Theoretical Investigation of the Effect of a Spin Transition on the Second-Order Molecular Hyperpolarizability of a Bis(salicylaldiminato)Fe^{II} Schiff Base Complex

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The intermediate neglect of differential overlap-based (INDO-based) sum-over-states (SOS) perturbution theory and the density functional theory (DFT) are used to explore the effect of a spin-crossover phenomenon on the quadratic molecular NLO response (β) of an Fe^{II}L complex in which the H_2L ligand is obtained from the Schiff base condensation of 5-nitrosalicylaldehyde with 1,4,7,10-tetraazadecane. The calculations based on crystal structures recorded at different temperatures reveal that the spin transition results in a β increase of about 25% of its initial value. This effect is mainly due to geometry modifications occurring upon spin transition. In addition, a temperature dependence of β is also pointed out for the first time.

Introduction

Multiproperty molecular materials are of growing interest, especially because they should provide opportunities for interplays between the properties, in relation to the emerging concept of molecular switches.[1] Ionic materials combining conductivity and magnetism,[2,3] conductivity and nonlinear optical (NLO) properties,[4,5] or magnetism and NLO properties[6,7] have already been reported. However, the achievement of an actual interplay is a challenging issue, once the buiding blocks carrying both properties have been engineered in the solid state.

Along this line, we have started the investigation of the NLO properties of a class of bis(salicylaldiminato) Schiff base complexes containing various paramagnetic metal centers.[8] Complexes with hyperpolarizabilities (β) higher than that of the free ligand were selected to ensure the contribution of the metal. Various paramagnetic NLO materials have now been reported, in this family of Schiff base complexes where the metal center acts as a donor[8,9] and in organic radicals,[9b,10,11] but the possibility of interplay has not been evidenced yet, even when a single entity is capable of magnetic and NLO response.

In the present contribution, we wish to report on a theoretical investigation of the influence of spin crossover on the second-order NLO response, as a first step toward the design of materials with switchable NLO behavior induced by magnetic properties. Spin crossover in a metal complex is known for inducing modifications in the coordination sphere, especially changes of the metal−ligand bond lengths up to 10%, in addition to different optical spectra, associated with the different spin states. In some cases, dramatic changes in the visible spectra were reported, with colors switching from white to deep red upon spin transition.[12] The β value of a chromophore is usually related to intense low-lying electronic transitions, having charge-transfer character, assuming a two-level description, which has already been successfully used for various metal−salen-based NLO chromophores.[8,9,13,14] Within this framework, β is expressed as a function of the energy of the transitions

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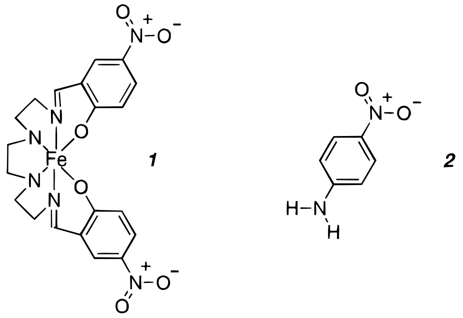
Scheme 1



(E), its oscillator strength (f), and the change in dipole moment ($\Delta\mu$) occurring during the transition through the following relation:[15]

$$\beta = \frac{3e^2\hbar f\Delta\mu}{2\mathrm{m}E^3}\,\frac{E^4}{(E^2-(2\hbar\omega)^2)(E^2-(\hbar\omega)^2)} \qquad (1)$$

In this relation, $\hbar\omega$ is the energy of the laser beam. Any complex with capabilities for one-dimensional metal-to-ligand charge transfer (MLCT) may exhibit the sizable $\Delta\mu$ value required for a large quadratic NLO response.

Up to now, the low-spin ($S = 0$) to high-spin ($S = 2$) transition occurring in iron(II) complexes has by far been the most widely investigated spin-crossover phenomenon.[16] Many of these complexes possess pseudocentrosymmetric electronic environments in relation to an octahedral coordination sphere. Therefore, they lack the extreme electronic asymmetry required for large $\Delta\mu$ values and hence a large second-order NLO response. However, the presence of a withdrawing substituent on the ligand may break the pseudocentrosymmetric character. Among various potential chromophores, we have selected [$\mathrm{Fe^{II}}$(5-$\mathrm{NO_2}$-sal-N(1,4,7,10))] (**1**, Scheme 1) as a suitable candidate for our investigations.[17] The reasons for this choice were first related to the topological similarities to typical benchmark push−pull *p*-nitroaniline (**2**, Scheme 1), $\mathrm{Fe^{II}}$ being expected to act as the donor, and the nitrobenzene moieties as the acceptor counterpart. The observation of an angle of about 110° between the two charge-transfer axes (Fe → $\mathrm{NO_2}$) in **1** ensures noncentrosymmetric electronic properties ($\beta \neq 0$), even if the centrosymmetry of the crystal must necessarily lead to vanishing macroscopic NLO response. Furthermore, the compound possesses the unique characteristic to exhibit a spin transition in two steps, which correspond to three different phases at high temperature ($S = 2$), low temperature ($S = 0$), together with a third phase at intermediate temperature, where one-half of the molecules (enantiomer Λ_2) are $S = 0$ and one-half (enantiomer Δ_2) are $S = 2$. The crystal structures have been previously reported for the three different phases.[17] The different sets of molecular geometries are summarized in Table 1. It is important to emphasize that these structures do not correspond to different allotropic forms, but to the same crystal recorded at different temperatures. Molecular geometries obtained from crystal structures always differ from gas-phase geometries due to undesirable effects of crystal packing. However, in the present case, the molecular environment is nearly identical for the three structures, and therefore, we can make the assumption that, to a large extent, the modifications of the molecular geometries result from temperature change and spin-state transition only.

Table 1. Set of Crystal Data Available for 1

	T (K)					
	103		153		292	
isomers	Λ_1	Δ_1	Λ_2	Δ_2	Λ_3	Δ_3
spin-state	0	0	0	2	2	2

In a first section, the experimental UV−visible spectrum of **1** will be presented and compared to the ZINDO[18] spectra calculated for every set of molecular coordinates available. The orbital analysis of β will be described precisely at the restricted Hartree−Fock (RHF) level, in the case of enantiomer Λ, for which $S = 0$ at 153 K (Λ_2). Then, the temperature dependence of β will be pointed out, and finally, the effect of the spin-crossover phenomenon will be investigated on the basis of crystal data recorded at the same temperature for both spin states (Λ_2 and Δ_2).

Experimental Section

Starting Materials and Equipment. The bis(salicylaldiminato)$\mathrm{Fe^{II}}$ Schiff base complex **1** has been synthesized as previously described.[17] The UV−visible spectra were recorded on a Hewlett-Packard 8452A spectrophotometer. The solvents were distilled under nitrogen. Due to air sensitivity, the solutions of **1** were prepared under an inert atmosphere in a glovebox.

Calculation of the Molecular Hyperpolarizability. The electronic spectra were calculated using the all-valence intermediate neglect of differential overlap (INDO) method.[18] The closed-shell restricted Hartree−Fock (RHF) formalism was adopted for the diamagnetic complexes (Λ_1, Δ_1, and Λ_2), while the open-shell restricted Hartree−Fock (ROHF) formalism was selected for the $S = 2$ (Δ_2, Λ_3, and Δ_3) analogues. INDO, in connection with the sum-over-state (SOS) formalism,[19] was employed for the calculation of the hyperpolarizabilities assuming a closed-shell configuration for any molecular structures, to evaluate the effect of geometry modifications on the NLO response. Details on the computationally efficient INDO/SOS method for describing second-order molecular optical nonlinearities have been reported elsewhere.[20] Calculations were performed using the ZINDO/1 Hamiltonian incorporated into the commercially available MSI software package ZINDO.[21] The monoexcited configuration interaction (MECI) approximation was employed to describe the excited states. The 100 energy transitions between the 10 highest occupied molecular orbitals and the 10 lowest empty ones were chosen to undergo CI mixing. Metrical parameters used for the calculations were taken from related crystal structure data.

The calculations of β modifications occurring upon spin conversion were conducted using the Gaussian94 program package,[22] within the framework of the density functional theory (DFT) at the B3PW91 level using a 6-31G* basis for

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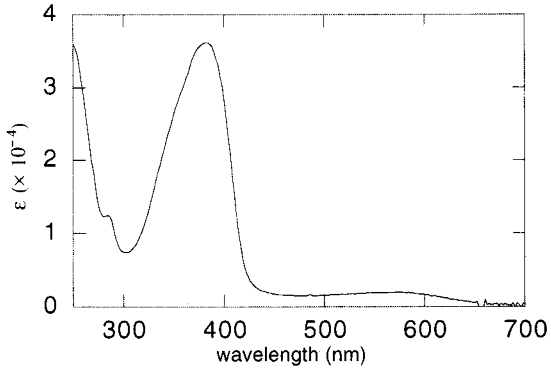

Figure 1. Optical spectrum of **1**, recorded in tetrahydrofurane.

all atoms, and a LANL2DZ basis for iron, for which a polarization basis was added.[23] Static hyperpolarizabilities were evaluated using the numerical finite field procedures. A field strength of 0.001 was chosen in any cases. The (SCF) convergence was reduced to 10^{-6} in the finite field procedure for the high−spin Δ_2. It was shown for Λ_2 that the β value is the same using either this reduced convergence criteria or the standard tighter one.

Results

Optical Properties of Compound 1. The electronic absorption spectrum of **1** recorded in tetrahydrofuran at room temperature is shown in Figure 1. The spectrum is dominated by an intense band in the 300−400-nm domain, with an absorption maxima at 382 nm (ϵ = 36200 L·mol^{-1}·cm^{-1}), and a shoulder at higher energy. Additional but very weak transitions are present at lower energies (500−600 nm, $\epsilon \leq 2000$ L·mol^{-1}·cm^{-1}). The intense transition exhibits a solvatochromic shift, with representative $\lambda_{\max}$ (solvent) of 348 (CH_3CN), 372 (MeOH), 386 (acetone), and 400 nm (DMSO). In some cases,[8b,9a,12,13] solvatochromism has been reported as strongly indicative of changes in dipole moments ($\Delta\mu$) upon electronic excitations in metal−salen complexes. This behavior, in accordance with eq 1, suggests some quadratic NLO capabilities for **1**.[24]

ZINDO-calculated spectra from the X-ray structures obtained at 103, 153, and 292 K are gathered in Table 2 and compared with the experimental data. In any case, the calculations reveal the same general features, with spectra dominated by an intense band located at 300−400 nm. The agreement between calculation and experiment is excellent, taking into account the experimental solvatochromism ($348 < \lambda_{\max} < 400$ nm). In particular, the presence of a shoulder is predicted by the calculation at a wavelength about 20 nm lower than that of $\lambda_{\max}$. Although the data suggest that spin crossover and temperature have little influence on the electronic spectrum, a red shift is noticeable, when the temperature is lowered. The good agreement between experimental and calculated spectra suggests a reliable electronic structure−NLO property relationship within the ZINDO formalism.

Molecular Orbital Analysis of β in the Closed-Shell Configuration. Our ZINDO release cannot calculate the hyperpolarizabilities of open-shell chromophores. Nevertheless, this software can be used to describe the molecular orbital origin of β in a closed-shell configuration ($S = 0$). Owing to similarities in the ZINDO-calculated spectra, we tentatively assume that the charge-transfer origin of the NLO response of **1** is roughly the same at any spin state and temperature. Therefore, in this section, we present only the results obtained for Λ_2.

Within the framework of the SOS perturbation theory, the molecular hyperpolarizability is related to all excited states of the molecule and can be partitioned into two contributions, so-called two-level and three-level terms. Analysis of term contributions to the molecular hyperpolarizability of bis(salicylaldiminato) Schiff base complexes indicates that the two-level term ($\beta_{2\text{level}}$) dominates the nonlinearity.[8,9] For the present iron(II) complex, $\beta_{2\text{level}}$ can mainly be related to the 1 → 8 and 1 → 9 transitions, as indicated in Table 3. In particular, the 1 → 8 transition contributes 68.2% to the nonlinearity. Therefore, we will assume here that understanding this transition provides qualitative understanding of β. The composition of the CI expansion reveals that the transition involves the 88(HOMO) → 89(LUMO) and 87 → 90 orbital transitions. These orbitals are shown in Figure 2. It clearly appears that the metal center and the oxygen of the phenolate act as the main donors (orbitals 87 and 88), while the nitro substituents are the acceptor counterparts in the degenerated orbitals 89 and 90. Therefore, the charge transfer results in a dipole moment change of 6.6 D along the 2-fold axis of the molecule (Table 3).

Temperature Dependence of β. The proven ZINDO/SOS formalism has long been successfully used to calculate the hyperpolarizabilities of various metal-containing NLO chromophores.[20] However, as previously pointed out, our ZINDO release is inoperative for open-shell chromophores, and the effect of spin crossover on β cannot be evaluated directly. Nevertheless, this procedure applied at the restricted Hartree−Fock level is used here to investigate the effect of geometry modification on β. The results are gathered in Table 4. A temperature dependence can be pointed out from the calculation. For instance, the enantiomer Λ exhibits a reduced β value, from 103 to 153 K, without spin conversion. The same behavior is found for the enantiomer Δ between 153 and 292 K. By contrast, the shift observed at 153 K between Λ_2 and Δ_2 must necessarily be ascribed to spin conversion instead of temperature effect. The calculated $\beta_{S=0}$ values and the extrapolated $\beta_{S=2}$ values, corrected from the spin-crossover shift, are finally reported in Figure 3 to give a crude evaluation of the temperature dependence of β. The trend for β reduction as the temperature increases is clearly evidenced. On the basis of this observation, the investigation conducted at 153 K on both spin states becomes essential to reach the only reliable evaluation of the β

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Table 2. Comparison of ZINDO Absorption Maxima (λ_{max} in nm) and Oscillator Strength (*f*), Calculated for Various Crystal Data of 1, with Experimental Spectrum

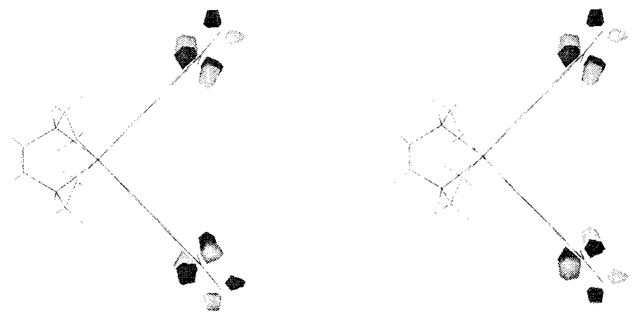
	T (K)						
	calc.						exp.
	103		153		292		300
enantiomer	Λ_1	Δ_1	Λ_2	Δ_2	Λ_3	Δ_3	
$\lambda_{max}(f)$	393(0.62)	376(0.56)	342(0.72)	364(0.74)	334(0.54)	334(0.54)	382
sh[a]	372	363	333	352	319	319	350−360

[a] Shoulder.

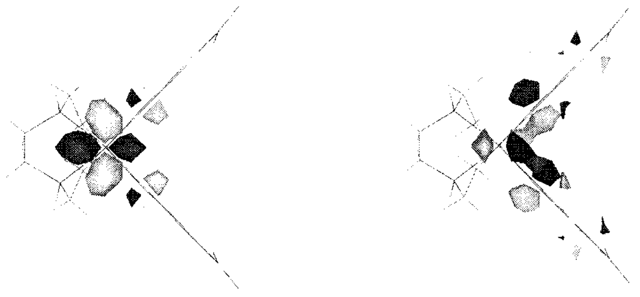
Table 3. ZINDO-Calculated Energies (λ_{max} in nm), Oscillator Strengths (*f*), Dipole Moment Changes between Ground and Excited State ($\Delta\mu$ in D), Contribution in the β_{2Level}, and Composition of the First Excited States of 1 Λ_2

transition	λ_{max}	*f*	$\Delta\mu$	state[a] (%)	composition[b] of CI expansion
1 → 8	342	0.72	6.6	68.2	$-0.691\chi_{88\to 89} - 0.665\chi_{87\to 90}$
1 → 9	333	0.28	3.4	13.3	$-0.545\chi_{88\to 90} - 0.515\chi_{87\to 89} + 0.465\chi_{88\to 92} + 0.360\chi_{87\to 91}$

[a] Contribution of the *i*th transition to the β_{2level} (state % = $\beta_{g\to e(i)}/\sum_{j=1}^{j=100}\beta_{g\to e(j)}$). [b] Orbital 88 is the HOMO and orbital 89 the LUMO for **1**.



LUMO (89) 90



HOMO (88) 87

Figure 2. Main molecular orbitals involved in the NLO response of **1**.

Table 4. ZINDO-Derived Hyperpolarizabilities[a] Calculated at Zero Frequency ($\beta(0)$) and at 1.907 μm, Using the Restricted Hartree−Fock Approximation

	T (K)					
	103		153		292	
enantiomer	Λ_1	Δ_1	Λ_2	Δ_2	Λ_3	Δ_3
$\beta(0)$	16.5	18.1	10.5	15.3	12.0	12.0
$\beta_{1.907}$	22.2	23.1	13.3	19.6	15.2	15.2

[a] In 10^{-30} cm^5 esu^{-1}.

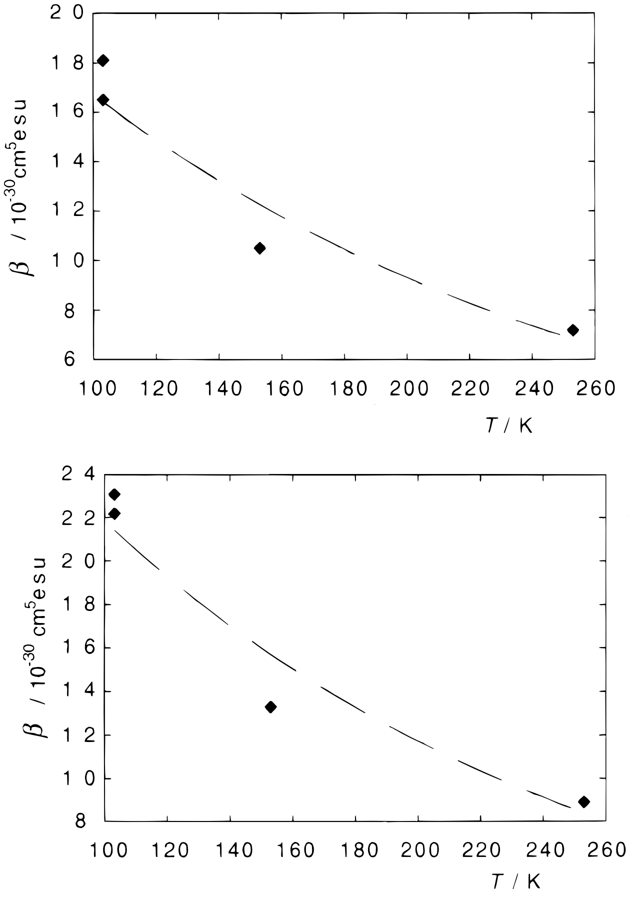


Figure 3. Temperature dependence of the hyperpolarizability of **1** extrapolated from Table 2, at zero frequency (top) and at 1.907 μm (bottom). The drawing of the dotted line is arbitrary.

dependence upon the spin-crossover phenomenon.

Effect of the Spin Transition on β. The hyperpolarizabilities of **1** calculated at 153 K for both spin states in nearly identical crystal environments are reported in Table 5. The data (static $\beta(0)$ hyperpolarizabilities) determined using the numerical finite field procedure included in Gaussian94 are compared to those reported in the previous section. The scope and limitations of the different β calculation methodologies have been reviewed.[20] It is noteworthy that significant differences in the magnitude of the hyperpolarizabilities are observed, depending on the calculation method. In particular, we have previously observed a tendency for overestimating β within the framework of the DFT theory at the B3PW91 level versus the ZINDO−SOS approach.[11]

Beyond these differences, the same trend for β enhancement upon spin conversion is observed, whatever the method used. However, the effect calculated by ZINDO, at the Hartree−Fock level, is about twice as large as that obtained by the finite field procedure, which account for both spin-state and geometry modi-

Table 5. Summary of Theoretical Data ($\beta(0)$ in 10^{-30} cm^5 esu^{-1} at 153 K) for Switching of NLO Response Induced by Spin Conversion in 1

	quantum approach			
	Λ_2	Δ_2	increase %	source of effect
ZINDO (restricted level)	10.5	15.3	46	geometry modification only
Gaussian	36.9	45.9	25	geometry and spin-state modification

fications. This could suggest that most of the switch is due to geometry changes, rather than spin-state changes.

Discussion

Chromophore synthetic chemistry is highly laborious, with the outcome of many tedious syntheses frequently being uncertain. In the past decade, theoretical computational quantum procedures have profoundly changed the science of chromophore design. To make progress toward advanced materials, experimentalists must apply chemical intuition in concert with insight provided by such computations to effectively guide synthetic strategies. In the context of spin transition and NLO effects, the traditional approach[18] offers limited chemical intuitions, as the interaction of a medium with light is regarded within the framework of a dielectric subjected to an electric field. In this approach, no magnetic effect will interfere with the NLO response. At a deeper theoretical level, the usual framework could be enlarged to encompass both electric and magnetic dipole transitions, leading to generalized mixed electric−magnetic contributions to the NLO tensor.[25] However, the ambition of the present report is not to provide a thorough description of the magnetic−NLO property relationship within a single molecule but rather to point out the indirect effect of structural changes occurring upon spin crossover on the molecular hyperpolarizability.

As a first result, the present calculations have revealed a temperature dependence of β. To the best of our knowledge, such a dependence has never been reported either experimentally or theoretically. Finding a rationale for this effect is not in the scope of our investigation. However, one can expect that molecular expansion induced by temperature would decrease the orbital overlaps, which would necessarily affect the charge-transfer properties and therefore the molecular hyperpolarizability. The reliability of calculations performed from crystal structures recorded on both sides of the spin transition is hampered by the fact that the effect of temperature and spin-state conversion can hardly be distinguished. Consequently, a reliable comparison must be conducted on crystal data in which two chromophores (Λ_2 and Δ_2) have different spin states at the same temperature, and in the same environment, as observed for **1** at 153 K. This can readily be assumed, taking into account the fact that, at higher temperature, Λ_3 and Δ_3 are crystallographically independent. Therefore, it is reasonable to infer that, to a large extent, they keep the same solid-state environment at 153 K. Such unique characteristics provide an exceptional opportunity for a theoretical investigation. It is worth pointing out that a comparison of the metal-to-ligand bond lengths does not show any evidence for a significant reduction in bond length usually observed for a molecule experiencing a spin conversion from the high-spin to low-spin form.[15] Therefore, the increase of 25% of the initial β value obtained upon spin crossover in **1** could be more pronounced in the case of Fe^{II} complexes exhibiting larger geometry modifications than those observed for **1**.

Up to now, a direct measurement of this effect has not been observed. This would require a noncentrosymmetric crystal structure and an investigation of the temperature dependence of the SHG properties. However, recent years have witnessed an interest for the incorporation of switchability into NLO materials.[26] Along this line most investigations have employed photoexcitation to stimulate molecular isomerization. A convincing switch should preferably be attached to an “on and off“ behavior whereby the “off“ state would correspond to a zero β tensor and the “on“ state to a nonzero value, a situation which has not been observed yet. Nevertheless, our study indicates that using magnetic transition for switchable NLO properties deserve more interest in the future.

Conclusion

[Fe^{II}(5-NO$_2$-sal-N(1,4,7,10))] undergoes a spin crossover (from $S = 0$ to $S = 2$) and is capable of quadratic NLO response, related to intense MLCT electron transition located in the 300−400-nm domain. Theoretical evidences are provided for an increase of the NLO response of about 25%, mainly due to modifications occurring in the coordination sphere upon spin-state transition. This report is the first evidence for an effect of a spin crossover on the quadratic NLO properties of a molecule. In addition, the temperature dependence of the hyperpolarizability has also been pointed out.

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