Optical Activity in Tris Bidentate Cobalt(III) Complexes. An ab Initio Study

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In this work we present the results of an ab initio study aimed at the prediction of the chiroptical spectra of dissymmetric bidentate Co(III) complexes at modest levels of theory. The restricted Hartree–Fock/random-phase approximation is employed to obtain excitation energies and rotatory strengths for tris(ethylenediamine)cobalt(III), tris(1,3-diaminopropane)cobalt(III), and tris(oxalato)cobaltate(III). Numerically, the calculated optical properties compare quite favorably to experiment. A modified RHF/ligand field CI procedure is employed to account for some of the error which is encountered at the RPA level. The features of the SCF wave functions and the structure of the RPA transition density matrices are found to be strikingly different from what would be predicted by classical ligand field theory. Our results are analyzed in terms of similarities to and differences from related efforts.

Introduction

The origin of the significant optical rotatory strength associated with the "d → d" transitions of dissymmetric transition metal complexes is a rather old challenge to theoretical chemistry, and one which never has been resolved satisfactorily. The problem has been considered by numerous authors since the early work of Moffitt.[1] Contributions prior to 1979 have been reviewed by Richardson.[2] Work since that time includes papers by Schipper and Rodger,[3] by Schipper,[4] and by Gerloch[5,6] and co-workers.

The difficulty is to obtain a value for the electric dipole term, $\langle \Psi_j|\mu|\Psi_i\rangle$ in the Rosenfeld equation,[7] which is large enough to account for the observed optical rotation associated with the magnetically allowed "d → d" transitions. These are generally considered to be metal-centered d → d transitions and as such would be La Porte forbidden with an electric dipole strength of zero. Most of the previous efforts have focused on the magnetically allowed excitations of T_{1g} octahedral parentage in "nearly octahedral" tris bidentate $M(A–A)_3$ complexes of cobalt(III) and chromium(III). For these cases, the problem reduces to the introduction of sufficient ungerade character into these transitions, which are of gerade character in the undistorted octahedron.

In most of the previous work the independent systems/perturbation (ISP)[2] approach, which has been applied successfully to many chiral organic systems, has been used. This model divides the system into an achiral chromophore, where the transition is taking place, and chiral surroundings, which perturb the chromophore to induce rotatory strength. Historically only Coulombic interactions between the chromophore and the surroundings have been considered, whereas exchange perturbations have been ignored. This approach has not been very successful for the case of transition metal complexes. Calculations of this type have yielded some promising results, but rely heavily on poorly defined parameters and various authors tend to disagree on the relative importance of different terms in the perturbation expansion. Recently Schipper[4] has demonstrated how the ISP perturbation approach can be extended to include exchange terms arising from weak overlap between the achiral chromophore and the chiral surroundings using his simplified group function (SGF) approach. However, at the present time no calculations have been reported using this formalism.

There has been a limited amount of work in which a molecular orbital approach was taken. The most direct precursors to the work reported here are papers by Strickland and Richardson[8] and Evans et al.[9] Most of these investigations considered only the metal 3d, 4s, and 4p orbitals and the 2s and 2p orbitals of the immediately ligating nitrogen or oxygen atoms. The most complete "all-atom" calculation was done with a minimal basis set and employed the extended Hückel (Wolfsberg–Helmholtz)[9,10] algorithm. In view of the high quality required of the wavefunction to yield accurate rotatory strengths due to the second order nature of the phenomenon,[11] such calculations need to be considered qualitative. They did, however, correctly reproduce the signs of the A_2 and E components of the band of octahedral T_{1g} parentage for some selected cases, and they also provided support for the assumption, that the vibronic mechanism[12] which accounts for most of the intensity in the linear absorption spectra is not responsible for the rotatory strengths of the T_{1g} band.

It has been shown in recent years, that ab initio calculations applied to transition metal complexes are not only feasible, but also of predictive quality, if designed with care.[13,14] This study was undertaken to examine the possibility of correctly predicting rotatory strengths at modest levels of theory and to aid in the selection of appropriate higher level methods which would improve accuracy while remaining computationally feasible. We believe, that a deeper insight into the origin of the optical activity can be gained by examining the results of such ab initio calculations.

Computational Details

The main body of this work encompassses the characterization of ligand field states and chiroptical properties of tris bidentate Co(III) complexes with the use of inexpensive ab initio methods, namely restricted Hartree–

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(5) Fenton, N.; Gerloch, M. *Inorg. Chem.* **1990,** *29,* 3718.

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(7) The expression for the rotatory strength of a specific excitation $i \rightarrow j$ is the Rosenfeld equation

$$R_{ij} = \mathrm{Im}\langle \Psi_i|\mu|\Psi_j\rangle \cdot \langle \Psi_j|m|\Psi_i\rangle$$

where μ is the electric dipole operator, m is the magnetic dipole operator, and Im indicates the imaginary part of a complex number.

(8) Strickland, R. W.; Richardson, F. S. *Inorg. Chem.* **1973,** *12,* 1025.

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(10) (a) Yeh, C.; Richardson, F. *Inorg. Chem.* **1976,** *15,* 682. (b) Hilmes, G.; Yeh, C.; Richardson, F. *J. Phys. Chem.* **1976,** *80,* 1798.

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Table I. Size/Contraction of the Basis Sets

basis set	Co	C, N, O	H
minimal	(13s/9p/6d)[5s/3p/3d]	(7s/4p)[2s/1p]	(3s)[1s]
split valence	(14s/10p/6d)[6s/4p/3d]	(9s/5p)[3s/2p]	(3s)[1s]
double ζ	(14s/11p/6d)[8s/6p/3d]	(9s/5p)[4s/2p]	(4s)[2s]

Fock (RHF) theory for the ground state and reference wave functions, and random-phase approximation[15] for the spectroscopic properties.

Single-point calculations were performed on four different complexes as described below. Calculations on hexaamminecobalt(III) ($[Co(NH_3)_6]^{3+}$) were made with two different geometries; the "octahedral" geometry where the nitrogens were placed in the octahedral positions and the hydrogens were oriented to give the highest possible overall symmetry, which is D_{3d}, and a "truncated tris(ethylenediamine)cobalt(III)" where the ammonia ligands were placed in positions which correspond to the amino groups in tris(ethylenediamine)cobalt(III). This distortion results in a chiral D_3 geometry. The main subjects of the study were three relatively small examples for tris bidentate cobalt(III) complexes, namely tris(ethylenediamine)cobalt(III) ($[Co(en)_3]^{3+}$), tris(1,3-diaminopropane)-cobalt(III) ($[Co(tn)_3]^{3+}$), and tris(oxalato)cobaltate(III) ($[Co(ox)_3]^{3-}$). The geometries which were used in the computations were derived from X-ray structures in the following fashion:

The structure of the cation in the $[Co(en)_3]Cl_3{\cdot}3H_2O$ crystal[16] was averaged to D_3 symmetry. The positions of the Hydrogen atoms were averaged to reflect symmetry equivalent bonds.

For the case of the $[Co(tn)_3]Cl_3{\cdot}H_2O$, the Co, N and C bond distances and angles were averaged from the crystal structure[17] to C_3 symmetry. Since the hydrogens are poorly defined in the structure, they were placed at calculated positions. The resulting geometry reflects the C_3-chair$_3$ conformation, which has been predicted[18] to be the lowest energy conformation.

The four independent crystallographic structures of the $[Co(ox)_3]^{3-}$ anion reported by Okazaki et al.[19] were averaged to D_3 symmetry. The oxalate ligands were kept planar.

Three different basis sets were considered to find the optimal balance between computational economy and accuracy. The smallest basis was derived from a minimal set.[20] The basis of intermediate size corresponded approximately to a split valence set in the number of functions, but contained large primitive sets[21] which were contracted with the use of the general contraction scheme.[22] The basis with the largest number of functions was formally of double zeta character, where the number of primitives used for this set was not much larger than what was used in the split valence set.[23] Details about the size and contraction of all sets can be found in Table I. All three basis sets were matched for internal balance in adherence to the $\Delta E/N$ criterion.[24] For the case of the cobalt, all three sets were modified in the standard way to ensure adequate description of the metal–ligand bond. Depending on the original set, appropriate replacements and augmentations to the representation of the 4s and 4p functions to account for the ligand field environment were selected in accordance with established methods.[24] The same set of d-functions[25] was used in all three sets, replacing the respective original functions.

The ground state of tris(ethylenediamine)cobalt(III) was examined at the HF level with all three different basis sets. Ground-state MP2 energies and RHF/RPA spectra were obtained with the minimal and split valence sets. RHF/RPA calculations with the smallest basis set were performed for all three bidentate complexes. All RPA calculations used the full valence space and a rather large number of virtual orbitals as configuration reference space. Some very preliminary studies employing a modified RHF/ligand field CI method[13] with single and double substitutions were applied to hexaamminecobalt(III).

Table II. $[Co(en)_3]^{3+}$ Ground-State Energy (au)

basis set	HF	MP2
minimal	−1945.94	−0.09
split valence	−1947.77	−0.07
double ζ	−1947.82	

The RHF/RPA work was executed with the program RPAC, version 8.6,[26] interfaced with Gaussian 90.[27] The RHF/LFCI calculations were performed with the Gamess 90[28] program. Most of the calculations involving the smaller ligands and the minimal basis set were performed on a VAX 6440 owned by Georgia Tech, with the appropriate VMS installations of the ab initio packages. The larger computations were excecuted on the Cray YMP/832 at the Pittsburgh Supercomputing Center.

Results

Preliminary Considerations. Results of the HF and HF/MP2 ground-state calculations with different basis sets are summarized in Table II. It is worth noting that the split valence and double-ζ basis sets exhibited almost identical performance with respect to the total energy. Furthermore, the orbital energies and LCAO compositions of the entire space of occupied valence orbitals are nearly identical, with completely identical sequencing of the orbitals. The structure of the valence space which resulted from the use of the minimal set presented in Table I was virtually identical to the valence space found with the larger bases. This was not the case for some other bases which were considered, and the smallest basis which was chosen as adequate for this study was the one which resulted in a valence space closely resembling the one obtained with the largest basis.

The MP2 calculations result in a very small total energy correction, indicating that the nondynamical correlation error for the closed shell HF wave function is probably small. A full valence CID calculation of the ground state of the hexaammine complex also resulted in a small correction to the total energy, with no evidence for a strongly multireference character of the wavefunction. Further indirect evidence for this can be found in the excitation energies from the RHF/RPA calculations. The excitations were consistently very slightly too high for the lower three states (T_{1g} parentage) and high for the upper three states (T_{2g} parentage), but never low. Some spectra were also calculated using the monoexcited CI or Tamm–Dancoff approximation,[29] which differs from the RPA in that ground-state correlation is completely neglected in the TD description of excitation properties.[15] The calculated spectra differ only slightly between the two methods, again indicating that ground state correlation is not very crucial for the qualitatively correct description of the spectroscopic properties of interest.

From the RHF/RPA calculation with the split valence basis it was determined, that any increase in the size of basis set beyond the smallest set chosen for this study does not improve the results for either the excitation energies or the predicted rotatory strengths. This was not surprising, as the approximation of the excited states as a superposition of only singly excited configurations would impose an inherent limit to the accuracy, which could not be overcome by improving on the reference wave

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(29) CI singles or monoexcited CI, also known as the Tamm–Dancoff Approximation. See also ref 15.

Table III. Measured and Calculated Chiroptical Data

complex		measd		calcd[a]		
		λ, nm	$10^{40}R$	λ, nm	$10^{40}R_v$	$10^{40}R_{oi}$
Λ-$[Co(en)_3]^{3+}$	E	475	+10.7	469	+19.0	+8.2
	A_2	462	−6.2	461	−11.9	−6.8
Λ-$[Co(tn)_3]^{3+}$	E	483	−0.83	478	−18.6	−3.8
	A_2	521	+0.39	484	+11.9	+4.4
Λ-$[Co(ox)_3]^{3-}$	E[b]	590	+70	535	+90	+34

[a] Rotatory strengths are in cgsu × 10^{40}; R_v is the velocity form and R_{oi} is the origin-independent form, as defined in ref 15. [b] Experimental data for $[Co(ox)_3]^{3-}$ are a rough estimate from the diluent crystal spectrum reported in ref 31.

Table IV. Canonical Molecular Orbitals in $[Co(en)_3]^{3+}$ Which Contain Significant Amounts of Metal d Orbital Character[a]

(a) Partial Molecular Orbital Data To Show the Symmetry and Energy of the Relevant Orbitals

energy, au	symmetry		no.
	O_h	D_3	
−0.360	e_g	e	64, 65[b]
−1.206	t_{2g}	e	44, 45
−1.215	t_{2g}	a_1	41
−1.239	t_{2g}	e	38, 39
−1.289	t_{2g}	e	35, 36
−1.299	t_{2g}	a_1	34

(b) Mulliken Analysis of the Canonical Orbitals Given in Part a as Percent Contribution per Atom Type in $[Co(en)_3]^{3+}$

atom	molecular orbital					
	34	35, 36	38, 39	41	44, 45	64, 65
Co	51	58	11	43	20	81
N	29	21	41	31	32	18
H (N)[c]	12	7	16	16	10	<1
C	6	11	25	9	30	<1
H (C)[d]	2	3	7	1	9	<1

[a] Note that the e orbitals are more delocalized than the a_1 orbitals. [b] Orbitals 64 and 65 are the LUMO set. [c] Hydrogen atoms bonded to nitrogen atoms. [d] Hydrogen atoms bonded to carbon atoms.

function. Calculations with even smaller basis sets were performed to isolate the most economical basis set, at which the accuracy attainable within this method would plateau. Our particular choice of basis set for the RPA studies of the larger complexes was based on these findings.

Calculated Optical Activities. The results which have been obtained for the chiroptical spectra for the three complexes with the use of the RHF/RPA formalism are presented in Table III. The experimental data are included for comparison. Generally, data of this type are obtained by recording the CD spectra of the solution and the oriented crystal of the optically pure conformer, assigning the E component from the crystal spectrum, and fitting the solution spectrum with Gaussian curves for integration. This was done for the case of the two diamino ligands.[30] The experimental data for the tris(oxalato)cobaltate(III) which are shown in Table III represent a rough estimate of the rotationally averaged CD intensity of the E component, which was derived from the diluent crystal spectrum recorded by McCaffery and Mason.[31] The oxalato complex is believed to be unstable in solution; therefore data for the A_2 component are absent.

The reported absolute magnitudes of the rotatory strengths, the excitation energies, and the A_2/E splitting are subject to environment effects and other factors which would not be accounted for by the calculation, as well as an inherent uncertainty due to the fitting process employed to separate the (overlapping) A and E components of the band. The absolute sign of the optical rotatory strength, however, does not normally change in response to experimental conditions. It is thought to be characteristic of a given ligand/conformer. This is generally true for the relative energies of the two components, as well.

Of all of the diamino ligands whose Co(III) complexes have been prepared and characterized in the described manner, 1,3-diaminopropane takes an exceptional position in two regards: Both the sign of the CD and the relative excitation energies for the A_2 and E components are opposite from what they are for all other ligands of this category.[30] Consequently, this particular complex represents a challenging test for any theoretical attempt at predicting CD spectra. Unfortunately, some other factors are not as favorable. In particular, the CD intensities are also much weaker than for most other complexes, and the molecule possesses several other conformers which are believed to be only slightly higher in energy than the C_3-chair$_3$ conformer, with presumably low interconversion barriers. Due to the uncertainty of the actual geometry of the complex in solution, the experimental data, particularly the magnitude of the splitting, need to be interpreted with some caution. The sign of the E band from the single crystal spectrum of the optically pure conformer, however, can be regarded as established beyond doubt.

In consideration of these factors, comparison to experiment cannot serve as an absolute measure of the calculated values' accuracy. On a more relative scale, the performance of a theoretical model can be evaluated by comparison to a superior model, or from the degree to which known relations between calculated properties are violated. In the case of the RPA scheme, the rotatory strengths are calculated both in the position and momentum representation, thereby providing such a quality index.[15]

For all the systems examined, the RPA method correctly predicts the relative position and the sign of the two components of the T_{1g} parentage CD band, which is remarkable in the light of the special status of the 1,3-diaminopropane ligand within the class of diamino ligands. Considering the approximations inherent at this level of theory, the CD intensities are reproduced as well with respect to experiment as can be expected from the quality of the wavefunction. The differences between the values calculated by the position and momentum formulations found here compare favorably with values previously reported using larger basis sets on smaller molecules.[32]

As expected from the octahedral selection rules, the magnetic transition moments of the A_2 and E transitions are virtually identical in a given complex and vary only slightly among the different complexes. The electric transition dipole moments, on the other hand, vary by roughly a factor of 4 between the oxalato and the diamino complexes, accounting for most of the variation in optical activity. Not surprisingly, the intensities for the 1,3-diaminopropane complex compare least favorably. By and large, the degree of inaccuracy present in these calculations can probably be attributed to the cumulative effect of different approximations, rather than to the presence of any one severe error.

Features of the Calculated Wave Functions. In the ligand field approximation the metal d oribtals are thought of as essentially atomic orbitals, which are perturbed by the presence of the ligands only slightly. If this view was to be correct in the sense of Schipper's[4] limiting case (ii), one would expect it to be borne out in the ab initio molecular orbitals. Recalling octahedral parentage, the following symmetry orbitals would be observed in the case of the trigonal, low-spin d^6 complexes: The doubly occupied, nonbonding π-type t_{2g} set splits into an a_1 orbital and an e set; the vacant, antibonding σ-type e_g set becomes an e set, while these MO's retain essentially atomic character.

This general pattern has indeed been reported in the literature[13,33] for HF calculations of certain complexes of Co(III) and Cr(III), where the metal 3d content of the e_g set was reported to be around 85%, and 92% or higher for the t_{2g} set. The vacant e_g set has long been recognized as the antibonding pendant to the

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(32) For some examples, see ref 15, Section VIII.

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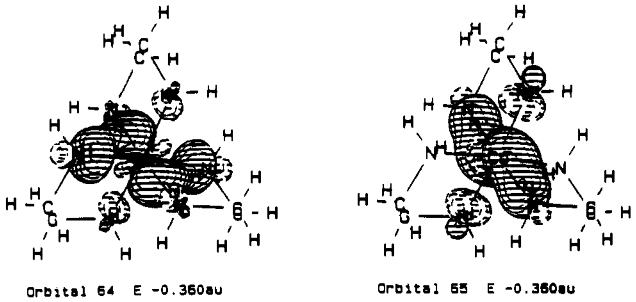

Figure 1. Orbital plots of the LUMO's in $[Co(en)_3]^{3+}$. The contour level is 0.05 au. The rather low contour level tends to overemphasize the contribution from the nitrogen lone pairs. The view is 10° from the 3-fold axis such that the top of the figure is further from the viewer than the bottom. The location of the nitrogen atoms, with respect to the plane of the paper, is as follows: above, starting with the top right nitrogen, then clockwise alternating below and above.

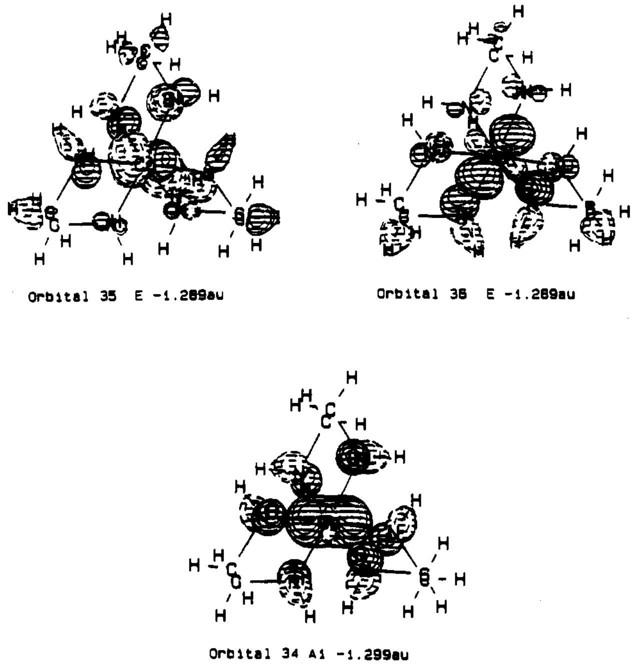

Figure 2. Orbital plots of a set of t_{2g} parentage orbitals with high Co d orbital content from the valence space of $[Co(en)_3]^{3+}$. Refer to Table IV for the orbital-labeling scheme. View and contour level are as in Figure 1.

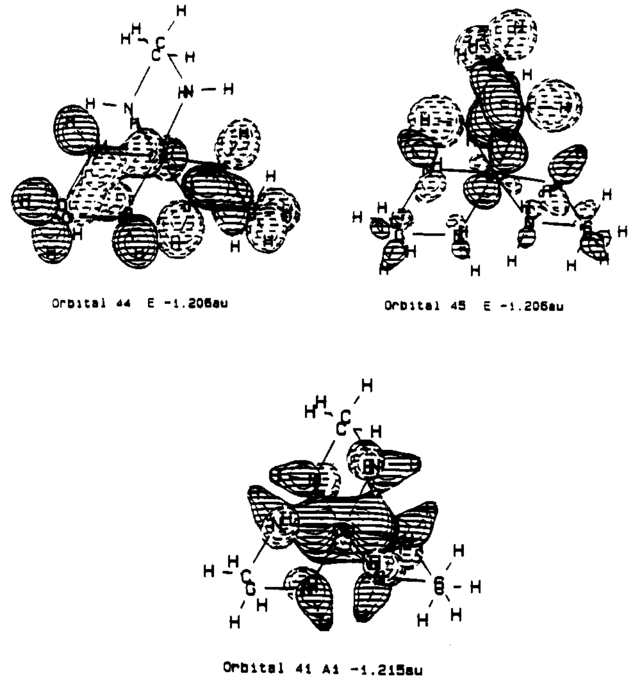

Figure 3. Orbital plots of a set of t_{2g} parentage orbitals with moderate Co d orbital content from the valence space of $[Co(en)_3]^{3+}$. Refer to Table IV for the orbital-labeling scheme. View and contour level are as in Figure 1.

σ-bond which is formed by the ligand lone pairs and the appropriately oriented metal d orbitals, which would lead to an admixture of lone pairs in these orbitals. The t_{2g} set, however, is thought of as nonbonding and consequently noninteracting, except for the case of π-back-donation to unsaturated ligands.

The canonical SCF orbitals which were obtained in the course of this work are of somewhat different structure. While the e_g set, which was observed as the LUMO set, was composed predominantly of metal d character, with some admixture from the ligand lone pairs, the t_{2g} parentage metal orbitals were found to interact via accidental near degeneracies with occupied ligand orbitals of appropriate symmetry parentage.

The near-degeneracy interactions between occupied metal and ligand orbitals were found to result in several sets of delocalized canonical orbitals of varying metal content (up to 60% d-character for $[Co(en)_3]^{3+}$). The resulting delocalized MO's fall into a rather narrow energy range, indicating that the interactions are weak. The patterns of the resulting valence orbitals are very similar for all the systems which were considered. A detailed Mulliken population analysis of the canonical orbitals which make the largest contribution to the excitation eigenvectors for $[Co(en)_3]^{3+}$ is presented in Table IV. The orbital energies and octahedral symmetry parentage of the orbitals are also given. Of the orbitals given in Table IV, orbitals 64 and 65 are the LUMO set of e_g parentage, all others are occupied orbitals whose "d portions" are of t_{2g} parentage. There are 63 occupied orbitals in $[Co(en)_3]^{3+}$, and the orbital count numbers are used for identification of the orbitals throughout the tables and figures. As can be seen from the labels, the occupied orbitals which contain significant amounts of d character are not among the HOMO's, which conforms with previous calculations.[33] 3D plots of the orbitals presented in Table IV are presented in Figures 1–3.

The choice of orbitals to be included in Table IV was dictated by the structure of the excited states, as will become evident later. The assignment of octahedral parentage was done simply by examining the molecular orbital coefficients.

Close examination of the Mulliken populations, the molecular orbital coefficients, and plots of the orbitals in question shows that for the case of the diamino ligands the interactions occur mainly with N–H and N–C σ-bonds. In the case of the oxalato ligand, the occupied d orbitals interact with the π-bonds on the ligand.

It should be noted that these observations are not inherently in disagreement with previous findings,[33] as we believe that none of the systems previously studied were very favorable for the occurrence of near-degenerate mixing of this type, due to a smaller number of candidate orbitals in the valence manifold.

In the delocalized representation used in this work, the representation of the excited states in the basis of canonical MO's differs from the classical ligand field picture. In the ligand field approximation the excited states are represented as d → d excitations within the manifold of five d orbitals. The ligand field symmetry terms for the six resulting one electron excitations in trigonal geometry have been reported by Liehr.[34] Only the lower three excitations of T_{1g} parentage are magnetic dipole allowed in the octahedral case, and give rise to most of the observed optical activity. Recalling octahedral parentage, they can be written as follows:

$$^1A_2\text{:}\quad (1/2)^{1/2}[e_-(t_{2g}) \rightarrow e_-(e_g) - e_+(t_{2g}) \rightarrow e_+(e_g)]$$

$$^1E_+\text{:}\quad -(1/2)^{1/2}[a_1(t_{2g}) \rightarrow e_+(e_g) + e_+(t_{2g}) \rightarrow e_-(e_g)]$$

$$^1E_-\text{:}\quad (1/2)^{1/2}[a_1(t_{2g}) \rightarrow e_-(e_g) + e_-(t_{2g}) \rightarrow e_+(e_g)]$$

If the canonical molecular orbitals obtained by the compu-

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[34] Liehr, A. *J. Phys. Chem.* **1964**, *68*, 665.

Table V. RPA Vectors[a] of the T_{1g} States of $[Co(en)_3]^{3+}$

occ	→	virt	E	E	A_2
34 (a_1)		64	0.220		
34		65		0.220	
35 (e)		64		0.119	0.249
35		65	0.119		
36 (e)		64	0.119		
36		65		0.119	0.249
41 (a_1)		64	0.274		
41		65		0.274	
44 (e)		64		0.060	0.126
44		65	0.060		
45 (e)		64	0.060		
45		65		0.060	0.126
38 (e)		64	0.028		
38		65		0.028	0.057
39 (e)		64		0.028	0.057
39		65	0.028		

[a] As calculated from the RPA amplitude coefficients X and Y which yield the square of the state vector coefficient $(X+Y)(X-Y)$, as defined in ref 15.

tational procedure indeed contain a set of orbitals which are almost pure atomic d orbitals, then the resulting excited states should be composed mostly of terms corresponding to the terms shown above. For cases where the ab initio molecular orbitals correspond closely to ligand field type orbitals, the ligand field states have been approximated successfully by means of the RHF/ligand field CI method.[13] This method is based on diagonalization of the configuration space spanned by five (usually state averaged) nearly atomic d orbitals, which generally are derived from RHF calculations.

Clearly, if the valence space of the complex does not contain any single set of nearly pure d orbitals, any approximation of the excited states by means of superpositions of excitations from a given reference state must be based on a larger configuration space. All of our RPA calculations included the full valence space and nearly all the virtual orbitals as reference space.

It was reassuring to find, that the lowest lying excitations indeed correspond to d → d transitions, and that 98% of the state vector was solely composed of excitations from molecular orbitals with high d orbital content into the LUMO's, which are nearly pure d orbitals in the ligand field sense. The leading terms of the RPA wave functions of the states which give rise to the optical activities in Table III are shown in Table V. For the orbital labeling scheme, refer to Table IV.

The RPA state vectors can be analyzed by relating them to Liehr's ligand field states. Instead of two terms of the type $e(t_{2g}) \rightarrow e(e_g)$ or $a_1(t_{2g}) \rightarrow e(e_g)$ with state vector coefficients of nearly $(1/2)^{1/2}$, as would be expected from classical arguments, there are several sets of terms corresponding to excitations into the "ligand field like" LUMO's. All these excitations originate from the orbitals with high or moderate d orbital content of t_{2g} parentage. In essence, the excitations are composed just like the symmetry functions derived by Liehr, with the notable difference that the single set of lignd field t_{2g} functions is replaced by a group of delocalized orbitals of high d content, all of which are of t_{2g} d parentage. As can be seen from Tables IV and V, the relative weight of the contributions of the individual excitations correlates with the d-orbital content of the resulting hole-states.

In order to shed some light on the mechanistic questions concerning the source of the electric transition dipole moment, we shall now examine the transition densities which are associated with the optically active transitions. A useful property of the transition density is that its various electric multipole moments provide the corresponding geometric transition moments.[35] The contributions of different parts of the molecule to the transition moment of interest can serve to identify the effective chromophore of a given excitation.

Table VI. Length Transition Dipole Moment by Atom Type ($D \times 10^2$)

	excitation/polarization		
atom	E/Y	E/X	A_2/Z
Co	0	0	0
N	−0.69	+0.69	−2.28
H (N)	−1.42	+1.42	−2.51
C	+1.00	−1.00	+1.68
H (C)	+0.11	−0.11	+0.31

Projection of the gross transition charges on each atom into the dipole moment along the axis of polarization thus yields the atom by atom contributions to the electric transition dipole. Again, tris(ethylenediamine)cobalt(III) was chosen for detailed examination. Table VI presents the individual contributions of the atoms summed into contributions per atom type. The sum of these contributions corresponds to the net electric transition dipole. The following properties of Table VI are of particular interest: The Co atom itself is not part of the effective chromophore, which was expected from the applicability of the octahedral selection rules to the immediate surroundings of the Co atom. It is very interesting to note that the largest contribution comes from the hydrogen atoms on the amino groups. This is somewhat unexpected, but provides an excellent explanation for the exceptionally strong gegenion effect[36] associated with the solution CD of the diamino complexes, which is brought about by hydrogen bonds with gegenions of suitable geometry.

From the information contained in the component analysis of the electric transition dipole moment and the composition of the orbitals which participate in the excitations, some conclusions regarding the mechanism which induces optical activity can be drawn. The greatest contribution to the electric dipole moment of the "d to d" transition moments comes from the immediate neighborhood of the ligating atoms, which is clearly chiral. The effective chromophore for the optical rotation can be thought of as arising from gerade/ungerade mixing of N–H and N–C σ-bonds whose gerade contributions mix with the t_{2g} cobalt d orbitals via near-degeneracy.

Higher Level of Theory. As would be expected from the very modest level of theory employed in this study, overall agreement with experimental data is less than perfect. Due to the size of the problem and the multireference nature of the excited states, only a limited amount of higher level treatment is feasible. The following section outlines some preliminary efforts which were made along these lines.

While the spectroscopic characteristics of the magnetic dipole allowed terms of T_{1g} parentage were described well with the RPA model, the transitions of T_{2g} parentage were calculated approximately 1 eV above the experimental values. A simple argument derived from classical ligand field theory can account for this systematic difference in the two sets of excitations and suggest appropriate corrections.

In the octahedral approximation, the T_{2g} transitions are of $(t_{2g})^6 \rightarrow (t_{2g})^5(e_g)^1$ type, and the $(t_{2g})^5(e_g)^1$ terms can interact strongly with terms of the appropriate symmetry from the $(t_{2g})^{5-x}(e_g)^{1+x}$ configurations, where $x = 1$–3. A crude estimate of this effect can be made by considering the standard ligand field electrostatic interaction matrices.[37] The ligand field parameters Δ, B, and C are ill defined with regard to the ab initio calculations and must be considered rough estimates, but it should be possible to make an order of magnitude estimate of the importance of correlation effects of this type. The following reasoning is applied to the case of the tris(ethylenediamine)cobalt(III): The RHF/RPA calculation yields excitations of 2.66 eV (T_{1g} av) and 4.68 eV (T_{2g} av),

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(35) Hansen, A. E.; Bouman, T. D. *J. Am. Chem. Soc.* **1985**, *107*, 4828.

(36) Mason, S.; Norman, B. *Proc. Chem. Soc., London* **1964**, 339.

(37) Griffith, J. S. *The Theory of Transition Metal Ions*; Cambridge University Press: Cambridge, U.K., 1961.

Table VII. RPA and LF/CISD Data for D_3 $[Co(NH_3)]^{3+}$

	excitation, eV		
state	RPA	LF/CI	exp[a]
$A_2(T_{1g})$	2.510	2.7	
$E(T_{1g})$	2.518	3.0	
$A_1(T_{2g})$	4.56	4.4	
$E(T_{2g})$	4.57		3.6

[a] Experimental value from the weak CD band of the $E(T_{2g})$ state in $[Co(en)_3]^{3+}$. Only the A_1 was calculated due to computational limits, while the E is the one for which an experimental value is known.

respectively. From this we get

$$16B = 4.68 - 2.66 \qquad 2.66 = \Delta - C$$

The resulting estimates for the ligand field parameters are taken to be

$$\Delta = 2.98\ \text{eV} \qquad B = 0.13\ \text{eV} \qquad C = 0.32\ \text{eV}$$

Substituting these values into the appropriate electrostatic interaction matrices lowers the energy of the T_{1g} excitation by 0.07 eV where the coefficient of the one-electron term in the eigenvector is 0.996, while the T_{2g} excitation is lowered by 0.52 eV with a one-electron coefficient of 0.91.

These calculations are not particularly sensitive to the choice of input parameters, and over a range of values they consistently indicate that the T_{1g} excitations should be adequately represented as superpositions of single excitations, while the T_{2g} set will contain a considerable amount of two electron excitation.

This back-of-the-envelope reasoning can be tested by carrying out the appropriate RHF/LFCI calculations. However, in the light of the previously discussed nature of the RHF wavefunctions for the compounds of interest, the CI reference space will have to be greater than the usual set of five nearly atomic d orbitals. The size of the computational problems is too large to readily solve for the appropriate higher roots of a full valence space CISD calculation, which is what would have to be done for a rigorous comparison between a full valence space RPA calculation and the corresponding CISD calculation. As mentioned previously, the full valence CIS results were found to differ little from the RPA results, thus justifying a comparison between RPA and CISD calculations in order to estimate the importance of doubly excited configurations in the description of the excited states.

To obtain a qualitative assessment of the situation, the following abbreviated study was performed: It was established that the general features of the hexaammine complex, distorted to D_3 geometry to represent a "truncated" bidentate ligand, closely resemble the features of the tris(diamino) complexes. The general features of the HF ground state and the RPA spectra are indeed very similar. A "modified" RHF/LFCI with single and double substitutions was then performed, where the configuration reference space contained the eight molecular orbitals, which give rise to the leading terms in the RPA excited-state vectors. Since the RPA state vectors contain more terms involving a larger reference space, the predicted excitation energies cannot be compared directly; however, a trend toward a relative lowering of the T_{2g} parentage excitations with respect to the T_{1g} parentage excitations should be quite obvious even at this level.

The predicted spectra are summarized in Table VII. The CISD vectors for the states of T_{1g} parentage contained no double excitations. Both the A_2 and the E states are high compared to the corresponding RPA results, which is to be expected from the much smaller reference space. The A_2/E splitting is larger at the CISD level, which is not surprising. The use of a smaller reference space would be expected to effect excitations of different symmetry differently.

More importantly, the A_1 excitation of T_{2g} parentage is lowered compared to the value obtained with the full valence space RPA calculation, despite the use of a much smaller configuration reference space. The CISD vector contains four doubly excited terms, whose coefficients are around 0.2 (compared to the singles coefficients of 0.45). This admixture of doubly excited states accounts for the energy lowering, as was expected on the basis of the electrostatic interaction expressions. These results permit the conclusion, that contributions from two electron excitations cannot be neglected in the representation of the T_{2g} excitations, and that their neglect probably accounts for most of the error in the RPA approximation.

Discussion

We have demonstrated that the chirospectral features associated with the magnetic dipole allowed "d → d" transitions in transition metal complexes can be discussed meaningfully at the level of RHF/RPA theory.

Several assumptions are inherent in the calculations at the RPA level. The excited states are represented as superpositions of single excitations from some suitable single determinant representation of the ground state. As we have demonstrated in the previous section, this representation of the excited states in terms of configurations from the reference space of one electron excitations is not always correct. Also, no provision for orbital relaxation upon excitation is made. It has been argued[38] that the error associated with the neglect of orbital relaxation is probably small for the class of compounds of interest here. At the level of theory which is discussed here, it is usually assumed that the effects of dynamical correlation are of comparable importance for all states under consideration. Any error arising from this assumption is probably small compared to errors induced by truncating the configuration reference space and by neglecting orbital relaxation.

The RPA method was shown to be quite accurate for those cases, where truncation of the configuration reference space at the level of one electron excitations was demonstrated to be acceptable by means of classical ligand field arguments. The feature which makes the RPA method particularly interesting for the study of optical activity is that it was developed specifically for the correct description of excitation properties correct to first order, i.e. with consideration of ground-state correlation.[15] The successful application to the cases treated here should encourage similar investigations with a slightly more general computational approach. Unfortunately, the currently available implementations of the RPA procedure, RPAC 8.6[26] and 9.0, are limited to systems with a closed-shell ground state. In order to be used routinely for the study of chiral transition metal complexes, any candidate method would have to be generalized to account for open-shell cases, as well as make provision for the inclusion of double excitations in the configuration reference space.

With regard to fitting our work into the domain of commonly accepted ideas, the most unexpected and possibly controversial aspect is the deviation from the representation of the complex's molecular orbitals in terms of predominantly metal orbitals and ligand orbitals, with nothing between. It has long been recognized that the vacant e_g orbitals do contain some slight admixture from ligand lone pair orbitals. Strong interactions between ligand valence orbitals and occupied metal d orbitals on the other hand, were thought to occur only for the case of back-donation to π-acceptor ligands, of which the amino ligand is not an example.

The observed orbital mixing is not so disturbing if one considers the large number of occupied orbitals with very similar orbital energies, which are present in these systems. The SCF wave function of $[Co(en)_3]^{3+}$ contains 41 valence orbitals which span an orbital energy range of only 0.7 au. Considering that, for D_3 geometry, they fall into only three symmetry types, a significant amount of interaction due to near accidental degeneracy would seem almost inevitable. The narrow energy range into which the resulting occupied MO's with high metal character fall indicates that the interactions with the ligand orbitals are weak, or in the

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(38) Vanquickenborne, L. G.; Hendrickx, M.; Postelmans, D.; Hyla-Kryspin, I.; Pierloot, K. *Inorg. Chem.* **1988**, *27*, 900.

terminology of the SFG approach,[4] that the overlap between the A^{inner} and A^{outer} portions of the extended chromophore is weak.

The observation that the occupied d orbitals delocalize in the molecular environment is not unique to any one ligand, geometry, or basis set, as it persists in almost unchanged form for all the systems which were included in this investigation, including the "octahedral" hexaammine complex. It is important to appreciate that the degree of delocalization which is present in the canonical HF orbitals is not a direct index for any observable quantity; indeed, the structure of the MO's taken by itself contains relatively little information. Since in the RPA, the excitation properties are computed in the basis of the canonical HF orbitals, it is necessary to examine the MO's to avoid calculations in a deficient valence space, as well as to aid in the interpretation of the resulting representation of the excited states.

The characterization of the extended chromophore was based solely on the structure of the transition density, not on the structure of the canonical MO's.

It now must be considered how the results of the delocalized calculations presented here can be reconciled with the classical interpretation of the spectroscopic properties of the complexes. Since the energy separation between the MO's which result from the near degeneracy interactions is small, and their contributions to the excitations correlate with their d orbital content, the effect on the excitation energies should be minor by comparison to models where the occupied d orbitals are assumed to be truly noninteracting. There could be a slight decrease of the relaxation of electron–electron repulsions which accompany the excitations. In the language of ligand field theory, this would result in a small decrease of the *B* parameter. The electric dipole strengths and consequently the rotatory strengths would be affected strongly due to the steric distribution of the effective chromophore in the delocalized description.

It may be useful to connect our results to some of the mechanisms proposed in previous efforts to account for the observed optical activity. Although our work was not specifically aimed at distinguishing between various models which have been considered in the past, some conclusions can be reached regardless.

Several mechanisms to account for the required ungerade character have been considered before: The "bent bond" mechanism introduced by Liehr[34] induces ligand character in the occupied t_{2g} orbitals by an angle of mismatch between the lone pairs on the ligating atoms and the octahedral axis. This model implies significant distortion of the immediate electronic environment of the Co away from octahedral symmetry. The steric distribution of the transition density which was obtained at the RPA level does not support such a mechanism.

The dynamic coupling ligand polarization model proposed by Mason and Seal[39] accounts for the ungerade character by coupling of the d → d transitions with higher energy electric dipole allowed transitions on the hydrocarbon portion on the ligand. Although our work was not aimed directly at distinguishing different coupled chromophore mechanisms, it did not supply any evidence to confirm such a mechanism. The largest contribution to the electric transition moments seems to be provided by the σ-bonds around the ligating nitrogen atoms in the case of the diamino ligands. In addition, the rotatory strengths obtained from the "truncated" hexaammine complex were slightly greater than the ones reported for $[Co(en)_3]^{3+}$, indicating that any contribution from the hydrocarbon portion of the ligand must be minor.

Although our work was not aimed at deriving a suitable ansatz for a rigorous independent systems (or coupled chromophore) approach, some conclusions about the applicability of the basic ISP ideas to the problem of optical activity in transition metal complexes evolved indirectly from our result. In light of the distribution of the effective dipole chromophore over the bonds surrounding the ligating atoms, the question arises as to whether the division or the extended chromophore into the required achiral chromophore and chiral surroundings can be made in any clear-cut manner.

The inability of the simple ISP model to account for overlap between the A and C subsystems seems to be largely eliminated by Schipper's recent extension of the perturbation approach to include electron exchange terms.[4] An examination of the charge rearrangement densities which accompany the excitations clearly indicates a movement of charge which would correspond to Schipper's "dative" MLET and LMET terms in the ISP/dative formalism. The delocalization of the MO's over the subsystem A^{inner} and A^{outer} which would result from a mapping of the dative contributions to the effective extended chromophore onto a canonical basis is clearly present in our results. Our results clearly support the possibility that the ISP/dative formalism might be a useful approach in investigating problems of this type. Indeed, the distribution of the effective dipole chromophore which we find in our work indicates that such a dative analysis is required for the qualitatively correct description of the extended chromophore in any ISP formalism. However, the tripartite division of the system into A^{inner}, A^{outer}, and C portions, where the dative terms transfer electrons between the A^{inner} and A^{outer} regions and the purely ISP "excitonic" terms couple the A and C portions, might be difficult to carry out in systems of the type studied here. The completely delocalized results presented here do not provide a precise guide as to how this division should be carried out. The breakdown of the gross transition density into contributions by atom suggests that the bonds surrounding the directly ligating atom provide most of the effective dipole chromophore; thus the A^{outer} portion of the chromophore would need to extend past the first coordination sphere.

Examination of our calculated charge rearrangement densities raises the question as to whether any portion of our rather small ligands can be assigned to a C portion of the system, which by definition is not involved in electron transfer with the rest of the system. The calculations consistently show that the cobalt loses electron density as expected with an increase in electronic charge in all portions of the ligands upon excitation, except the amine hydrogens which lose charge. Since the gain in electron density in the hydrocarbon portion of the ligand is approximately twice the amount lost by the amine hydrogens, it is difficult to see how a C portion could be defined.

Conclusions of a more definite nature would be possible if more systems were to be examined with both delocalized and localized RPA theory, and some actual calculations using the ISP/dative formalism were carried out.

Since ab initio methods and computational capacity have reached a point where their application to transition metal compounds can be considered routine, we feel that it would be worthwhile to explore optical and chiroptical properties of transition metal complexes by means of different ab initio methods to obtain the insight necessary to propose more economical means of arriving at them.

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[39] Mason, S.; Seal, R. *Mol. Phys.* **1976**, *31*, 755.