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Role of Metal Electronic Properties in Tuning the Second-Order Nonlinear Optical Response of Coordination Complexes. A Combined Experimental and Theoretical Investigation of a Homologous Series of (*N*,*N′*-Disalicylidene-1,2-phenylenediaminato)M(II) (M = Co, Ni, Cu) Complexes

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Abstract: The role of metal electronic configuration in determining the second-order nonlinear optical response of the homologous series of planar, thermally robust M(salophen) (M = Co, Ni, Cu) transition metal complexes is investigated by electric field induced second harmonic generation experiments and ZINDO quantum chemical calculations. Both the experimental data and those derived from the theoretical calculations (which are in good agreement) indicate that, on passing from closed-shell d^8 Ni(II) to the open-shell d^9 Cu(II) and d^7 Co(II) analogues, hyperpolarizability values increase by a factor of ~3 and ~8, respectively. These indicate a major role of metal electronic configuration in determining the second-order nonlinear optical response. Partially resonant solution-phase hyperpolarizability values as high as $(-170 \pm 40) \times 10^{-30}$ cm^5 esu^{-1} ($\hbar\omega = 0.92$ eV; $\mu\beta = 1340 \times 10^{-48}$ esu $\approx 2\times$ that for 4-(*N*,*N*-dimethylamino)-4′-nitrostilbene) are observed for the Co(salophen) complex. The greater second-order responses of the Cu(II) and Co(II) complexes can be understood in terms of the different natures of the contributing electronic excited states. In particular, the large nonlinearities of Cu(salophen) and Co(salophen) are due to more intense low-energy charge-transfer transitions and the existence of either higher (M = Cu) or lower (M = Co) lying metal-to-ligand charge-transfer states. While, for the closed-shell Ni(salophen) complex, the two-state model represents a suitable approximation for describing the nonlinearity, it breaks down in the case of Cu(salophen) and Co(salophen), since other states contribute to the response. Experimental linear and nonlinear optical features are fully consistent with the theoretical calculations.

Introduction

Recently, transition metal organometallic and coordination complexes have emerged[1−6] as potential building blocks for second-order nonlinear optical (NLO) materials.[7] Compared to organic molecules, metal complexes offer a larger variety of structures, comparable or, in some cases, higher environmental stability (e.g., metallophthalocyanines), and a much greater diversity of tunable electronic properties by virtue of the coordinated metal center. To date, however, both experimental[1−6] and quantum chemical[8,9] investigations have been largely limited

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(1) (a) Long, N. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 21 and references therein. (b) Loucif, R.; Delaire, J. A.; Bonazzola, L.; Doisneau, G.; Balavoine, G.; Fillebeen-Khan, T.; Ledoux, I.; Puccetti, G. *Chem. Phys.* **1992**, *167*, 369. (c) Doisneau, G.; Balavoine, G.; Fillebeen-Khan, T.; Clinet, J.-C.; Delaire, J.; Ledoux, I.; Loucif, R.; Puccetti, G. *J. Organomet. Chem.* **1991**, *421*, 299. (d) Calabrese, J. C.; Cheng, L.-T.; Green, J. C.; Marder, S. R.; Tam, W. *J. Am. Chem. Soc.* **1991**, *113*, 7227. (e) Cheng, L.-T.; Tam, W.; Eaton, D. F. *Organometallics* **1990**, *9*, 2856. (f) Cheng, L.-T.; Tam., W.; Meredith, G. R.; Marder, S. R. *Mol. Cryst. Liq. Cryst.* **1990**, *189*, 137.

(2) (a) Bourgault, M.; Mountassir, C.; Le Bozec, H.; Ledoux, I.; Puccetti, G.; Zyss, J. *J. Chem. Soc., Chem. Commun.* **1993**, 1623. (b) Thami, T.; Bassoul, P.; Petit, M. A.; Simon, J.; Fort, A.; Barzoukas, M.; Villaeys, A. *J. Am. Chem. Soc.* **1992**, *114*, 915.

(3) Di Bella, S.; Fragalà, I.; Ledoux, I.; Diaz-Garcia, M. A.; Lacroix, P. G.; Marks, T. J. *Chem. Mater.* **1994**, *6*, 881.

(4) (a) Lequan, M.; Branger, C.; Simon, J.; Thami, T.; Chauchard, E.; Persoons, A. *Adv. Mater.* **1994**, *6*, 851. (b) Laidlaw, W. M.; Denning, R. G.; Verbiest, T.; Chauchard, E.; Persoons, A. *Nature* **1993**, *363*, 58. (c) Zyss, J.; Dhenaut, C.; Chauvan, T.; Ledoux, I. *Chem. Phys. Lett.* **1993**, *206*, 409.

(5) For recent powder SHG studies involving organometallic complexes and inorganic polymers, see: (a) Coe, B. J.; Foulon, J. -D.; Hamor, T. A.; Jones, C. J.; McCleverty J. A.; Bloor, D.; Cross, G. H.; Axon, T. L. *J. Chem. Soc., Dalton Trans.* **1994**, 3427. (b) Wright, M. E.; Toplikar, E. G. *Macromolecules* **1992**, *25*, 6050. (c) Bandy, J. A.; Bunting, H. E.; Garcia, M.-H.; Green, M. L.; Marder, S. R.; Thompson, M. E.; Bloor, D.; Kolinsky, P. V.; Jones, R. J.; Perry, J. W. *Polyhedron* **1992**, *11*, 1429. (d) Marder, S. R.; Perry, J.; Tiemann, B.; Schaefer, W. P. *Organometallics* **1991**, *10*, 1896. (e) Chiang, W.; Thompson, M. E.; Van Engen, D. In *Organic Materials for Nonlinear Optics II*; Hann, R. A., Bloor, D., Eds.; Royal Society of Chemistry: London, 1991; p 210. (f) Pollagi, T. P.; Stoner, T. C.; Dallinger, R. F.; Gilbert, T. M.; Hopkins, M. D. *J. Am. Chem. Soc.* **1991**, *113*, 703.

(6) For a review of early NLO studies involving organometallic and coordination complexes, see: Nalwa, H. S. *Appl. Organomet. Chem.* **1991**, *5*, 349.

(7) For recent general reviews of NLO materials, see, for example: (a) *Optical Nonlinearities in Chemistry*; Burland, D. M., Ed. *Chem. Rev.* **1994**, *94*, No. 1. (b) *Molecular Nonlinear Optics: Materials, Physics and Devices*; Zyss, J., Ed.; Academic Press: Boston, 1993. (c) Prasad, N. P.; Williams, D. J. *Introduction to Nonlinear Optical Effects in Molecules and Polymers*; Wiley: New York, 1991. (d) *Materials for Nonlinear Optics: Chemical Perspectives;* Marder, S. R., Sohn, J. E., Stucky, G. D., Eds.; ACS Symposium Series 455; American Chemical Society: Washington, DC, 1991. (e) *Nonlinear Optical Properties of Organic Molecules and Crystals*; Chemla, D. S., Zyss, J., Eds.; Academic Press: New York, 1987; Vols. 1 and 2.

(8) Kanis, D. R.; Ratner, M. A.; Marks, T. J. *Chem. Rev.* **1994**, *94*, 195.

(9) (a) Kanis, D. R.; Lacroix, P. G.; Ratner, M. A.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10089. (b) Kanis, D. R.; Ratner, M. A.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 10338.

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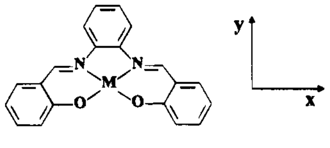
Table 1. Experimental[a] and ZINDO-Derived Linear Optical Spectroscopic and Nonlinear Optical Response Parameters[b] for M(salophen) Complexes

	λ_{max}		r_{ge}		μ_g		$\Delta\mu_{ge}$		β_{vec}		
compound	exptl ($\epsilon \times 10^{-4}$)	calcd	exptl	calcd	exptl	calcd	exptl	calcd	exptl	calcd	β_0^{calcd}
Co(salophen)	388 (1.5)	391	6.01	7.34	*c*	7.7	−4.0	−4.7	$-170 \pm 40^{d,e}$	−105.1	−40.1
Ni(salophen)	480 (0.9)	387	4.74	5.97	7.0 ± 0.5	8.5	−5.1	−5.2	−20.5 ± 2	−17.3	−11.5
Cu(salophen)	428 (2.1)	413	7.27	8.56	7.0 ± 0.2	8.1	−4.1	−3.1	−50.0 ± 5	−53.7	−37.2

[a] Chloroform solution. [b] λ_{max} in nanometers; r_{ge}, μ_g, and $\Delta\mu_{ge}$ in debyes; β_{vec} and β_0 in 10^{-30} cm^5 esu^{-1} ($\hbar\omega = 0.92$ eV). For definition of the parameters see text. [c] Complex insufficiently soluble for accurate measurements. [d] Estimated using the calculated dipole moment. [e] The larger estimated uncertainty is due to the low solubility of the Co(salophen) complex.

Chart 1



M(salophen); M = Co, Ni, Cu

to the molecular NLO response of metal chromophore families having the same metal (e.g., ferrocenyl derivatives),[1a−e,9b] or to families having isoelectronic metal fragments (e.g., group VI carbonyl derivatives).[1e,f,9a] No comprehensive experimental and/or theoretical studies have been carried out to probe how second-order molecular NLO response depends upon the electronic properties of the coordinated metal center, i.e., upon the results of varying the metal ion through a homologous series. Such studies are of relevance to the design and optimization of molecular NLO response for new, thermally stable chromophores which would take advantage of the versatility offered by metal complexation.

We present here the first comparative experimental/theoretical investigation of the molecular second-order NLO properties of a homologous series of planar (*N,N′*-disalicylidene-1,2-phenylenediaminato)M(II) (M(salophen); M = Co, Ni, Cu) complexes[10] (Chart 1) to explore the role of the metal electronic properties in the second-order NLO response. The study combines a self-consistent field linear combination of atomic orbitals (SCF-LCAO) approach, within the proven intermediate neglect of differential overlap (INDO/S)−sum over states (SOS) formalism[8,11] recently implemented for open-shell doublet electronic states,[12] to calculate the molecular hyperpolarizability, $\beta(-2\omega;\omega,\omega)$, with experimental hyperpolarizability data acquired by electric field induced second harmonic generation (EFISH) techniques.[13] We emphasize that the goal of this initial investigation is to probe the effects of the metal electronic configuration on $\beta(-2\omega;\omega,\omega)$. Therefore, it has necessarily been limited to unsubstituted M(salophen) complexes, thus avoiding electronic effects on $\beta(-2\omega;\omega,\omega)$ due to the donor and/or acceptor substituents (which will be the subject of a later paper).

Results and Discussion

We have recently communicated[3] the second-order NLO properties of a series of thermally stable, *closed-shell* donor−acceptor bis(salicylaldiminato)nickel(II) complexes, the NLO response of which is dramatically "switched on" by the metal complexation. The comparison of Ni(II) complex NLO properties with those of the *open-shell* Cu(II) and Co(II) homologues offers an interesting case study. The reaction between *N,N′*-disalicylidene-1,2-phenylenediamine (H_2salophen) with the M(II) (M = Co, Ni, Cu) ions leads to the formation of thermally stable M(salophen) complexes: diamagnetic[14] wine-red Ni(salophen) and the paramagnetic[14,15] reddish-brown Cu(II) and brown Co(II) analogues. All of these complexes are planar,[16−18] differing in metal electronic configuration, d^8 in the case of the Ni(II) complex,[14] d^9 for the Cu(II) complex,[14,15] and low-spin d^7 for the Co(II) complex.[14,15,19] In spite of these electronic structure differences, both experimental and theoretical data indicate that the complexes possess nearly identical ground-state dipole moments (μ_g; Table 1), thus suggesting a similar charge distribution in the ground state of the molecules.

The M(salophen) complexes exhibit a very good thermal stability. For example, the Co, Ni, and Cu complexes exhibit decomposition temperatures (T_d)[20] of 330, 350, and 300 °C in air, respectively (360, 360, and 325 °C under N_2), as established by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA; see Experimental Section for details). Moreover, Cu(salophen) survives, without decomposition, heating at 280 °C for 30 min (under N_2), as demonstrated by the reversibility of the DSC trace observed upon subsequent cooling and reheating to the 30−350 °C range, as well as by elemental analysis and the UV−vis spectra of the thermolyzed samples.

The linear optical absorption spectra of the present M(salophen) complexes in solution are compared in Figure 1, and relevant data are tabulated in Table 1. The absorption spectrum of Ni(salophen) consists of three intense bands (ϵ = 8000−28000) in the region between 290 and 540 nm and of a weak structure ($\epsilon < 200$) in the region between 540−620 nm, the latter presumably involving contributions from "d−d" transitions.[21] On passing to Cu(salophen), the two more intense, shorter wavelength features, mainly associated with intraligand $\pi \rightarrow \pi^*$ transitions,[21] coalesce into a single band, while the strong, longer wavelength band, having a similar band shape in both Ni and Cu spectra, is blue-shifted (~50 nm). This band, absent in the optical spectrum of the free ligand,[3] exhibits an appreciably different intensity in the two complexes (ϵ = 9000 in Ni(salophen) vs 21 000 in Cu(salophen)). The optical transition associated with this band involves both the ligand and the metal center and is the excitation mainly responsible for the NLO

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(10) Communicated in part: Di Bella, S.; Fragalà, I. Abstract of Papers. In *Perpectives in Inorganic Chemistry*, XXIII National Inorganic Chemistry Meeting, Bressanone (BZ), Italy, 1994; B6, p 66.

(11) Di Bella, S.; Marks, T. J.; Ratner, M. A. *J. Am. Chem. Soc.* **1994**, *116*, 4440.

(12) (a) That is, systems having a single unpaired electron. (b) Di Bella, S.; Fragalà, I.; Marks, T. J.; Ratner, M. A. To be submitted for publication.

(13) For discussions of the EFISH technique see: (a) Oudar, J. L. *J. Chem. Phys.* **1977**, *67*, 446. (b) Reference 7c, p 106.

(14) Nagar, R.; Sharma, R. C.; Parashar, R. K. *Spectrochim. Acta* **1990**, *46A*, 401.

(15) Valko, M.; Klement, R.; Pelikán, P.; Boca, R.; Dlhán, L.; Böttcher, A.; Elias, H.; Müller, L. *J. Phys. Chem.* **1995**, *99*, 137.

(16) Montgomery, H.; Morosin, B. *Acta Crystallogr.* **1961**, *14*, 551.

(17) Cassoux, P.; Gleizes, A. *Inorg. Chem.* **1980**, *19*, 665.

(18) Bresciani Pahor, N.; Calligaris, M.; Delise, P.; Dodic, G.; Nardin, G.; Randaccio, L. *J. Chem. Soc., Dalton Trans.* **1976**, 2478.

(19) (a) Nishida, Y.; Kida, S. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 143. (b) Hitchman, M. A. *Inorg. Chem.* **1977**, *16*, 1985. (c) Urbach, F. L.; Bereman, R. D.; Topich, J. A.; Hariharan, M.; Kalbacher, B. J. *J. Am. Chem. Soc.* **1974**, *96*, 5063.

(20) Moylan, C. R.; Twieg, R. J.; Lee, V. Y.; Swanson, S. A.; Betterton, K. M.; Miller, R. D. *J. Am. Chem. Soc.* **1993**, *115*, 12599.

(21) (a) Crawford, S. M. *Spectrochim. Acta* **1963**, *19*, 255. (b) Bosnich, B. *J. Am. Chem. Soc.* **1968**, *90*, 627.

Table 2. Absorption Maxima of the Lowest Energy Charge-Transfer Optical Transition for M(salophen) Complexes in Solvents of Different Polarities

	λ_{max} (nm)					
complex	CCl_4	benzene	chloroform	ethyl acetate	acetone	methanol
Co(salophen)[a]	398 (442)	392 (436)	388 (434)	388 (434)	386 (430)	*b*
Ni(salophen)	494	488	480	480	478	466
Cu(salophen)	438	434	428	428	424	414

[a] Values in parentheses refer to the higher wavelength shoulder (see text). [b] In methanol solution a complete modification of the optical absorption spectrum of Co(salophen) is observed presumably due to solvent coordination.

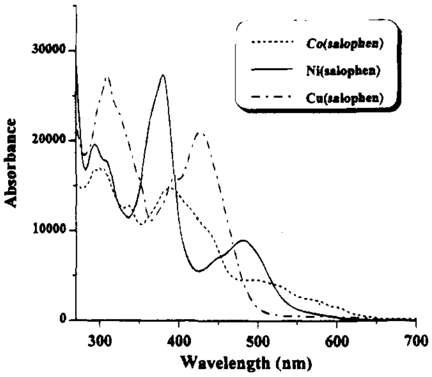

Figure 1. Optical absorption spectra of M(salophen) complexes in chloroform solution.

response (vide infra). Moreover, this band exhibits a negative solvatochromism, i.e., a hypsochromic (blue) shift with increasing solvent polarity (Table 2), thus indicating a negative dipole moment change between the ground and the excited state and, hence, significant charge-transfer (CT) character for the associated optical transition.

The absorption spectrum of Co(salophen) is quite different from that of the Ni(II) and Cu(II) homologues (Figure 1). In fact, in the region $\lambda > 350$ nm, in addition to the CT band (Table 2) which is further blue-shifted (~40 nm) with respect to that of Cu(salophen), a shoulder is apparent at longer wavelengths, and a new band envelope ($\epsilon = 1500-4500$) is present in the region between 480 and 620 nm. All of these new features are expected[19] to involve both the ligand and the metal center. Analogously to the CT band, the aforementioned shoulder also exhibits an appreciable negative solvatochromism (Table 2).

Second-order NLO properties of the present complexes are also compiled in Table 1 and compared with ZINDO-derived theoretical values. Here β_{vec} is the vector part of the β_{ijk} tensor which is obtained in an EFISH experiment. The agreement between experimental and theoretical data is good. On passing from Ni(salophen) to the Cu(II) analogue, the solution-phase EFISH hyperpolarizability β_{vec} value surprisingly increases in magnitude by a factor of 2.5, from -20.5 to -50.0×10^{-30} cm^5 esu^{-1} at $\hbar\omega = 0.92$ eV. This indicates a strong dependence of the NLO response upon the metal electronic configuration. The essentially nonresonant[22] β_{vec} value of Cu(salophen) is rather large for a non-donor–acceptor substituted metal chromophore.[1-6] In fact, it is comparable to those observed in *donor–acceptor-substituted* Ni(salophen) derivatives[3] and is larger than that commonly observed in many similarly substituted organometallic complexes.[1]

The most dramatic case of metal-tuned β enhancement occurs in the Co(II) complex (Table 1). In fact, on passing from Ni(salophen) to the Co(II) analogue, β_{vec} increases by nearly an order of magnitude (to $(-170 \pm 40) \times 10^{-30}$ cm^5 esu^{-1} at $\hbar\omega = 0.92$ eV). This partially resonant β_{vec} value represents one of the largest reported to date in an EFISH experiment on an organometallic[1] or coordination complex.[2,3] The $\mu \cdot \beta_{1340}$ product (-1310×10^{-48} esu), which is the relevant parameter for poled polymer applications,[23] is ~2× greater than that reported for efficient, thermally robust second-order organic π electron chromophores such as the prototypical donor–acceptor stilbene 4-(*N,N*-dimethylamino)-4′-nitrostilbene (DANS; $\mu \cdot \beta_{1300} = 662 \times 10^{-48}$ esu).[20,24]

The ZINDO-derived M(salophen) β_{vec} values (Table 1) are in generally good agreement with the experimental, EFISH-derived data and predict an increase in β_{vec} of ~3× and ~6× on substituting Cu(II) and Co(II) for Ni(II), respectively. The dominant contribution to β_{vec} derives from the *yyy* component of the β_{ijk} tensor, where *y* is the direction along the principal (dipole moment) axis of the molecule. Contributions from all other components amount to less than ~5% of the *yyy* component. Within the framework of the SOS perturbation theory, the molecular hyperpolarizability can be related to all the excited states of the molecule in terms of energy, $\hbar\omega_{ng}$, transition dipole moment, r_{gn}, and dipole moment variation, $\Delta\mu_{gn}$, between ground and excited states. The hyperpolarizability determined by a sum over states expression can be partitioned into two contributions,[8] so-called two-level ($\beta_{ijk,2}$) terms and three-level ($\beta_{ijk,3}$) terms, such that $\beta_{ijk}(2\omega;\omega,\omega) = \beta_{ijk,2} + \beta_{ijk,3}$. Each two-level component in the sum for $\beta_{ijk,2}$ contains only two states, the ground and one excited state, while the three-level contributions involve a ground state and two excited states. Analysis of term contributions to the molecular hyperpolarizabilities of the present complexes indicates that the two-level terms dominate the NLO response (Table 3), as is usually the case.[8] Therefore, analysis of variables influencing $\beta_{ijk,2}$ can be used to understand the NLO response of the present complexes and its dependence upon the metal electronic properties. Moreover, the good agreement between relevant experimental and theoretical linear and nonlinear optical properties (Table 1) suggests that this theoretical formalism can be used with confidence to describe the second-order NLO response of the present complexes.

In the case of Ni(salophen), analysis of the theoretical results indicates that a single two-level term dominates the $\beta_{ijk,2}$ sum (Table 3). In other words, in this case the simple two-state model[8,13a] is a very good approximation, and the $\beta_{ijk,2}$ sum reduces to eq 1 where $\hbar\omega$ is the incident (laser) radiation

$$\beta_{yyy}(-2\omega;\omega,\omega) = \frac{3e^2}{2}\frac{\hbar\omega_{eg}r_{ge}^{2}\Delta\mu_{ge}}{[(\hbar\omega_{eg})^2 - (\hbar\omega)^2][(\hbar\omega_{eg})^2 - (2\hbar\omega)^2]} \tag{1}$$

frequency, and $\hbar\omega_{eg}$, r_{ge}, and $\Delta\mu_{ge}$ are, respectively, the energy,

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[22] The calculated dispersive enhancement of β_{vec} for Cu(salophen) is expected to be very low (see β_0 in Table 1). On the other hand, the static β_0 deduced according to the two-state model[13a] is -26.5×10^{-30} cm^5 esu^{-1}. This estimate should be considered qualitative at best, in view of the demonstrated nonvalidity of the two-state model in the case of the Cu(salophen) complex (vide infra).

[23] (a) Burland, D. M.; Miller, R. D.; Walsh, C. A. *Chem. Rev.* **1994**, *94*, 31. (b) Marks, T. J.; Ratner, M. A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 155.

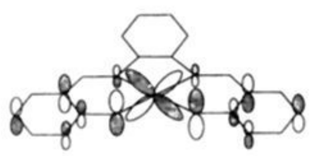
[24] Cheng, L.-T.; Tam, W.; Stevenson, S. H.; Meredith, G. R.; Rikken, G.; Marder, S. R. *J. Phys. Chem.* **1991**, *95*, 10631.

Table 3. Contributions of Two-Level ($\beta_{yyy,2}$) and Three-Level ($\beta_{yyy,3}$) Terms to the Main Tensor Component (β_{yyy}) of the Quadratic Hyperpolarizability (10^{-30} cm^5 esu^{-1}; $\hbar\omega = 0.92$ eV) for M(salophen) Complexes and the Energy ($\hbar\omega_{eg}$) and Composition of the Dominant Excited State Involved in the ($\beta_{yyy,2}$) Terms

compound	β_{yyy}	$\beta_{yyy,2}$	$\beta_{yyy,3}$	state (%)[a]	$\hbar\omega_{eg}$ (eV)	composition[b]	principal character
Co(salophen)	−99.88	−55.74	−44.14	D11 (43)	3.17	$0.20\chi_{60\to65} - 0.89\chi_{62\to64}$	Co (d_{xz}), O ($2p_z$), Ph (π) → C=N (π^*), Ph (π^*)
Ni(salophen)	−16.11	−23.21	7.10	S2 (95)	3.21	$0.17\chi_{61\to65} + 0.28\chi_{62\to65} - 0.90\chi_{63\to64}$	Ni (d_{xz}), O ($2p_z$) → C=N (π^*)
Cu(salophen)	−53.20	−40.18	−13.02	D5 (55)	2.99	$-0.58\chi_{62\to66} - 0.73\chi_{63\to65} - 0.16\chi_{63\to68}$	Cu (d_{xz}), O ($2p_z$), Ph (π) → C=N (π^*), Ph (π^*)

[a] S = singlet excited state; D = doublet excited state. Values in parentheses refer to the percent contribution of the excited state to $\beta_{yyy,2}$. [b] MO 63 is the HOMO in Ni(salophen) and Co(salophen). In the latter it represents the partially filled orbital. MO 64 is the HOMO in Cu(salophen) and represents the partially filled orbital.

the transition dipole moment, and the dipole moment variation, between the ground and first CT excited state. Therefore, the second-order NLO response of Ni(salophen) can be related to a single excited state involving the lowest energy CT transition. Both the experimental solvatochromic and theoretical data indicate that this transition is accompanied by a moderately negative dipole moment change between the ground and excited states (thus accounting for the measured negative β_{vec} value) and by an appreciable transition dipole moment value (Table 1). Analysis of the mixing coefficients of the CI expansion indicates that the Ni(salophen) HOMO (**1**) and LUMO (**2**) orbitals are mainly involved in the transition (Table 3). Analysis of these MOs indicates that the HOMO is principally composed of Ni ($3d_{xz}$) and O ($2p_z$) orbitals, while the LUMO involves the C=N groups and the π system within the phenylene ring.



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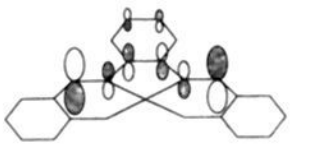

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On passing to Cu(salophen), the theoretical results indicate that the two-level contribution associated with the lowest CT excited (D5, Table 3) state accounts for ~55% of the $\beta_{yyy,2}$ sum. This contribution is comparable in magnitude to the $\beta_{yyy,2}$ sum found in Ni(salophen). Analysis of mixing coefficients of the configuration interaction (CI) expansion indicates that, in contrast to Ni(salophen), other Cu(salophen) MOs in addition to the SHOMO[25] and LUMO contribute substantially in the CI mixing (Table 3). The enhanced intensity of the lowest energy CT excitation (in terms of r_{ge}) observed both experimentally and theoretically as well as the smaller experimental and calculated $\Delta\mu_{ge}$ values of Cu(salophen), relative to those of Ni(salophen) (Table 1), are consequences of greater charge delocalization in the excited state. The sum of two-level terms involving the higher lying excited states results in a ~45% contribution to $\beta_{yyy,2}$. In particular, various higher lying states, having significant metal-to-ligand charge-transfer (MLCT) character,[26] contribute to the nonlinearity. Therefore, the stronger low-energy CT transition in addition to these higher lying MLCT states is responsible for the larger hyperpolarizability of Cu(salophen).

In the case of Co(salophen), analysis of two-level term contributions indicates that the D11 CT excited state accounts for *only* ~43% of the $\beta_{yyy,2}$ sum (Table 3). In analogy to the Ni(II) and Cu(II) complexes, this excited state mainly involves a transition from the SHOMO (Co ($3d_{xz}$), O ($2p_z$) in character) to the LUMO (C=N, π^*), mediated by the phenylene ring orbitals, thus resulting in appreciable experimental and calculated r_{ge} and $\Delta\mu_{ge}$ values, comparable to those of the Cu(II) complex (Table 2). The larger observed and calculated nonlinearity of Co(salophen) is due to the existence of additional low-lying MLCT states, as observed in the optical absorption spectrum (Figure 1, Table 2), involving the $3d_{xz,yz}$ metal orbitals and the C=N (π^*) and Ph (π^*) MOs. Moreover, in contrast to the Ni(II) and Cu(II) complexes, the theoretical analysis indicates that the $\beta_{yyy,3}$ sum also contributes substantially to the nonlinearity of Co(salophen) (Table 3).

Conclusions

This paper presents the first detailed experimental and theoretical investigation of the metal-dependent second-order NLO response of a homologous series of coordination (M(salophen)) complexes. Even if the ground-state properties of the complexes are rather similar (in terms of charge distribution), both experimental and theoretical data indicate that the excited states are appreciably different, and that the observed linear optical spectroscopic features on passing from Co(II) to Ni(II) and Cu(II) are consistent with the energetic stabilization of metal 3d subshells along the series. These electronic structural differences are reflected in the different second-order NLO response which is significantly larger in the Cu(II) and Co(II) complexes. While, for closed-shell Ni(salophen), the two-state model represents a suitable approximation for describing the nonlinearity, it clearly breaks down in the case of open-shell Cu(II) and Co(II) complexes, since other higher or lower lying states, respectively, having MLCT character, contribute to the nonlinearity. EFISH β_{vec} data as well as related β-determining parameters are fully consistent with the ZINDO-derived responses. The results of this study provide further evidence of the powerful capabilities of the ZINDO−SOS model even for predicting the frequency-dependent hyperpolarizability of open-shell doublet states and the attraction of coordination complexes as robust, highly efficient chromophores for second-order NLO materials.

Work is in progress to further probe the role of the metal d electron configuration on NLO response as well as to target and synthesize optimized high-hyperpolarizability transition metal chromophores.

Experimental Section

Starting Materials. Copper(II) acetate monohydrate ($Cu(Ac)_2 \cdot H_2O$; Aldrich) was used without purification. H_2salophen, Ni(salophen), and Co(salophen) were synthesized and purified as described elsewhere.[3,27] Chloroform solutions of Co(salophen) were stable under ambient atmosphere in the absence of Lewis bases.[27] Moreover, optical absorption spectra recorded under a nitrogen atmosphere using deoxygenated chloroform were found to be identical to those obtained under air.

Synthesis of Cu(salophen). A blue solution of $Cu(Ac)_2$ (1.26 g, 6.3 mmol) in 80 mL of H_2O was added to a boiling yellow solution of

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[25] The HOMO is represented by the partly filled MO.

[26] The overlapped nature of the lower wavelength feature in the optical spectrum of Cu(salophen) has precluded experimental evaluation of solvatochromic effects.

[27] (a) Chen, D.; Martell, A. E. *Inorg. Chem.* **1987**, *26*, 1026. (b) Marzilli, L. G.; Marzilli, P. A.; Halpern, J. *J. Am. Chem. Soc.* **1971**, *93*, 1374.

H_2salophen (2 g, 6.3 mmol) in 200 mL of ethanol, with stirring. After an initial dark green coloration, a brown precipitate was obtained. The mixture was stirred under reflux for 1.5 h. It was then allowed to cool to room temperature. The precipitate was collected, washed with an H_2O/ethanol mixture, and dried. The microcrystalline red-brown product was recrystallized from an absolute ethanol/chloroform mixture and dried in vacuo (1.9 g, 80% yield). The product is soluble in most common organic solvents, and is very soluble in chloroform. EI MS (70 eV, 30 °C) *m/z* (relative intensity): 377, 379 (M^+, 100, 45). Anal. Calcd for $C_{20}H_{14}N_2O_2Cu$: C, 63.56; H, 3.73; N, 7.41. Found: C, 63.11; H, 3.59; N, 7.22.

Physical Measurements. Elemental analyses were performed on a Carlo Erba 1106 elemental analyzer. Electron ionization (EI) and fast atom bombardment (FAB) mass spectra were recorded on a Kratos MS 50 double-focusing mass spectrometer equipped with a standard FAB source. Thermal measurements were performed with a Mettler 3000 system equipped with a TG 50 thermobalance, a TC 10 processor, and a DSC 30 calorimeter. The weight of the samples was between 15 and 20 mg for TGA and 4−8 mg for DSC. Thermal analyses were made either in air or under prepurified nitrogen using a 10 °C/min heating rate.

Spectroscopy. UV−vis spectra were recorded with a Beckman DU 650 spectrophotometer, and λ_{max} values are considered accurate to ±2 nm. Optical absorption spectra of M(salophen) in chloroform solution, recorded in the 5×10^{-3} to 2×10^{-6} M range, followed the Beer−Lambert law, thus indicating that the complexes are monomeric in solution.

The transition dipole moment, r_{ge}, between the ground and the excited states was evaluated from the oscillator strength, f, of the associated absorption band by the relationship[28]

$$r_{ge} = (2.13 \times 10^{-30} \nu f)^{1/2}\ (\text{esu·cm}) \qquad (2)$$

where ν is the energy (cm^{-1}) of the absorption maxima. The oscillator strength was determined from the integrated intensity of the absorption band by the expression[28]

$$f = 4.381 \times 10^{-9} \int \epsilon_\nu \, d_\nu \qquad (3)$$

The dipole moment variation between the ground and the excited states, $\Delta\mu_{ge}$, was determined from the solvatochromism of the relevant absorption band by means of the Lippert−Mataga equation[29]

$$\nu_{CT} = \nu_{CT}^{g} + C_1 \frac{n^2 - 1}{2n^2 + 1} + C_2 \left[\frac{D - 1}{D + 2} - \frac{n^2 - 1}{n^2 + 2}\right] \qquad (4)$$

where ν_{CT} is the frequency (cm^{-1}) of the optical transition in a particular solvent and D and n are the dielectric constant and refractive index of the solvent, respectively. The intercept, ν_{CT}^{g} is the frequency of the transition in the gas phase, and $C_2 = 2\mu_g\Delta\mu_{ge}/hca^3$ where μ_g is the ground-state dipole moment, h and c are Planck's constant and the speed of light, respectively, a is the Onsager radius, and $\Delta\mu_{ge}$ is the dipole moment change. The constant C_2 was determined from the least-squares fit of eq 4 to the absorption maxima of the CT band in 13 different solvents. $\Delta\mu_{ge}$ was calculated from C_2 with the measured value of the ground-state dipole moment and a value of the Onsager radius (6.5 Å) estimated from the solute molar volume.[11]

EFISH Measurements. Second-order molecular hyperpolarizability analyses were performed using a Q-switched mode-locked Nd:YAG laser operating at 1.34 μm ($\hbar\omega = 0.92$ eV) by the electric field induced second harmonic generation method.[13] The laser delivers pulse trains of total duration envelope around 90 ns, each pulse duration being 160 ps. The molecules to be measured were dissolved in chloroform (used as a reference) at various concentrations, x, between 5×10^{-3} and 10^{-4} M. The sign of $\bar{\beta}_{vec}$ (where $\bar{\beta}_{vec} = \beta_{yyy} + \beta_{yxx} + \beta_{yzz} \approx \beta_{yyy}$ for a one-dimensional charge-transfer molecule) was determined by studying the variation of the macroscopic susceptibility, $\Gamma(x)$, as a function of x. If $\bar{\beta}_{vec}$ is negative, Γ first decreases with increasing x, and cancels out when the contribution from the solvent is exactly compensated by that of the dissolved NLO molecule. The $\Gamma(x)$ value then increases because it is dominated by the contribution of the solute. Further details of the experimental methodology and data analysis are reported elsewhere.[13a,30] EFISH measurements were performed using fresh chloroform solutions.

The ground-state dipole moment was determined by the standard method of Guggenheim.[31]

Theoretical Methods. The all-valence INDO/S (intermediate neglect of differential overlap) formalism,[32] in connection with the sum over excited particle−hole states (SOS) formalism,[33] was employed. Details of the computationally-efficient ZINDO−SOS-based method for describing second-order molecular optical nonlinearities have been reported elsewhere.[8,34] Standard parameters and basis functions were used.[32] In the present approach, the closed-shell restricted Hartree−Fock (RHF) formalism was adopted for the Ni(II) complex, while the open-shell restricted Hartree−Fock (ROHF) formalism was adopted for the Cu(II) and Co(II) analogues. Thus, the closed-shell $^1A_1$ ground-state configuration was studied for the Ni(II) complex, while the $^2A_2$ $(d_{xy})^1$ and $^2A_1$ $(d_{z^2})^1$ ground states were studied for the Cu(II) and Co(II) complexes, respectively. The monoexcited configuration interaction (MECI) approximation was employed to describe the excited states (singlet states for the Ni(II) complex and doublet states for the Cu(II) and Co(II) analogues). In all calculations, the lowest 160 energy transitions between SCF and MECI electronic configurations were chosen to undergo CI mixing and were included in the SOS. Further theoretical details of the implementation of the ZINDO code to the calculation of hyperpolarizability of open-shell doublet systems are reported elsewhere.[12] Metrical parameters used for the calculations were taken from related crystal structure data.[16−18,35] Calculations were performed assuming a C_{2v} planar geometry.

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(28) Reference 7c, p 114.

(29) Mataga, N.; Kubota, T. *Molecular Interactions and Electronic Spectra;* Marcel Dekker: New Work, 1970; p 371.

(30) Ledoux, I.; Zyss, J. *Chem. Phys.* **1982**, *73*, 203.

(31) Guggenheim, E. A. *Trans. Faraday Soc.* **1949**, *45*, 203.

(32) (a) Zerner, M.; Loew, G.; Kirchner, R.; Mueller-Westerhoff, U. *J. Am. Chem. Soc.* **1980**, *102*, 589. (b) Anderson, W. P.; Edwards, D.; Zerner, M. C. *Inorg. Chem.* **1986**, *25*, 2728. (c) Bacon, A. D.; Zerner, M. C. *Theor. Chim. Acta (Berlin)* **1979**, *53*, 21. (d) Ridley, J.; Zerner, M. C. *Theor. Chim. Acta (Berlin)* **1973**, *32*, 111.

(33) Ward, J. F. *Rev. Mod. Phys.* **1965**, *37*, 1.

(34) Kanis, D. R.; Marks, T. J.; Ratner, M. A. *Int. J. Quantum Chem.* **1992**, *43*, 61.

(35) Gaetani Manfredotti, G.; Guastini, C. *Acta Crystallogr.* **1983**, *C39*, 863.