seven neutral organic molecules in organic solvents has shown promising results for three out of six solvents, but poor results for the others.

In order to illustrate the strong influence of the polar solvent water on the spectrum of the +3 charged complexes, and the almost negligible effect of the less polar solvent ethanol on the neutral complex $[Co(acac)_3]$, Figure 5 displays the CD spectra of $[Co(tn)_3]^{3+}$ and $[Co(acac)_3]$ that have been calculated with and without the COSMO solvent model. For $[Co(tn)_3]^{3+}$ very poor agreement with experiment is obtained from gas-phase calculations because of the strong underestimation of the charge-transfer excitation energies in the simulated spectrum. This situation is substantially improved when the solvation model is included, due to a blue-shift of the lowest charge-transfer CD band by more than 6 × $10^3$ $cm^{-1}$. The final position of this CD band (see Figure 1) is still somewhat too low in energy in comparison with experiment. The exact reason for this error cannot be determined at the present stage, but is likely due to a combination of approximations in the calculations. See also the paragraph devoted to a discussion of possible sources of

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errors. For [Co(acac)$_3$], almost no net effect due to solvent effects is obtained. The solvent has a nonnegligible effect on the rotatory strength of most of the individual transitions. Despite this, the resulting $\Delta\epsilon$ values of the respective simulated spectra are very similar for [Co(acac)$_3$]. We note that [Co(tn)$_3$]$^{3+}$ and [Co(acac)$_3$] represent extremes for solvent effects among our samples. [Co(en)$_3$]$^{3+}$, being the only other +3 charged complex, exhibits the second strongest solvent effects which also lead to a pronounced blue-shift of the charge-transfer excitations. For most other complexes, moderate effects are obtained that in all cases improve the simulated spectra when compared to experiments.

In the following paragraphs we discuss some individual spectra in more detail.

**[Co(en)$_3$]$^{3+}$.** [Co(en)$_3$]$^{3+}$ is the antetype of a chiral transition metal complex and has been thoroughly studied in the past. The structure of [Co(en)$_3$]$^{3+}$ is not very rigid. There exist 4 conformers for both the $\Delta$ and the $\Lambda$ stereoisomer that are distinguished by whether the plane of the chelate ring adopts a parallel (*lel*) or oblique (*ob*) orientation with respect to the $C_3$ symmetry axis of the complex. The energy difference between the two conformations is rather small, and consequently all conformers will be present in solution at room temperature and undergo rapid interconversion between the *ob* and *lel* conformations of the chelate rings. This is also confirmed by NMR studies.[11,73] We have studied the *lel*$_3$ and the *ob*$_3$ conformers as examples. The *lel*$_3$ conformer was in 1959 theoretically estimated to be lower in energy than *ob*$_3$ by about 7.5 kJ/mol.[74] Our calculations for the gas phase predict the *ob*$_3$ conformer to be more stable by about 5.5 kJ/mol, in accordance with recent work by Freedman et al.[30] (4.2 kJ/mol B3LYP/LanL2DZL). The stabilities of the *ob*$_2$*lel* and *lel*$_2$*ob* conformers were in ref 30 found to range between those of *ob*$_3$ and *lel*$_3$.

The electronic CD spectrum for [Co(en)$_3$]$^{3+}$ in the UV/vis range is not extremely sensitive with respect to the orientation of the chelate rings, and its qualitative features for both conformers are quite similar. In gas-phase calculations, the excitation energies for the d-to-d and the lowest charge-transfer transitions differ by less than 50 and 500 cm$^{-1}$, respectively, with equal signs and similar magnitudes for the rotatory strengths. However, the differences are somewhat larger for calculations based on the COSMO solvent model. Also, the computed optical rotation has a different sign for the two conformers. An investigation of d-to-d transitions in chiral Co$^{\mathrm{III}}$complexes that will also include a detailed analysis of the difference between the CD of the *lel*$_3$ and *ob*$_3$ conformers is currently under way.[75] The following discussion is based on the results for the slightly more stable *ob*$_3$ conformer.

The orbital diagram for [Co(en)$_3$]$^{3+}$ in aqueous solution (COSMO) is displayed in Figure 4. The HOMO−LUMO gap is approximately 3.1 eV (25 × 10$^3$ cm$^{-1}$). In the TD-DFT method this represents a zeroth order approximation for the excitation energy. As we have already noted, the HOMO−LUMO gap is typically overestimated by the BP functional for this type of compound because it predicts a too strong covalent interaction between the ligands and the metal d-orbitals. While the HOMO and HOMO−1 of [Co(en)$_3$]$^{3+}$ represent almost pure metal d-orbitals, the LUMO has approximately 40 ligand contributions. Accordingly, a very high LUMO energy is obtained, yielding an overestimation of the lowest excitation energies in zeroth order. Unfortunately, the final converged TD-DFT result of 27 × 10$^3$ cm$^{-1}$ for the d-to-d excitations is even higher in energy, whereas the lowest CD band for the d-to-d singlet transitions is experimentally observed at 21 × 10$^3$ cm$^{-1}$. However, sign and order of magnitude of the lowest d-to-d CD band ($\alpha$ in Figure 1) as well as the energetic ordering ($E < A_2$) of the respective excitations are correctly predicted in the calculations, and thus the theoretical spectrum agrees well with the experimental one after red-shifting the lowest pair of d-to-d transitions by 6 × 10$^3$ cm$^{-1}$. The sign and energetic ordering of the individual $A_2$ and E components have experimentally been determined (see ref 11 for an overview). The orbital analysis of the excitations shows in accordance with the literature[11,63] that the pair of d-to-d CD bands is caused by a comparatively small splitting of the $t_{2g}$ metal orbitals in $O_h$ into $a_1$ and e components (in $D_3$) upon trigonal distortion. The higher of the d-to-d transitions ($A_2$) is in the orbital picture represented by a pure HOMO−1 to LUMO excitation, and the lower one (E) is represented by a 50/50 mixture of HOMO−1 to LUMO and HOMO to LUMO transitions, respectively. The small negative band ($\beta$ in Figure 1) in the experimental CD spectrum at about 24 × 10$^3$ cm$^{-1}$ thus is due not to an individual transition but to an artifact of the overlapping positive and negative CD bands of the lowest energy pair of d-to-d excitations. The relative magnitudes of the rotatory strengths for these transitions, and their energies, depend slightly on the *ob* or *lel* conformation of the chelate ring. It is expected that the negative CD band $\beta$ results from the spectrum of the *lel* conformations;[76−79] therefore its absence in the simulated *ob*$_3$ conformer spectrum is in agreement with the experimental data. We will investigate this issue in more detail in a subsequent publication.[75]

The next higher positive weak CD band ($\gamma$ in Figure 1), experimentally at about 29 × 10$^3$ cm$^{-1}$, is caused by another d-to-d transition of E ($T_{2g}$ in $O_h$) symmetry. It is theoretically predicted at 31.6 × 10$^3$ cm$^{-1}$. The spectrum becomes more complicated in the charge-transfer region. The CD is here caused by transitions from ligand orbitals (see Figure 4) into the LUMO. Except for a pair of CD bands (labeled $\delta$ and $\epsilon$ in Figure 1) between 40 and 45 × 10$^3$ cm$^{-1}$, the theoretical and experimental spectrum qualitatively agree rather well.

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We are not able to definitively discard the possibility that this pair ($t_{1u}$ ($O_h$) to LUMO) corresponds to the experimentally observed pair of charge-transfer CD bands ($\phi$ and $\eta$) at 48 and 57 × $10^3$ cm$^{-1}$, respectively, but is underestimated in energy even upon inclusion of solvent effects. However, since the CD spectra for the other complexes qualitatively agree with experiments, it is more likely also in the case of $[Co(en)_3]^{3+}$ that the experimental CD bands are caused by a larger number of ligand-to-d transitions, as is the $\phi/\eta$ pair of CD bands in the simulated theoretical spectrum. Further, the splitting between the $\delta/\epsilon$ pair of excitations is far from being able to reproduce the experimental difference of 9 × $10^3$ cm$^{-1}$ between $\phi$ and $\eta$.

**$[Co(tn)_3]^{3+}$.** The complex $[Co(tn)_3]^{3+}$ is chemically very similar to $[Co(en)_3]^{3+}$ in the way the ligand binds to the metal. Accordingly, the qualitative features of the excitation spectra (i.e., energetic ordering and sign of the E and $A_2$ transitions) are the same. Nevertheless, differences in the relative strengths of the d-to-d transitions cause the sign of the CD spectrum in the d-to-d region to be different for the two complexes Moreover, is it obvious from a comparison of the spectra in Figure 1 that the different number of atoms in the chelate rings has a substantial effect on the energy of the lowest charge-transfer band. It is experimentally red-shifted by about 7 × $10^3$ cm$^{-1}$ for $[Co(tn)_3]^{3+}$ as compared to $[Co(en)_3]^{3+}$. Computationally, a shift of similar magnitude is obtained. As for $[Co(en)_3]^{3+}$, the lowest calculated charge-transfer excitation energies appear to be underestimated by a few thousand wavenumbers, which is also supported by a comparison of the simulated with the experimental absorption spectrum in Figure 2. But also in this case the splitting between the lowest charge-transfer pair of excitations is not able to reproduce the experimental splitting between the charge-transfer CD bands, and a rather large number of additional excitations need to be considered in order to reproduce the two experimentally observed charge-transfer CD bands.

We have found that in the case of $[Co(tn)_3]^{3+}$ the orientation of the plane of the chelate rings (*ob* or *lel*) with respect to the $C_3$ symmetry axis of the complex has a much more pronounced impact on the CD spectrum than was found for $[Co(en)_3]^{3+}$. The data presented here has been obtained for the *lel*$_3$ conformer, which is believed to be in high abundance in solutions[76,77] and was found to be 5.9 kJ/mol more stable than the *ob*$_3$ conformer in our computations.

**$[Co(acac)_3]$ and $[Co(en)_2(acac)]^{2+}$.** The cases of $[Co(en)_2(acac)]^{2+}$ and $[Co(acac)_3]$ are somewhat different from the other complexes since excitations into low-lying empty ligand $\pi^*$-orbitals, in particular ligand $\pi$-to-$\pi^*$ excitations, also contribute to the CD spectrum. The features of the theoretical and the experimental CD spectrum in Figure 1 agree remarkably well with each other, especially for $[Co(acac)_3]$. It can be seen that a large number of excitations contribute to the spectrum, which makes an assignment difficult. The various CD bands of $[Co(acac)_3]$ have been previously assigned to d-to-d (α and $\beta$ in Figure 1), ligand-to-d ($\gamma$), and ligand *$\pi$-to-$\pi^*$*excitations ($\delta$ and $\epsilon$), respectively.[11] Our analysis of the TD-DFT results indicates that the case is not as clear-cut except for the bands α and $\beta$ which are indeed due to d-to-d transitions alone. In partial agreement with the previous assignments, the range from 20 to 34 × $10^3$ cm$^{-1}$ is dominated by ligand-to-d charge-transfer excitations, and the range above 40 × $10^3$ cm$^{-1}$ by ligand $\pi$-to-$\pi^*$ excitations. However, in $\gamma$, $\delta$, and $\epsilon$, there is also (although generally of low to medium intensity) involvement of transitions with pronounced d-to-ligand-$\pi^*$ character, and ligand-to-d and *$\pi$-to-$\pi^*$* excitations contribute to both the $\gamma$ and $\delta$ CD bands. For instance, according to our analysis the most intense CD transition contributing to band $\delta$ (of E symmetry) represents ligand-to-d transitions, and its four neighbor excitations at lower energy (E, $A_2$, E, $A_2$ in descending energy order) represent mixtures of d-to-ligand, $\pi$-to-$\pi^*$, and ligand-to-d transitions. In summary, the spectrum is rather complicated, and ligand-to-d and ligand $\pi$-to-$\pi^*$ excitations cannot be cleanly separated. The situation for $[Co(en)_2(acac)]^{2+}$ is similar.

In contrast to the spectra of the other complexes, for $[Co(acac)_3]$ (and also $[Co(en)_2(acac)]^{2+}$ after inclusion of solvent effects) it is necessary not only to red-shift the d-to-d transitions but the whole spectrum by 4 × $10^3$ cm$^{-1}$ in order to obtain good agreement with experiment. The acac ligand differs from the other ligands in this study because it represents a comparatively “hard” species that forms a much more ionic bond to the metal.[80] Therefore, we might expect that approximations in the density functional have somewhat different consequences than for the covalent binding ligands. It is unlikely that currently neglected solvent effects require the shift of excitation energies in the presence of the acac ligand, since both charge and solvent are different for the two complexes and similar shifts for the other complexes do not appear to be necessary.

**Sources of Errors in the Computations.** Regarding the CD bands $\delta$ and $\epsilon$ of the simulated spectrum of $[Co(en)_3]^{3+}$ in Figure 1, and similarly for $[Co(tn)_3]^{3+}$ and some of the other complexes, it is likely that deficiencies of the density functionals cause the respective excitations to occur at too low energies. Further, we also attribute the overestimation of the d-to-d transitions in all complexes to deficiencies in the density functionals. It has to be noted that much effort has been put into improving TD-DFT excitation energies for smaller molecules, which is often accomplished by ensuring that the Kohn−Sham potential has the proper asymptotic limit and that appropriate diffuse basis functions are employed.[40−43] However, for the present samples we are concerned with valence excitations for which the asymptotic region plays little or no role, and therefore deficiencies in the functionals that influence the electronic structure in the valence region are to blame.

In Figure 1 the CD spectrum of the *ob*$_3$ conformer of $[Rh(en)_3]^{3+}$ is shown for comparison to $[Co(en)_3]^{3+}$. The required shift for the d-to-d excitations is only approximately 1.2 × $10^3$ cm$^{-1}$ and compares well with the 0.9 × $10^3$ cm$^{-1}$ average deviation of excitation energies that has been obtained for

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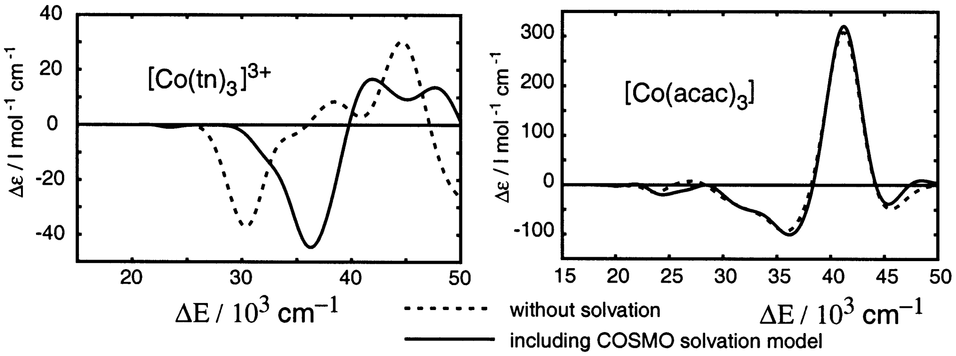

**Figure 5.** Comparison of simulated CD spectra for [Co(tn)$_3$]$^{3+}$ and [Co(acac)$_3$] with and without modeling of solvent effects in the ground state calculations (no corrections to the excitation energies are applied here). The solvent effects on the charge-transfer excitations are much more pronounced for the +3 charged complex [Co(tn)$_3$]$^{3+}$.

various Ru complexes in ref 44. The much better performance of the TD-DFT method for the 4d metal Rh as compared to Co indicates that deficiencies of the functional are likely to be responsible for the errors in the d-to-d excitation energies. It is well-known that approximate functionals perform much better for heavier elements, and in particular that 3d metals are much more sensitive to approximations in the functionals than 4d or 5d metals. The same is true for the treatment of correlation effects in wave function based ab initio methods.[39]

On the other hand, as we have already noted, the shapes of the spectra are rather well reproduced in the present calculations. This strongly suggests that mainly the energy splittings between occupied and unoccupied Kohn−Sham orbitals, as zeroth order approximations to the excitation energies, are in error here. At the same time the orbital shapes, and their energetic ordering, allow for a reasonably accurate prediction of the signs and magnitudes of the rotatory strengths and order of the excitations. That the electron density obtained from gradient-corrected density functional calculations appears to predict molecular properties quite well, while the occupied−unoccupied orbital energy differences (in particular the HOMO−LUMO gap) can be substantially in error, has been previously noted by us.[65,81] This fact has also implicitly been used for many years by the authors of ref 82 for the justification of a method in which orbital energy differences, but not the orbitals, are corrected in order to improve the results of DFT NMR calculations.

Regarding errors in the charge-transfer region, it has recently been convincingly argued[83] that TD-DFT excitation energies based on approximate density functionals can suffer from errors if a substantial change in the electron density due to the excitation occurs. This is certainly the case for the charge-transfer excitations in our samples. In some contrast to the d-to-d excitations, errors in the charge-transfer excitation energies can to a large extent be attributed to the approximate treatment of the response of the molecule to the external light beam being used to measure the absorption and CD spectrum. It can be shown[84] that both dominant errors in the orbital energies as well as the most important errors related to the response are of the same physical origin and occur because of an incomplete elimination of the artificial self-interaction of electrons that is intrinsic to all currently popular approximate density functionals.[85]

In summary, we conclude that errors in the excitation energies both for the charge-transfer region and for the d-to-d transitions are related to a particular approximation in the density functional approach. This approximation causes problems regarding the orbital energies (affecting mostly the d-to-d transitions), and problems regarding the description of the response of the molecule to a light beam, which are believed to be most significant for excitations with significant charge transfer.

Besides this, the yet incomplete treatment of solvent effects could also be responsible for deviations between the simulated CD spectra and the experimental ones. An example is the lowest-energy charge-transfer band of [Co(tn)$_3$]$^{3+}$ (see, e.g., Figure 5). As already mentioned in the section about solvent effects, it is at the present stage not possible for us to determine which of the approximations in the computations is the main reason for the remaining errors in the computed CD bands, or whether they are due to a combination of them. Other approximations in the computational model that could potentially have a noticeable effect on the outcome of the CD simulations are the neglect of the presence of the counterion, the neglect of vibrational effects, the neglect of the current dependence of the density functional (which is believed to be of some importance for TD-DFT calculations[48,86,87]), and the neglect of the frequency dependence of the molecular response (which is not believed to be of high importance in molecular TD-DFT computations for the UV−vis energy range and low light intensities[88]).

Another issue is the possibility of different conformations of the complexes being present in solution. Preliminary

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results for $[Co(tn)_3]^{3+}$ indicate that some improvement of the simulated CD spectrum will be obtained by considering a small percentage of *ob* conformations and computing an averaged CD spectrum. For the complexes with flexible five-membered chelate rings (the en ligand) we have found the influence of the ring conformation to be much smaller, though not negligible. Details will be published elsewhere. Inaccuracies in the optimized geometries for a specific conformation cannot be ruled out as an additional source of errors, but will be of less importance than conformational changes. Because of the already good qualitative, sometimes quantitative, agreement with experiment that we have obtained in the present study, it is rather unlikely that improving on the aforementioned approximations will significantly change the assignment of the spectra, though it can of course be expected that an improved computational model will lead to better quantitative agreement with experimental data.

## 4. Summary and Outlook

We have in this work presented a theoretical study of the CD spectra of chiral $Co^{III}$ complexes that covers the whole range of the experimental spectra. $[Rh(en)_3]^{3+}$ has also been studied for comparison. The calculations are based on our recent implementation for rotatory strengths within the time-dependent density functional approach.[24,48] Solvent effects on the spectra have been estimated by using a continuum solvation model for the ground state calculation. The shapes of the simulated spectra are not strongly altered through the inclusion of the solvent model in the ground state calculations, and they agree in most cases qualitatively with the experimental ones. However, large effects on the energy of CD bands and the rotatory strengths of individual transitions are obtained in particular for highly charged systems. For simple cases an assignment and an interpretation of the CD spectra could potentially also be based on gas phase calculations. In order to obtain a reasonable agreement of experimental and simulated spectra not only regarding its shape but also regarding the correct positions of the CD bands, however, we find that it is necessary to consider solvent effects for charged species in polar solvents. Further improvement of the results can be expected from an additional treatment of the solvent's response to the excitation. We also point out that due to the complexity of each spectrum in the charge-transfer region a comparison between theory and experiment is greatly facilitated by plotting the respective simulated “spectra”. For a quantitative comparison it is important to be aware of the systematic differences between TD-DFT simulations (both solvent and gas phase) and experimental data, viz., an overestimation of the d-to-d excitation energies due to deficiencies of the density functionals, and a tendency for an underestimation of some of the charge-transfer excitation energies for the same reason. These deficiencies strongly affect 3d metal complexes but will be of much less influence for 4d or 5d metals.

Differences in the CD spectra for different conformations of chelate rings are expected for some of the complexes. Their structures are not rigid, and the experimental spectra are determined by contributions from all possible conformers. A respective study by us for $[Co(en)_3]^{3+}$, $[Co(tn)_3]^{3+}$, and other complexes is currently under way.

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**Supporting Information Available:** Optimized structures for the complexes as well as parts of the outputs from the TD-DFT computations with detailed numerical data for the excitation energies, the oscillator strengths, and the rotatory strengths (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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