

CD Spectra of Polynuclear Complexes of Diimine Ligands: Theoretical and Experimental Evidence for the Importance of Internuclear Exciton Coupling

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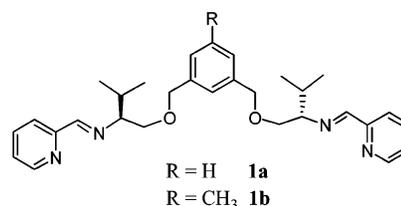
Abstract: We have recently reported on dinuclear complexes Λ, Λ -[Co₂L₂Cl₂](CoCl₄) of two novel chiral ligands (**1a** and **1b**) which contain pyridyl-imine chelate groups (Telfer, S. G.; Sato, T.; Kuroda, R. *Chem. Commun.* **2003**, 1064–1065). The absolute configuration of the cobalt(II) centers was unambiguously assigned by X-ray crystallography. However, the sign of the exciton couplets in their CD spectra was opposite to that expected on the basis of the stereochemistry of the metal centers. We present a rationalization of these anomalous spectra in terms of an “internuclear” exciton coupling model which takes into account the coupling of chromophores located on *different* metal centers. We have performed a series of semiempirical (ZINDO) calculations which provide quantitative support to this model. These findings show that the absolute configuration of the metal centers in a polynuclear complex may be incorrectly assigned on the basis of CD data if internuclear coupling effects are not taken into consideration. We summarize the CD spectral data of number of other chiral polynuclear complexes from the literature, including dinuclear complexes bridged by the 2,2'-bipyrimidine ligand, complexes of the HAT ligand, and dinuclear triple-stranded helicates. The amplitude of the CD spectra of many of these complexes is not additive with the number of chromophores. These anomalous spectra can be accounted for by taking internuclear coupling effects into consideration.

Introduction

The stereochemistry of coordination compounds, though long investigated,¹ has undergone something of a renaissance in recent years.^{2–4} Given their central role in coordination chemistry,^{5,6} it comes as no surprise that diimine ligands such as 2,2'-bipyridine (bipy) and 1,10-phenanthroline (phen) have been at the forefront of this field.^{7,8} It is well established that if multiple diimine chelates are coordinated to an octahedral metal center, characteristic split Cotton effects appear in the CD spectrum due to exciton coupling of their degenerate ligand-centered π - π^* transitions.^{9–11} For example, enantiopure [Ru(bipy)₃]²⁺

produces an intense bisignate curve centered around 280 nm (see Chart 1). A well established rule relates the sign of this curve with the absolute configuration of the metal center. Given this straightforward correlation, circular dichroism (CD) spectroscopy has become the method of choice for the assignment of the absolute configuration of complexes of diimine ligands.

We have recently reported on the synthesis and coordination chemistry of ligands **1a** and **1b** which contain diimine chromophores.^{12,13} Upon reaction with CoCl₂, these ligands form dinuclear complexes [Co₂L₂Cl₂](CoCl₄), and we were able to solve the X-ray crystal structures of both complexes. In both



of these dinuclear complexes, the two metal centers were unambiguously identified as having the Λ configuration. Thus,

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- (1) For example, see: Alfred Werner's 1913 Nobel lecture (<http://www.nobel.se/chemistry/laureates/1913/werner-lecture.html>) or translations of some selected papers on the topic of stereochemistry in Kauffman, G. B. *Classics in Coordination Chemistry Part I*; Dover Publications: New York, 1968.
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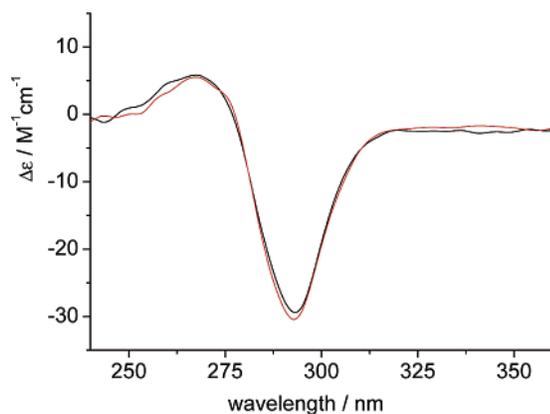


Figure 1. The CD spectra of Λ,Λ -[Co₂(**1a**)₂Cl₂](CoCl₄) (black) and Λ,Λ -[Co₂(**1b**)₂Cl₂](CoCl₄) (red) recorded in CH₃CN.

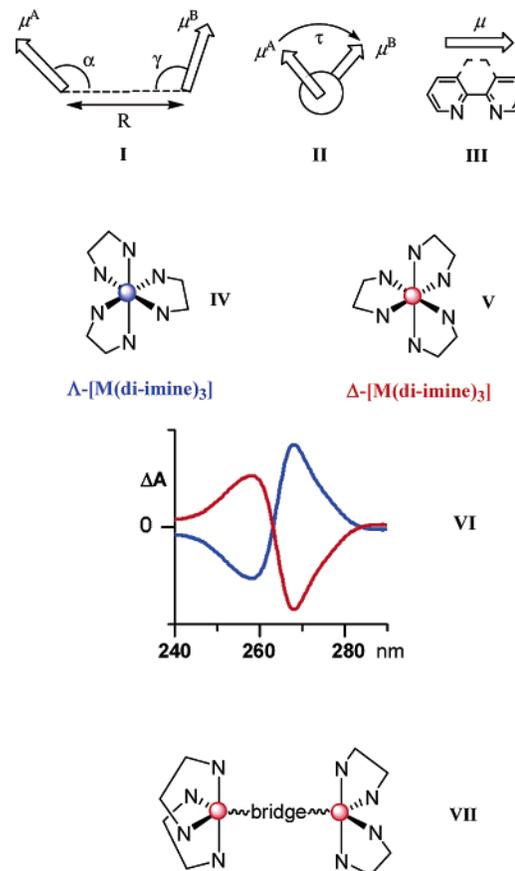
we were surprised to observe that the CD spectrum of this complex displays an exciton couplet in the region of the diimine π - π^* transition which is negative at lower energy (Figure 1). A CD curve with this sign is usually associated with metal centers having the Δ configuration.¹⁴ In the present report, we would like to present a rationalization of these anomalous CD spectra. This rationalization is based on a qualitative analysis of the spectra in terms of exciton theory and on semiempirical calculations. We then extend this analysis to the CD spectra of other polynuclear complexes of diimine ligands which have appeared in the literature.

Background

When three bidentate ligands such as bipy or phen coordinate to an octahedral metal center, the resulting complex is chiral. Despite their close spatial proximity in the complex, there is no charge transfer (electron exchange) between these ligands. However, the ligands are not completely insulated from one another: through-space Coulombic interactions between their large electric dipole transition moments mean that a single photon can cause all three chromophores to be excited.⁹ This is termed exciton coupling.^{15,16}

The sign and intensity of the Cotton effects arising from the exciton coupling of two degenerate transitions are determined solely by the magnitude and relative geometry of their transition dipole moments.^{11,16} The relative geometry of two transition dipole moments μ^A and μ^B can be defined by the angles α , γ , and τ and the distance between them, R (**I** and **II** in Chart 1). The transition moment of the lowest energy π - π^* transitions of the ligands bipy and phen is aligned along the long axis, as shown by **III**. For [M(diimine)₃]²⁺ complexes, the relative disposition of the ligands (and hence their transition moments) is well-defined due to the structural rigidity imposed by the metal center. The transition moments of the three ligands can couple in three different modes, and it can be shown a priori that the net effect of these coupling modes will be a split bisignate CD curve.¹¹ Importantly, the energy ordering of the

Chart 1



positive and negative Cotton effects is directly related to the absolute configuration of the metal center.

Typical CD spectra of Λ -[M(diimine)₃]²⁺ and Δ -[M(diimine)₃]²⁺ complexes (**IV** and **V**, respectively, M = Fe^{II} and Ru^{II}, e.g.) in the region of their lowest-energy π - π^* transitions are depicted schematically in **VI**. These spectra exhibit archetypal exciton couplets, viz closely spaced Cotton effects of opposite sign and approximately equal intensity. As expected for a pair of enantiomers, there is a mirror-image relationship between the CD curves of the Δ and Λ complexes.

The above summary pertains to mononuclear complexes. We term this type of exciton coupling (between chromophores located on the *same* metal center) as *intranuclear exciton coupling*. In polynuclear complexes (**VIII**), there is potentially another mode of coupling, that between chromophores located on *different* metal centers. We term this latter exciton interaction as *internuclear exciton coupling*, and this represents the central focus of the present paper.

The strength of internuclear exciton coupling will be dependent on the same geometrical and transition dipole strength factors as discussed above, however the following points are of particular significance in this context:

(i) The amplitude of the Cotton effects arising from coupling between two chromophores is inversely proportional to R^2 .¹⁷

(ii) The net CD curve of a compound containing more than two interacting chromophore pairs can be approximated by a summation of the CD intensity arising from the individual exciton couplets; i.e., the spectra should be additive.^{16,18,19}

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There is a large body of literature concerning the CD spectra of stereoisomerically pure polynuclear transition metal complexes.² However, despite the theoretical possibility of long-distance exciton coupling in dinuclear complexes being raised some 35 years ago,²⁰ to the best of our knowledge the present study represents the first analysis of experimental CD spectra within an internuclear coupling framework. The metal ions in the complexes which are discussed in this paper act solely as structural units and are *not* regarded as being integral to the chromophores under investigation. Therefore, the methodology and results outlined in this paper can be directly applied to purely organic systems which contain multiple interacting chromophores. However, it should be noted that the metal centers generally endow a high degree of structural rigidity upon the complexes discussed in this paper. This facilitates exciton coupling analysis as the chromophores are held at fixed distances and in well-defined relative orientations.

Computational Approach and Methods

In the present paper, we describe a computational approach to investigating the CD spectra of the diimine chromophores of transition metal complexes. In order to perform a large number of calculations and to obtain results within a reasonable time frame, we have employed the computationally efficient semiempirical ZINDO-1 method for calculating the excitation energies and rotational strengths of the various chromophores.^{21–28} This method is known to reproduce the excitation energies of organic chromophores with good accuracy and is particularly well-suited to N-heterocyclic compounds.²⁹ For all calculations, we have used models to represent the complexes of interest. In general, these models comprise only the atoms of the actual chromophores, that is we have omitted atoms such as the metal ions and the bridges between the chelate groups. With respect to the former, it has been shown that complexation to a metal center leaves the $\pi-\pi^*$ transition of diimine ligands largely unchanged.³⁰ Also, no attempt has been made to account for solvation effects which may also be important in these systems.³¹ Accordingly, rather than attempting to reproduce the experimentally observed spectra, our focus has been on probing the relative intensities of the various exciton couplets, along with developing a general model for the interaction of diimine chromophores of polynuclear transition metal complexes.

With respect to plots of the calculated CD spectra which are presented in the following sections, for purposes of clarity, we have used *only* the rotational strengths corresponding to the long-axis polarized $\pi-\pi^*$ transitions of the chromophores of interest. It should be emphasized that in reality spectra will be considerably more complicated due to CD intensity arising from other transitions. For reference, all calculated rotational strengths are listed in the Supporting Information.

The theoretical CD spectra in this paper have been calculated from the theoretical excitation energies and rotational strengths via well established procedures.³² Assuming a Gaussian function for the spectrum profile of a single electronic transition, the CD intensity $\Delta\epsilon_{0a}$, arising from a $|0\rangle \rightarrow |a\rangle$ transition, can be expressed using the rotational strength R_{0a} and the excitation energy E_{0a} as³³

$$\Delta\epsilon_{0a}(E) = 2.457 \times 10^{38} R_{0a}(E_{0a}/\sigma) \exp[-((E - E_{0a})/\sigma)^2] \quad (1)$$

where $\Delta\epsilon_{0a}$ and R_{0a} are expressed in the units of $M^{-1} \text{ cm}^{-1}$ and cgs, respectively. The overall CD curve is obtained by superimposing contributions from the individual electronic excitations,

$$\Delta\epsilon(E) = \sum_a \Delta\epsilon_{0a}(E) \quad (2)$$

The parameter σ in eq 1 represents the width of the Gaussian function (half of the $1/e$ width). We have used a value of $\sigma = 0.18 \text{ eV}$ throughout this paper and have plotted the calculated spectra as a function of wavelength (rather than directly as a function of E).

The excitation energies and the rotational strengths have been calculated using the ZINDO-1 method implemented in the Gaussian98 program.³⁴ All the possible one-electron excitations from the ground-state configuration were allowed in the ZINDO-CI calculations. The actual calculation of the rotational strengths used the imaginary part of the scalar product of the magnetic dipole and the electric dipole transition moments according to the theory of Rosenfeld,³⁵

$$R_{0a} = \text{Im}[\langle 0 | \boldsymbol{\mu} | a \rangle \cdot \langle a | \boldsymbol{m} | 0 \rangle] \quad (3)$$

where $\boldsymbol{\mu}$ and \boldsymbol{m} are the electric dipole and magnetic dipole operators, respectively. Two types of representations are possible for the electric dipole moment, i.e. the length form and the velocity form,

$$\begin{aligned} \langle 0 | \boldsymbol{\mu} | a \rangle &= -e \cdot \langle 0 | \boldsymbol{r} | a \rangle \\ &= -e(\hbar^2/m_e) \cdot \langle 0 | \nabla | a \rangle / E_{0a} \end{aligned} \quad (4)$$

where \boldsymbol{r} and ∇ are sums over electrons of the position and gradient operators, respectively. We have employed the velocity form representation since this gives better coordinate-origin independence of the rotational strengths.

The geometries of the chromophore systems will be described in the later sections. In all cases, planarity of the chromophores was imposed to eliminate any CD signals which might arise due to the chiral conformations of the individual chromophores, and the Coordinate files for all model systems are provided as Supporting Information. Where necessary, geometry optimizations of individual chromophores were performed using density functional theory with the B3LYP functional³⁶ with the cc-pVDZ basis set.³⁷

Results and Discussion

CD Spectra of Λ, Λ -[Co₂L₂Cl₂]²⁺ (L = 1a, 1b) Complexes.

The complexes Λ, Λ -[Co₂L₂Cl₂]²⁺ (L = 1a, 1b) both display

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Table 1. Important Geometrical Parameters for the Pyridyl-Imine Chromophore Pairs in the Λ, Λ -[Co₂(**1a**)₂Cl₂]²⁺ Complex and Qualitative and Quantitative Predictions of the CD Intensity Arising from the Exciton Coupling of These Chromophore Pairs^a

	AB	AC	AD	
Geometrical Parameters^b				
chromophore separation (Å)	5.09	6.85	7.32	
α (deg)	89.2	51.3	87.7	
γ (deg)	88.6	52.8	85.0	
τ^c (deg)	133.0	46.8	249.3	
Qualitative Predictions Based on Exciton Theory				
sign of lower energy band	positive	negative	negative	
sign of higher energy band	negative	positive	positive	
Quantitative Predictions Based on ZINDO Calculations^d				
lower E band	wavelength (nm)	273.8	279.8	273.8
	rotational strength (au)	0.576	-0.396	-0.808
higher E band	wavelength (nm)	272.9	275.3	273.4
	rotational strength (au)	-0.450	0.298	0.761

^a The inter-chromophore vector is defined as a line connecting the respective C_{imine} atoms, and the electric dipole transition moment was presumed to lie along the C_{imine}-C_{2-pyridyl} bond. ^b Chromophore separation defined the distance between the midpoints of the C_{imine}-C_{2-pyridyl} bonds. ^c Defined with respect to **II** (Chart 1). ^d 1 au = 2.357 × 10⁻³⁸ cgs.

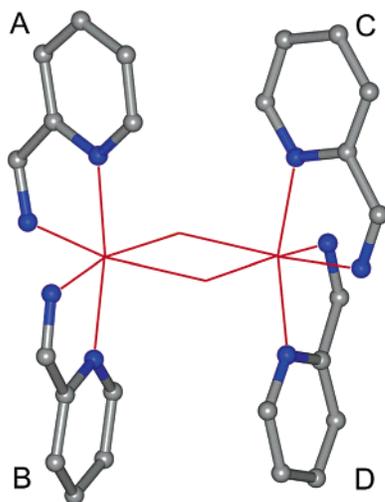


Figure 2. Model chromophore system used for the analysis of the CD spectra of the Λ, Λ -[Co₂L₂Cl₂]²⁺ complexes (L = **1a**, **1b**). The red lines indicate the bonds to the (omitted) cobalt(II) centers and the bridging chloride ions. H atoms have been omitted for clarity. Blue, nitrogen; gray, carbon.

an intense absorption band around 280 nm which corresponds to the lowest energy π - π^* transition of their four pyridyl-imine chromophores. The electric dipole transition moment of this transition is oriented along the C_{2-pyridyl}-C_{imine} bond, analogous to the long-axis polarized transition in 2,2'-bipyridine (**I**). In the CD spectra of these complexes, intense signals are observed in the region 250–320 nm which arise from exciton coupling of these transitions. The arrangement of the four chromophores of Λ, Λ -[Co₂(**1a**)₂Cl₂]²⁺ is depicted in Figure 2. Although the analysis of the CD spectra of polynuclear complexes typically focuses on the exciton coupling of ligands located on the same metal center, the close spatial proximity of the chromophores located on different metal centers (Table 1) suggests that *internuclear* coupling should also be taken into account.

There are three distinct exciton coupling modes for the four chromophores of the Λ, Λ -[Co₂L₂Cl₂]²⁺ complexes: AB (intranuclear), AC and AD (both internuclear). The qualitative application of exciton theory indicates that both internuclear exciton couplets (AC and AD) will produce CD curves which are *negative* at lower energy (Table 1). On the other hand, the intranuclear couplet (AB) will lead to a CD curve which is *positive* at lower energy (as expected for the arrangement of

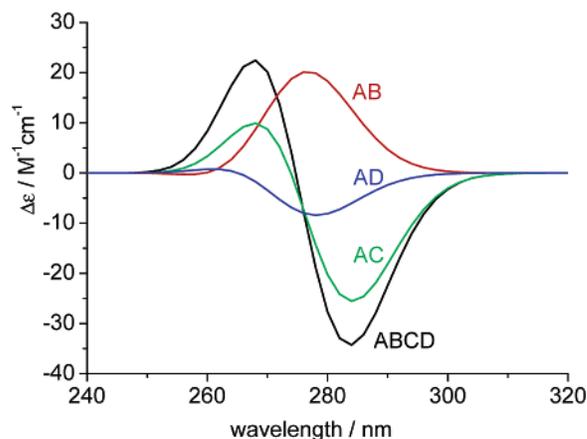


Figure 3. CD spectra calculated for the ABCD chromophore system (black), along with the CD curves calculated for the individual AB (red), AC (green), and AD (blue) chromophore pairs.

diimine chromophores around a metal center of the Λ configuration; see **IV** in Chart 1). The observed CD spectrum of Λ, Λ -[Co₂L₂Cl₂]²⁺ will be (approximately) a sum of these three individual exciton contributions. Thus, the shape of the observed spectrum will depend crucially upon the *relative intensity* of the individual exciton coupling contributions. We have used a computational approach to determine these intensities, as described in the following sections.

A series of semiempirical ZINDO calculations on the ABCD chromophore system (Figure 2) has been performed. The atomic coordinates of this model system were based on the X-ray crystallographic data for Λ, Λ -[Co₂(**1a**)₂Cl₂] (CoCl₄), though the individual chromophores were made planar so as to be in achiral conformations. The overall arrangement of the chromophores has approximate *D*₂ symmetry. The lowest energy π - π^* transition of an isolated chromophore was predicted to occur at 273.7 nm and be energetically well separated from other transitions.

First, the Cotton effects arising from the three chromophore pairs (AB, AC, and AD) were calculated individually. The calculated rotational strengths are listed in Table 1, and the predicted CD curves are shown in Figure 3. For all three chromophore pairs, the lowest energy π - π^* transition gives rise to an exciton couplet around 273 nm, viz a pair of energetically close rotational strengths which are similar in magnitude but opposite in sign. The energy ordering of these

rotational strengths was found to be different for the internuclear and intranuclear couplets. The results are in full accord with the qualitative predictions made above and, moreover, show that all three coupling modes should make significant contributions to the observed spectrum.

It may seem curious that the CD curves calculated for the AB and AD pairs are monosigned. This is primarily due to the fact that the oppositely signed rotational strengths are calculated to be very close in energy; i.e., their CD intensity will mostly cancel (see Table 1). Due to the slight imbalance in the magnitude of these two rotational strengths, the expected couplet is eliminated, and a curve corresponding to the stronger component is actually observed. Some similar monosigned curves appear in the following sections for the same reasons. Bisignate curves can be obtained by employing a very small value for the bandwidth (σ); however this concomitantly leads to highly distorted spectra with unrealistic $\Delta\epsilon$ values.

The spectrum calculated using the full ABCD chromophore model displays an intense negative Cotton effect with a peak at 285 nm, and a positive component of lesser intensity with a maximum at around 268 nm (Figure 3). Thus, the ZINDO calculations clearly imply that the sign of the CD spectrum of the Λ, Λ -[Co₂L₂Cl₂]²⁺ complexes will be dictated by the internuclear exciton couplets. This accounts for the appearance of a negative exciton couplet in the observed CD spectrum despite the metal centers both having the Λ absolute configuration. These results clearly show that the absolute configuration of the metal centers in a polynuclear complex may be *incorrectly assigned on the basis of CD data if internuclear coupling effects are not taken into consideration*.

Dependence of the CD spectrum on the Inter-Chromophore Separation. The Co...Co distance in the complex Λ, Λ -[Co₂(**1a**)₂Cl₂]²⁺ is 3.54 Å.¹² If the internuclear distance is increased, for example by using alternative bridging ligands, the AB chromophore pair will be further separated from the CD chromophore pair. To investigate the impact which this would have on the CD spectrum, a series of spectra was calculated for a variety of effective internuclear separations. The relative orientation of the chromophores was held fixed. The spectra calculated for the full ABCD chromophore model are presented in Figure 4, while those for the individual AC and AD couplets are presented in the Supporting Information (Figures S1 and S2). In Figure 4, it can be seen that the calculated CD spectrum is extremely sensitive to the distance between the chromophore pairs: the negative band centered around 285 nm dramatically loses intensity if the distance increases by just a fraction of an angstrom. Eventually, the separation of the chromophore pairs leads to the appearance of a positive Cotton effect around 278 nm. These findings are in keeping with intuitive expectations; the separation of the chromophore pairs diminishes the contribution of the internuclear couplets to the overall spectrum; thus the negative band at lower energy disappears, and the spectrum converges to that of the intranuclear couplet.

These results do however suggest that diimine chromophores which are located on different metal centers in complexes of the type [(diimine)₂M(bridge)M(diimine)₂] can interact, albeit weakly, even when the internuclear separation is reasonably large. Accordingly, internuclear exciton coupling effects are expected to contribute to the observed CD spectra of such

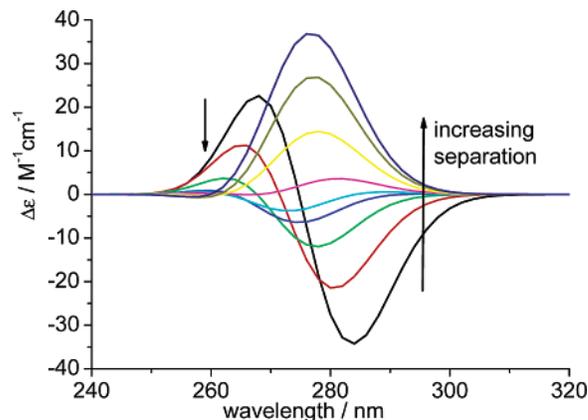


Figure 4. Plot showing the dependence of the calculated circular dichroism spectrum of the ABCD chromophore model system on the distance between the AB and CD chromophore pairs. The effect of internuclear exciton coupling is seen to diminish as the distance between the chromophore pairs is increased. The first spectrum (black curve) was calculated for an effective internuclear separation of 3.54 Å, following which this distance was increased by 0.2, 0.5, 1.0, 1.5, 2.5, 5.0, 10.0, and 20.0 Å.

complexes which feature commonly encountered bridging ligands such as halides, alkoxides, 2,2'-bipyrimidine, oxalate, etc.

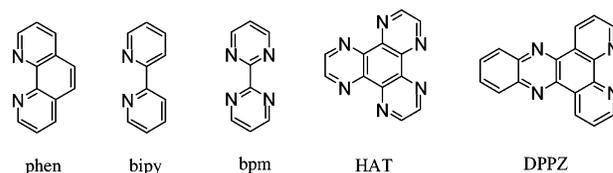
Application of the Internuclear Coupling Model to Polynuclear Complexes Reported in the Literature. There are many examples of stereoisomerically pure complexes of diimine ligands which have appeared in the literature. A large number of these feature octahedral metal centers, and the assignment of their absolute configuration has generally relied on the analysis of exciton coupling effects in their CD spectra.^{2,10,38} Given our above findings, we conducted a literature search to see whether there may be other polynuclear complexes in which internuclear exciton coupling effects are operative. We have focused on three important classes of compound (Chart 2):

(i) Enantiopure complexes of the type [(diimine)₂Ru(bridge)-Ru(diimine)₂]ⁿ⁺ which have two Ru(diimine)₂ units linked by a bridging ligand. Only complexes possessing C₂ symmetry about the bridging ligand were analyzed, i.e., those with two identical Ru(diimine)₂ units.

(ii) Enantiopure complexes of the HAT³⁹ ligand with diimine co-ligands.

(iii) Enantiopure helicates featuring ligands with diimine chelate groups.

Chart 2



(i) Bridged Dinuclear Complexes of the Type [(Diimine)₂-Ru(bridge)Ru(diimine)₂]ⁿ⁺. Octahedral ruthenium(II) complexes are generally kinetically inert thus stable toward racemization. Two [Ru(diimine)₂] units can be linked together to form a dinuclear complex by suitable bridging ligands, and a large number of such complexes have also been isolated in a

(38) Keene, F. R. *Chem. Soc. Rev.* **1998**, *27*, 185–193.

(39) HAT = 1,4,5,8,9,12-hexaazatriphenylene.

Table 2. CD Spectral Data Reported in the Literature for a Selection of Stereoisomerically Pure Mono- and Dinuclear Ruthenium(II) Complexes Containing Diimine Ligands^a ($A = \Delta\epsilon_2 - \Delta\epsilon_1$ ($M^{-1} \text{ cm}^{-1}$))

	λ/nm ($\Delta\epsilon_1$)	λ/nm ($\Delta\epsilon_2$)	A	ref
Complexes of phen and bipy				
Δ -[Ru(phen) ₂ (pyridine) ₂] ²⁺	259 (50)	269 (-110)	-160	40
Λ -[Ru(phen) ₂ (bipy)] ²⁺	260 (-250)	273 (185)	+435	41
Λ -[Ru(bipy) ₂ (phen)] ²⁺	266 (-110)	294 (243)	+353	41
Δ -[Ru(bipy) ₂ (phen)] ²⁺	265 (82)	291 (-209)	-291	42
Λ -[Ru(phen) ₂ DPPZ] ²⁺	254 (-178)	267 (363)	+541	43
Complexes of bpm				
Δ -[Ru(phen) ₂ bpm] ²⁺	256 (143)	267 (-243)	-386	44
Δ, Δ -[(phen) ₂ Ru(bpm)Ru(phen) ₂] ⁴⁺	258 (64)	295 (-43)	-162	42
		281 (-98)		
		295 (-108)		
Λ, Λ -[(phen) ₂ Ru(bpm)Ru(phen) ₂] ⁴⁺	259 (-55)	281 (90)	+145	42
		295 (94)		
		278 (-111)		
Δ, Δ -[(Me ₂ bipy) ₂ Ru(bpm)Ru(Me ₂ bipy) ₂] ⁴⁺	256 (65)	278 (-111)	-176	45
Λ, Λ -[(Me ₂ bipy) ₂ Ru(bpm)Ru(Me ₂ bipy) ₂] ⁴⁺	256 (-53)	278 (109)	+162	45
Δ -[Ru(2)bpm] ²⁺	284 (35)	301 (-97)	-132	46
Δ, Δ -[(2)Ru(bpm)Ru(2)] ⁴⁺	280 (29)	299 (-112)	-141	46
Complexes of Ligands 3–8				
Λ -[(phen) ₂ Ru(3)] ²⁺	257 (-120)	268 (235)	+355	47
Λ, Λ -[(phen) ₂ Ru(3)Pd(3)Ru(phen) ₂] ⁶⁺	257 (-245)	268 (470)	+715	47
Λ -[(bipy) ₂ Ru(4)] ²⁺	271 (-165)	290 (251)	+416	48
Λ, Λ -[(bipy) ₂ Ru(5)] ⁴⁺	271 (-162)	290 (419)	+581	48
$\Lambda, \Lambda, \Lambda$ -[(bipy) ₂ Ru(6)] ⁶⁺	272 (-231)	291 (569)	+800	48
Λ, Λ -[(phen) ₂ Ru(7)Ru(phen) ₂] ⁴⁺	255 (349)	270 (-285)	-634	49
Δ, Δ -[(phen) ₂ Ru(7)Ru(phen) ₂] ⁴⁺	255 (-370)	270 (327)	+697	49
Λ, Λ -[(phen) ₂ Ru(8)Ru(phen) ₂] ⁴⁺	255 (443)	270 (-510)	-953	49
Δ, Δ -[(phen) ₂ Ru(8)Ru(phen) ₂] ⁴⁺	255 (-520)	270 (539)	-1059	49

^a See Charts 2 and 3 for abbreviations and the numberings of chromophores.

stereoisomerically pure form. For example, von Zelewsky's group has shown that the complex Δ -[Ru(2)bpm]²⁺ can be isolated in a diastereomerically pure form and further converted to the dinuclear complex Δ, Δ -[(2)Ru(bpm)Ru(2)]⁴⁺.⁴⁶ Some CD spectral data for Δ -[Ru(2)bpm]²⁺ and Δ, Δ -[(2)Ru(bpm)Ru(2)]⁴⁺ in the region corresponding to the exciton coupling of the diimine chromophores are presented in Table 2 (see Charts 2 and 3 for the structures of the chromophores). Remarkably, the CD spectrum of Δ, Δ -[(2)Ru(bpm)Ru(2)]⁴⁺ is only marginally more intense than that of Δ -[Ru(2)bpm]²⁺, despite the latter effectively having two enantiopure [Ru(diimine)₃] centers. A similar observation can be made for the CD spectra of Λ, Λ - and Δ, Δ -[(phen)₂Ru(bpm)Ru(phen)₂]⁴⁺, which are less intense than those of the mononuclear Δ -[Ru(phen)₂bpm]²⁺, [Ru(phen)₂(bipy)]²⁺, and [Ru(phen)₂DPPZ]²⁺^{42,43} complexes. In another example, both enantiomers of the complex [(Me₂bipy)₂Ru(bpm)-Ru(Me₂bipy)₂]⁴⁺ (Me₂bipy = 4,4'-dimethyl-2,2'-bipyridine) display CD spectra of approximately the same intensity as their mononuclear precursors.⁴⁵

The CD spectra of these polynuclear complexes are less than the sum of their parts. Can this anomaly be rationalized in terms of an internuclear exciton coupling model? Figure 5 depicts the five chromophores of one member of this family of complexes, Λ, Λ -[(bipy)₂Ru(bpm)Ru(bipy)₂]. The bpm ligand provides a rigid and short bridge between the two metal centers. There is the potential for three distinct exciton coupling modes among

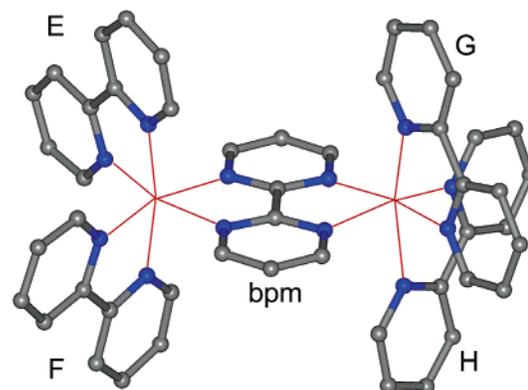


Figure 5. Arrangement of the diimine chromophores in the Λ, Λ -[(bipy)₂Ru(bpm)Ru(bipy)₂] complex. This EFGH-bpm chromophore model system was used for the ZINDO calculations. The red lines indicate bonds to the metal centers. The H atoms have been omitted from this diagram for clarity. Blue, nitrogen; gray, carbon.

the four bipyridyl chromophores: EF (intranuclear), EG and EH (both internuclear). On the basis of exciton theory, the sign of the CD signal arising from the two internuclear couplets is predicted to be *opposite* to that of the intranuclear couplet, a situation similar to the ABCD chromophore set discussed above.

The analysis of exciton coupling between the bipyrimidine bridging ligand and the bipyridine ligands, which is also expected to contribute some intensity to the CD spectrum, is somewhat more complicated due to the fact that the chromophores are nonidentical. The lowest energy π - π^* transition of the bipyrimidine ligand is polarized along its long axis. From a qualitative point of view, we may therefore expect that the phase of the bpm-bipy couplets (E-bpm and F-bpm) will be the same as the bipy-bipy intranuclear couplets and that the two bands will be found close to the transition energies of the two chromophores.^{9,11} However, as the bipy and bpm transitions

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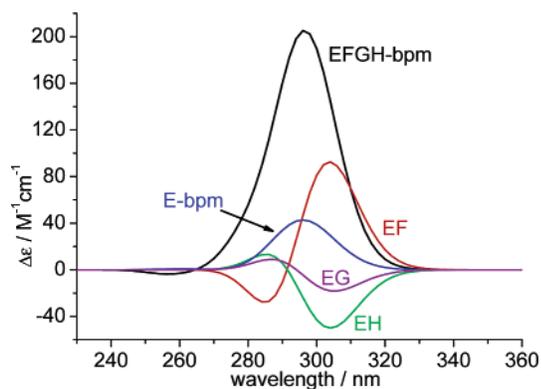


Figure 6. CD spectra calculated for the full EFGH-bpm model system, along with the calculated curves for the individual EF (red), EG (purple), EH (green), and E-bpm (blue) chromophore pairs.

are nondegenerate, the CD intensity arising from bpm–bipy exciton coupling will be inherently weaker than that arising from the EF couplet.⁹

We set about further investigating these dinuclear bpm-bridged systems using the computational approach which had proven successful for our dinuclear cobalt(II) complexes. Our calculations employed the chromophore model system depicted in Figure 5. The geometry of the bipy (planar with C_{2v} symmetry) and the bpm (planar with D_{2h} symmetry) chromophores were optimized independently with the density functional method and then combined to build up the D_2 symmetric model. The effective metal–ligand bond lengths and angles in this model were matched with those of the *meso*-[(Me₂-bipy)₂Ru(bpm)Ru(Me₂bipy)₂]⁴⁺ complex which has been characterized by X-ray crystallography.⁴⁵

The results of the ZINDO calculations in the region of the long-axis polarized transitions of the chromophores are presented in Figure 6. As predicted above on a qualitative basis, the sign of the CD intensity arising from the two internuclear couplets (EH and EG) is opposite to that of intranuclear couplets (EF, E-bpm). The intensities of the internuclear exciton couplets are relatively low, and the overall CD spectrum is dominated by the intranuclear coupling modes. These results demonstrate that the overall sign of the CD spectra of dinuclear bpm-bridged complexes such as [(bipy)₂Ru(bpm)Ru(bipy)₂]⁴⁺ will still reflect the absolute configuration of the metal centers. However, internuclear exciton coupling is predicted to still be significant, and its effect will be to reduce the overall spectral intensity. Thus, these computational results precisely match what is observed experimentally, and we may conclude that an internuclear coupling model offers a rational explanation of the anomalously low intensities of CD spectra of dinuclear bpm-bridged complexes.

A series of calculations was then performed to determine the effect on the CD spectrum of separating the chromophore pair EF from the pair GH. This corresponds to an increase in the effective internuclear separation. The bpm ligand was omitted from the model. Figure 7 shows a plot of the relative amplitude of the exciton couplet as a function of the effective internuclear separation. The first point on the graph represents the model depicted in Figure 5 (minus the bpm ligand) for which the effective internuclear separation was 5.6 Å. When the chromophore pairs are separated, the amplitude of the exciton couplet increases toward a limiting value. This value represents the CD

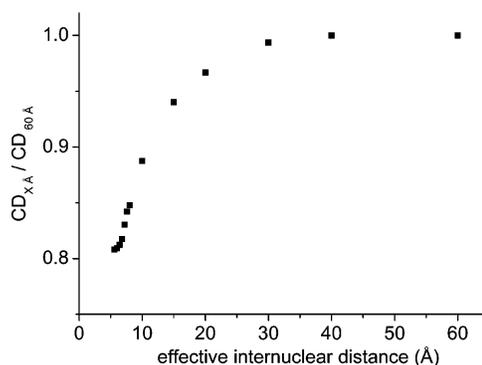
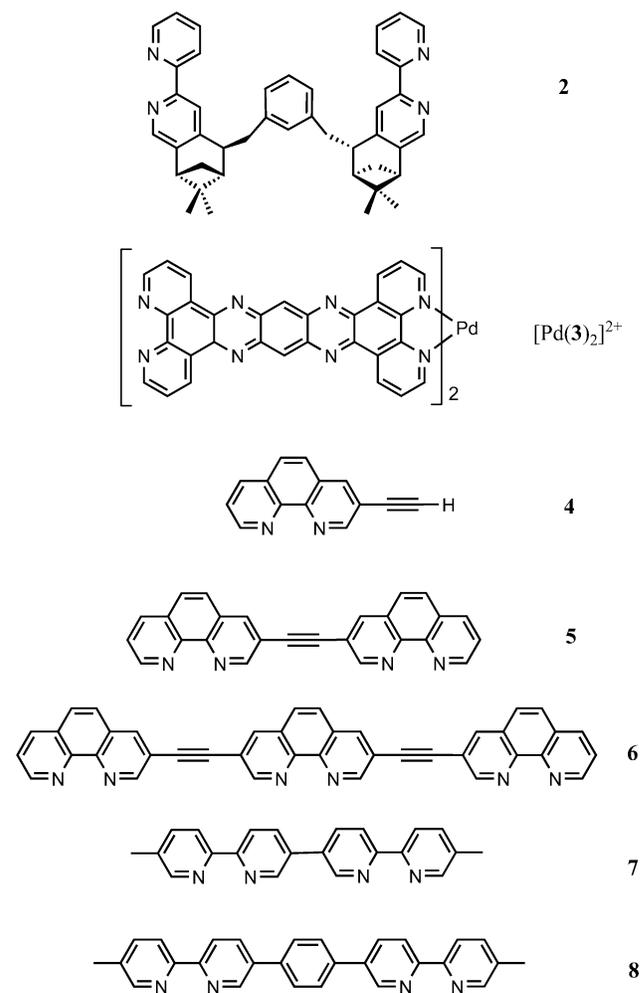


Figure 7. Dependence on the effective internuclear separation of the amplitude of the exciton couplet in the calculated CD spectrum of the EFGH chromophore set. The y axis scale corresponds to the ratio of the amplitude of the exciton couplet calculated at an internuclear separation of X Å to that calculated at 60 Å.

intensity arising from two completely noninteracting “Λ-[Ru-(bipy)₂]” units.

These calculations show that contribution of intranuclear exciton coupling to the CD spectra observed for [(diimine)₂Ru(bridge)Ru(diimine)₂] complexes will be strongly dependent on the length of the bridging ligand, as also predicted by exciton coupling theory. These theoretical results can be compared with experimental CD data for complexes with bridges of various lengths. For example, Lehn’s group has reported on a rigid

Chart 3



rodlike $[(\text{phen})_2\text{Ru}(\mathbf{3})\text{Pd}(\mathbf{3})\text{Ru}(\text{phen})_2)]^{6+}$ complex where the two ruthenium(II) centers are held 35 Å apart by an extended metal-organic exo-ditopic bridging ligand $[\text{Pd}(\mathbf{3})_2]^{2+}$ (Chart 3).⁴⁷ The intensity of the CD spectrum of $[(\text{phen})_2\text{Ru}(\mathbf{3})\text{Pd}(\mathbf{3})\text{Ru}(\text{phen})_2]^{6+}$ is exactly twice that of its pseudo-monomer $[\text{Ru}(\text{phen})_2(\mathbf{3})]^{2+}$ (see Table 2). This observation implies that internuclear exciton coupling effects make a negligible contribution to the observed CD spectrum. This is in complete accord with the computational results presented in Figure 7 which predict that a bridge of this length would preclude measurable internuclear coupling interactions between the $[\text{Ru}(\text{phen})_2(\text{diimine})]$ units.

Stereoisomerically pure polynuclear complexes comprising $[\text{Ru}(\text{bipy})_2]$ units linked by the bis(bidentate) and tris(bidentate) phenanthroline ligands **5** and **6** (Chart 3) have also been reported.⁴⁸ The CD spectra of the complexes $\Lambda, \Lambda - [((\text{bipy})_2\text{Ru})_2 - (\mathbf{5})]^{4+}$ and $\Lambda, \Lambda, \Lambda - [((\text{bipy})_2\text{Ru})_3(\mathbf{6})]^{6+}$ can be compared with their mononuclear analogue $\Lambda - [(\text{bipy})_2\text{Ru}(\mathbf{4})]^{2+}$ (Table 2). For all three complexes, bisignate curves due to the exciton coupling of the $\pi - \pi^*$ transitions of the diimine chromophores are centered around 280 nm. The amplitude of these CD signals as a function of the number of $[\text{Ru}(\text{bipy})_2(\text{diimine})]$ chromophores deviates from linearity; however this deviation is less pronounced than for the bpm-bridged complexes discussed above. Thus, it appears that these complexes represent a case where internuclear exciton coupling has only a moderate impact on the observed CD spectrum. This can be accounted for by the rotational freedom about the acetylene bonds in the ligands **5** and **6**. This will allow the $[(\text{bipy})_2\text{Ru}(\text{diimine})]$ units to rotate with respect to one another; therefore the internuclear coupling will be relatively weak.⁵⁰

$\Lambda, \Lambda - [(\text{phen})_2\text{Ru}(\text{L})\text{Ru}(\text{phen})_2]^{4+}$ (L = **7**, **8**) are further examples of bridged dinuclear complexes wherein internuclear exciton couplings have pronounced effects on the observed CD spectrum. **7** and **8** are very similar ligands which present near-identical bipyridyl chromophores to each $[\text{Ru}(\text{diimine})_3]$ subunit. We may therefore expect that the CD intensity arising from intranuclear exciton coupling will be similar for the complexes of both ligands. The intensity of the CD spectra of these complexes in the region of the lowest energy $\pi - \pi^*$ transition of the bipyridyl chromophores is strikingly different, however, with the spectrum of $\Lambda, \Lambda - [(\text{phen})_2\text{Ru}(\mathbf{8})\text{Ru}(\text{phen})_2]^{4+}$ being far more intense than that of $\Lambda, \Lambda - [(\text{phen})_2\text{Ru}(\mathbf{7})\text{Ru}(\text{phen})_2]^{4+}$. A consideration of internuclear exciton coupling effects shows why this may be so. The *para*-phenylene bridge separating the bipy chelates of ligand **8** will place the two $[\text{Ru}(\text{diimine})_3]$ subunits of $\Lambda, \Lambda - [(\text{phen})_2\text{Ru}(\mathbf{8})\text{Ru}(\text{phen})_2]^{4+}$ further apart than in $\Lambda, \Lambda - [(\text{phen})_2\text{Ru}(\mathbf{7})\text{Ru}(\text{phen})_2]^{4+}$. Consequently, the impact of internuclear exciton coupling effects on the CD spectrum will be far greater for the complex of **7** than for the complex of **8**.

This kind of analysis may also be illuminating for other polynuclear ruthenium(II)–diimine complexes in the literature which exhibit CD spectral intensities which do not scale linearly

with the number of chromophores.^{51–54} It is noteworthy that MacDonnell's group have found that although a linear fit exists between the CD intensity of the MLCT band (500 nm) and the "enantiomeric excess" of Ru(II) stereocenters for a series of polynuclear complexes,⁵² the same is not true for the ligand-centered bands.⁵⁵

(ii) Complexes of the HAT Ligand. A series of complexes containing one, two, or three $[\text{Ru}(\text{phen})_2]$ units chelated around the 3-fold symmetric HAT ligand (Chart 2) has been reported by Keene's group.⁵⁶ All the complexes were prepared stereospecifically by using enantiopure Δ - or Λ - $[\text{Ru}(\text{phen})_2(\text{CO})_2]^{2+}$ as a starting material. The intensities of the CD spectra reported for these complexes is presented in Table 3. It is clear that the observed intensities do not scale in a linear fashion with the number of $[\text{Ru}(\text{phen})_2]$ units. Given the short internuclear separation in these complexes (Ru–Ru distance ca. 6.9 Å), we considered whether internuclear exciton coupling effects may account for this anomaly.

Table 3. CD Spectral Data Reported in the Literature for a Selection of Stereoisomerically Pure Mono- and Dinuclear Ruthenium(II) Complexes of the HAT Ligand⁵⁶ ($A = \Delta\epsilon_2 - \Delta\epsilon_1$ ($\text{M}^{-1} \text{cm}^{-1}$))

	λ/nm ($\Delta\epsilon_1$)	λ/nm ($\Delta\epsilon_2$)	A
$\Delta - [((\text{phen})_2\text{Ru})(\text{HAT})]^{2+}$	254 (150)	264 (−186) 294 (−118)	−336
$\Delta, \Delta - [((\text{phen})_2\text{Ru})_2(\text{HAT})]^{4+}$	255 (304)	270 (−210) 296 (−257)	−514
$\Delta, \Delta, \Delta - [((\text{phen})_2\text{Ru})_3(\text{HAT})]^{6+}$	259 (336)	278 (−220) 295 (−236)	−556

A model (with D_3 -symmetry) depicting the chromophores present in the trinuclear $\Lambda, \Lambda, \Lambda - [((\text{diimine})_2\text{Ru})_3\text{HAT}]^{6+}$ complex is presented in Figure 8. The rigidly fixed orientations of the chromophores allow a qualitative analysis of the internuclear coupling based on the relative orientation of the electric dipole transition moments. For the mononuclear complex, $\Delta - [(\text{phen})_2\text{Ru}(\text{HAT})]^{2+}$, there are three potential intranuclear exciton couplets: IJ, I-HAT, and J-HAT. These will be of the same phase but will occur at different energies, as discussed above for the bipy/bpm chromophore set. Upon formation of the dinuclear complex, $\Delta, \Delta - [((\text{phen})_2\text{Ru})_2\text{HAT}]^{4+}$, naturally there will be a doubling of the number of intranuclear couplets to six. Concomitantly, four internuclear exciton coupling modes will be switched on, namely two pairs of degenerate couplets: IL and JK, and IK and JL. The CD intensity arising from these couplets will be of opposite sign to the intranuclear couplets. This may be the basis of the nonadditivity of the intensities of the CD spectra of the mono- and dinuclear complexes. The addition of a third $[\text{Ru}(\text{phen})_2]$ unit increases the number of intranuclear couplings to nine, while the total number of intranuclear modes trebles to twelve. Thus, the relative contribution from the internuclear coupling modes to the overall CD

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(50) If there is completely free rotation about these bonds, the internuclear exciton coupling would drop to zero due to averaging of all possible relative alignments of the "internuclear" transition moments (see: Tinoco, I., Jr. *Adv. Chem. Phys.* **1961**, *4*, 113–160). This is unlikely to be the case, however, and certain rotational conformations will probably be favoured, in which case internuclear exciton coupling will still contribute to the observed CD spectrum.

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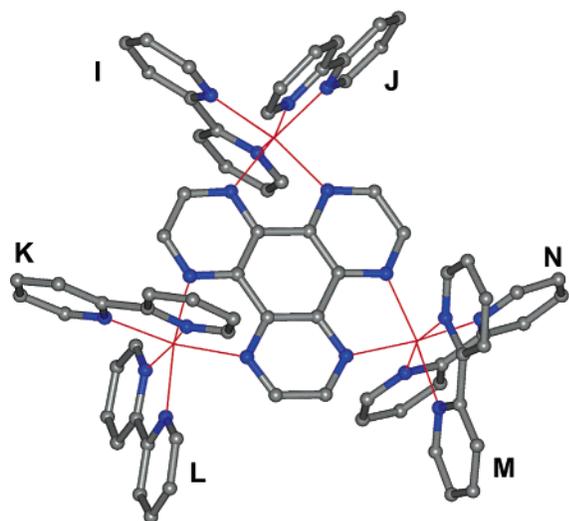


Figure 8. Model depicting the arrangement of the diimine chromophores in a $\Lambda, \Lambda, \Lambda$ -[((diimine)₂Ru)₃HAT]⁶⁺ complex. The red lines indicate bonds to the metal centers. All H atoms have been omitted for clarity.

intensity will be much greater for the trinuclear complex than the dinuclear complex, accounting for their similar experimentally observed amplitudes.

(iii) Dinuclear Helicates and Related Complexes. Transition metal helicates are intrinsically chiral, and several have been isolated in a stereoisomerically pure form.^{57,58} Lacour's group has shown that the dinuclear triple-stranded helicate [Fe₂(**9**)₃]⁴⁺ (Chart 4) can be resolved into its enantiomers with chiral phosphorus(V)-based TRISPHAT anions.⁵⁹ The CD spectrum of enantiopure Δ, Δ -[Fe₂(**9**)₃]⁴⁺ was recorded, and the data are presented in Table 4 along with those for its mononuclear analogue Δ -[Fe(bipy)₃]²⁺. For both complexes, a bisignate curve centered around 295 nm was observed which can be ascribed to exciton coupling of the lowest energy π - π^* transitions of the diimine chromophores. A comparison of the intensities of the peaks reveals that the CD spectrum of Δ, Δ -[Fe₂(**9**)₃]⁴⁺ is weaker than that of Δ -[Fe(bipy)₃]²⁺, despite the former effectively having two enantiopure [Fe(diimine)₃] centers.

The rigidity of the [Fe₂(**9**)₃]²⁺ helicate ensures that the diimine chromophores are fixed in a certain relative orientation. We performed a series of ZINDO calculations on the chromophore model presented in Figure 9 which comprises two Δ -[Fe(bipy)₃]²⁺ subunits (OPQ and RST). This model was constructed by manually positioning the planar bipy chromophores (geometry individually optimized with DFT) to give the *D*₂ symmetric arrangement. Parameters such as the effective metal–metal distance (7.65 Å) and the relative orientation of the two [Fe(bipy)₃] subunits were matched with those obtained by X-ray crystallography for the Δ, Δ -[Fe₂(**9**)₃]⁴⁺ cation of *rac*-[Fe₂(**9**)₃]⁴⁺.⁶⁴

Table 4. CD Spectral Data for a Selection of Helicates with Diimine Ligands and Related Complexes Which Have Been Reported in the Literature^a ($A = \Delta\epsilon_2 - \Delta\epsilon_1$ (M⁻¹ cm⁻¹))

	λ/nm ($\Delta\epsilon_1$)	λ/nm ($\Delta\epsilon_2$)	<i>A</i>	ref
Helicates				
Δ, Δ -[Fe ₂ (2) ₃] ²⁺	295 (242)	315 (-529)	-771	60
Δ, Δ -[Fe ₂ (9) ₃] ²⁺	286 (56)	306 (-290)	-346	59
Δ, Δ -[Fe ₂ (10) ₃] ²⁺	302 (249)	322 (-445)	-794	61
Δ, Δ -[Fe ₂ (11) ₃] ²⁺	291 (103)	309 (-252)	-355	62
Nonhelical Dinuclear Complexes				
Λ, Λ -[Fe ₂ (12) ₃] ²⁺	289 (-417)	307 (792)	+1209	63
Related Mononuclear Complexes				
Δ -[Fe(bipy) ₃] ²⁺	284 (>150)	300 (->500)	->650	30

^a See Charts 2 and 4 for abbreviations and numberings of chromophores.

Chart 4

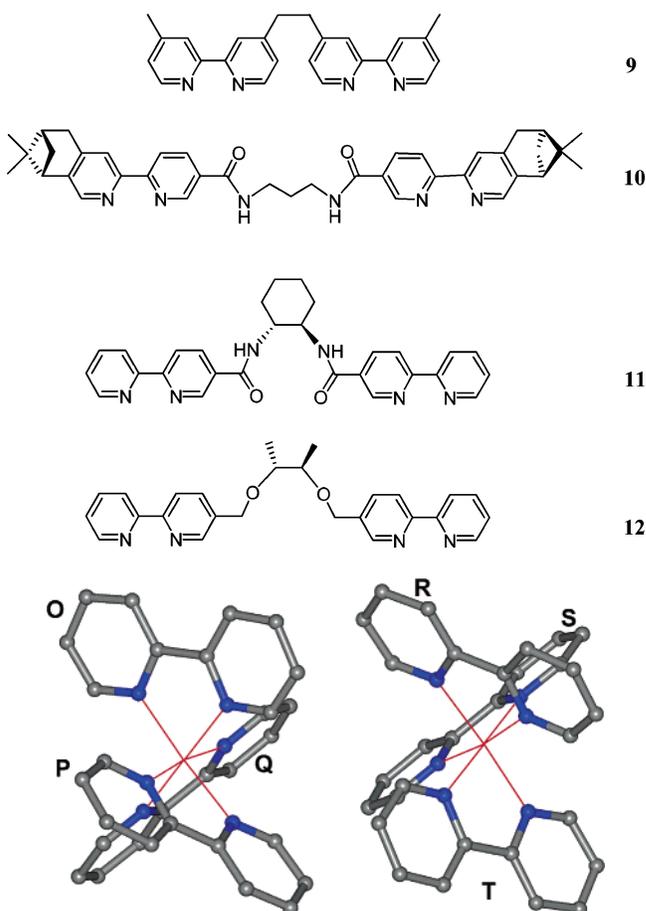


Figure 9. Arrangement of the diimine chromophores in the Δ, Δ -[Fe₂(**9**)₂]⁴⁺ helicate. The red lines indicate bonds to the metal centers. This chromophore model was used for the ZINDO calculations. All H atoms have been omitted for clarity.

The close spatial proximity of the internuclear chromophore pairs in the Δ, Δ -[Fe₂(**9**)₃]⁴⁺ cation is highlighted by Figure 9. There are three distinct potential internuclear exciton couplets: OR, OS, and OT. The distance between the midpoint of the bipyridyl bonds of these chromophore pairs is 7.63 Å, 8.47 Å, and 9.24 Å, respectively. The corresponding distance for the intranuclear couplet (OP) is 4.85 Å. The calculated CD spectral intensities for the exciton coupling of the long-axis polarized π - π^* transitions of these chromophore pairs is shown in Figure 10. The intranuclear couplet (OP) leads to a negative exciton couplet in this region, as expected for two diimine chromophores

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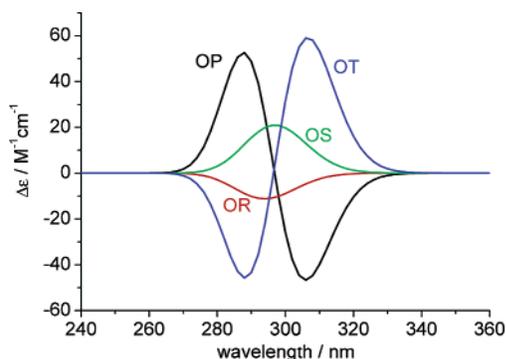


Figure 10. Calculated CD intensity for the individual chromophore pairs of the OPQRST chromophore model system.

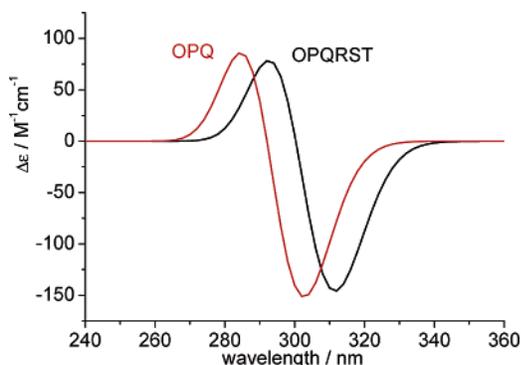


Figure 11. CD spectra calculated for the OPQRST hexa-chromophore model (black curve) and the OPQ tri-chromophore system (red curve). The sign and relative intensity of these spectra parallel those observed experimentally for Δ, Δ -[Fe₂(**9**)₃]⁴⁺ and Δ -[Fe(bipy)₃]²⁺.

coordinated to a metal center with the Δ absolute configuration. The OT internuclear pair gives a positive exciton couplet, while the OS and OR pairs both lead to negative couplets. For these latter two couplets, the CD curves appear as monosigned spectra in Figure 10 due to substantial overlapping of oppositely signed contributions, as discussed above for the ABCD chromophore system. The intensities of all four individual couplets are predicted to be of comparable magnitude, thus we may expect that they will all contribute significantly to the observed spectrum of the Δ, Δ -[Fe₂(**9**)₃]⁴⁺ helicate. It is worthy of note that, despite having the largest interchromophore separation, the OT pair produces the most intense curve due to a favorable relative orientation of the two chromophores. This underscores the necessity to consider *both the separation and the orientation* of chromophore pairs when analyzing their exciton coupling.

The spectrum calculated for the full chromophore model (OPQRST) of the [Fe₂(**9**)₂]⁴⁺ helicate is shown in Figure 11. For the sake of comparison, the spectrum calculated for the tris-chromophore (OPQ) model is also shown. The latter model system represents a mononuclear Δ -[M(bipy)₃] complex, and the calculations predict that it will produce a negative exciton couplet centered around 292 nm. This prediction is in keeping with well established experimental results for Δ -[M(bipy)₃] complexes.¹⁰ The CD spectrum predicted for the dinuclear helicate model (OPQRST) has a negative exciton couplet centered at around 300 nm. The intensity of this signal is comparable to that predicted for the mononuclear (OPQ) system. The sign, energy ordering, and relative intensity of these calculated spectra parallel those of the experimentally observed spectra of Δ, Δ -[Fe₂(**9**)₃]⁴⁺ and Δ -[Fe(bipy)₃]²⁺ which demon-

strates that the consideration of internuclear exciton coupling can rationalize the anomalously weak CD spectra of dinuclear helicates.

The surprisingly weak intensity of the CD spectra of dinuclear iron(II) helicates has been commented on in the literature.¹⁰ The possibility that racemization is responsible for these observations has been raised, though this can be deemed highly unlikely in light of the work of Williams et al. who demonstrated that a triple stranded dinuclear cobalt(II) helicate racemizes at room temperature with a half-life of 13 h.⁶⁵ In the context of alternative explanations for the weak CD spectra of these helicates, it should also be mentioned that trigonal distortion (from D_3 toward D_{3h} symmetry) of the coordination spheres of the metal ions in these helicates would also serve to reduce the intensity of their CD spectra by weakening the intranuclear exciton coupling of the diimine chromophores. However, analysis of the X-ray crystal structure of [Fe₂(**9**)₃]⁴⁺ indicates that such distortions are limited.

Further experimental evidence for the importance of internuclear exciton coupling effects in dinuclear helicates which contain diimine ligands comes from CD spectral data listed in Table 4. In all cases, the intensity of the CD spectra of the helicates is anomalously low as compared to analogous mononuclear complexes. However, despite the similarity of both the chromophores and the overall helicate structure, there is considerable variation in CD amplitude among these complexes. This can be accounted for in terms of an internuclear coupling model by the following. As outlined above, the intensity of a signal arising from the exciton coupling of two chromophores is inversely proportional to the square of the distance separating them.¹⁷ Thus, if the distance between the two sets of chromophores (OPQ and RST) is increased, the relative contribution of the internuclear exciton couplets to the observed CD spectrum will decrease rapidly. This would be manifest by an increase in the amplitude of the bands centered around 300 nm (see Figure 10). It is reasonable to assume that the separation of the sets of chromophores will be proportional to the length of the bridge between the two bipyridyl units and, hence, will increase in the order **9** < **11** < **10** \approx **2**. The data in Table 4 show that the amplitude of the CD spectra of the corresponding [Fe₂L₃]⁴⁺ helicates increases in the same order. These experimental observations thus lend strong support to the internuclear exciton coupling model.

One further point can be made which highlights the utility of this approach for the structural characterization of polynuclear complexes. Fletcher's group has investigated iron(II) complexes of ligands **11** and **12**.^{62,63} On the basis of ES-MS and NMR data, it was concluded that both ligands form complexes of the stoichiometry [Fe₂L₃]⁴⁺. However, the Δ, Δ -[Fe₂(**11**)₃]⁴⁺ complex was assigned a triple stranded helicate structure, while Λ, Λ -[Fe₂(**12**)₃]⁴⁺ was proposed to comprise a pair of Λ -[Fe(**12**)] units, in which the ligands are tetradentate, linked by a third ligand which bridges in a bis(bidentate) fashion (Figure 12). In the latter structure, the free rotation of the Λ -[Fe(**12**)] units, and their relatively large separation, will limit the contribution of internuclear exciton coupling effects to the experimentally observed spectrum. Accordingly, the CD spectrum around 300 nm should be dominated by intranuclear exciton coupling, and

(65) Charbonniere, L. J.; Gilet, M.-F.; Bernauer, K.; Williams, A. F. *Chem. Commun.* **1996**, 39–40.

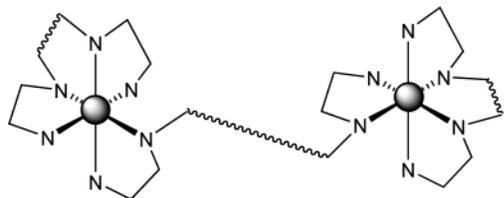


Figure 12. Schematic of the proposed structure of Λ,Λ -[Fe₂(**12**)₃]⁴⁺.

its intensity should be far greater than related helicates. This is indeed observed; the amplitude of the CD spectrum of Λ,Λ -[Fe₂(**12**)₃]⁴⁺ is more than three times greater than that of Δ,Δ -[Fe₂(**11**)₃]⁴⁺ and, as expected for two essentially non-interacting [Fe(di-imine)₃] centers, is nearly twice that of Λ -[Fe(bipy)₃]²⁺.

Conclusion

The analysis of exciton coupling effects in the CD spectra of polynuclear complexes of diimine ligands is the most common method used to assign the absolute configuration of the metal centers. Prior to the present study, this analysis has focused exclusively on exciton coupling between chromophores located on the *same* metal center. We have shown that the coupling between chromophores located on *different* metal centers can dominate the observed CD spectra of polynuclear complexes. As a result, there is the potential for the absolute configurations of the metal centers in a polynuclear complex

to be incorrectly assigned on the basis of CD data if internuclear exciton coupling effects are not taken into consideration. A review of the literature shows that many polynuclear complexes display CD spectra of anomalously low intensity. These spectra can be rationalized in the framework of an internuclear exciton coupling model. We have also shown how this model may find application for the structural characterization of polynuclear complexes. We envisage the approach employed here will be directly applicable to both the qualitative and quantitative analysis of many other systems which contain multiple interacting chromophores, including purely organic systems.

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Supporting Information Available: Experimental details of the synthesis and characterization of Λ -[Ru(phen)₂(bpm)](PF₆)₂, the coordinates of all chromophore model systems (as.xyz files), tables listing all of the calculated rotational strengths for all chromophore model systems in the region 240–320 nm, and plots of CD spectra calculated for the AC (Figure S1) and AD (Figure S2) couplets of the ABCD model system as a function of the effective internuclear separation. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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