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Sizable Second-Order Nonlinear Optical Response of Donor–Acceptor Bis(salicylaldiminato)nickel(II) Schiff Base Complexes

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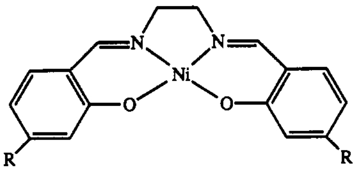
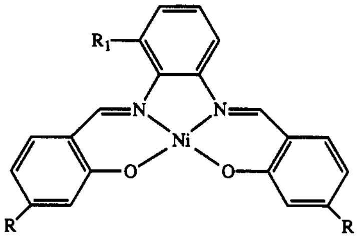
Considerable interest is currently associated with the synthesis of thermally stable, molecule-based materials having large second-order nonlinear optical (NLO) responses.[1] Crucial prerequisites for achieving large second-order NLO responses are that the individual constituents have large molecular responses and that they be arranged in a noncentrosymmetric architecture.[1] Considerable effort has been directed toward the molecular engineering of such structures, and a variety of strategies has emerged.[1] This activity has, however, focused primarily on organic systems due to the high polarizability of the π-electron networks and, hence, to the large second-order molecular responses.[1,2] Despite these extensive studies, only recently have transition metal organometallic and, to a far lesser extent, coordination complexes emerged as potential building blocks for second-order NLO materials.[3–6] Coordination complexes offer a large variety of novel structures, the possibility of high environmental stability, and a diversity of tunable electronic properties by virtue of the coordinated metal center.[6] We report here the synthesis, linear optical spectroscopic, and sizable second-order nonlinear response of a thermally robust series of donor-acceptor substituted bis(salicylaldiminato)nickel(II) complexes. The basic strategy is to assemble noncentrosymmetric chelate molecules by straightforward condensation[7–10] of substituted salicyclaldehydes with 1,2-diamines such as ethylenediamine (H_2salen) and *o*-phenylendiamine (H_2salophen), followed by Ni^{+2} incorporation[11,13] (Chart 1). We also present a theoretical analysis, using the well-established ZINDO-SOS formalism,[5,14] which elucidates the origin of the NLO response and how it depends upon molecular architecture.

Chart 1



R = H	Ni(salen) (1)
R = OMe	Ni(*4*-OMe-salen) (2)



R = H;	R_1 = H	Ni(salophen) (3)
R = H;	R_1 = NO_2	Ni(sal-*3*-NO_2-ophen) (4)
R = OMe;	R_1 = NO_2	Ni(*4*-OMe-sal-*3*-NO_2-ophen) (5)

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(6) Sizable hyperpolarizabilities have been reported for octupolar trisbipyridineruthenium complexes.[3b]

(7) All Schiff's bases were prepared using standard procedures[8] involving reaction of the appropriate salicylaldehyde[9] with the corresponding diamine[10] (2:1 molar ratio) in ethanol. The yellow imines were purified by recrystallization from ethanol.

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(10) H_2salophen and H_2(*3*-NO_2-salophen) (Aldrich) were purified by sublimation in vacuo.

(11) (a) The complexes were prepared[8a,12] by reaction of an aqueous or methanolic solution of nickel acetate ($Ni(OAc)_2 \cdot 4H_2O$)[9] with an alcoholic solution of the corresponding Schiff's base ligand. The complexes were then purified by recrystallization from ethanol and/or chloroform. The complexes were characterized by EI, FAB mass spectrometry, and UV–vis, ^1H NMR spectroscopy.[11b] The complexes gave satisfactory elemental analyses.[11b] (b) See supplementary material.

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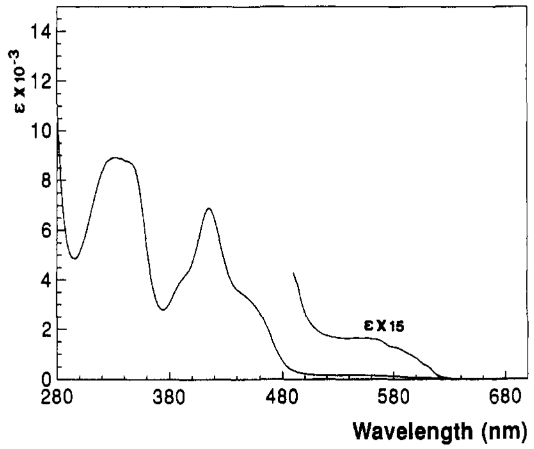

Figure 1. Optical absorption spectrum of Ni(salen) in chloroform solution.

The present four-coordinate Ni(II) complexes consist of acentric, essentially planar structures with significant thermal stability as judged by TGA measurements. For example, **3** and **5** exhibit <1% weight loss up to 250 °C.[16] The free ligands possess centrosymmetric trans-planar,[17] or distorted cis-like structures,[18] pressaging, vanishing or smaller (compared to the metal complexes) NLO response (vide infra). These Ni(II) complexes exhibit interesting linear optical spectroscopic features which will be seen to be related to the second-order NLO response. The optical absorption spectrum[19] (>280 nm) of archetypical Ni(salen) (Figure 1) consists of two overlapping principal features assigned[20] to two different types of transitions. There is a broad band ($\epsilon \approx 8800$ in $CHCl_3$ solution) in the region between 300 and 360 nm involving mainly intraligand $\pi \rightarrow \pi^*$ transitions, and a relatively intense structure in the 400–480-nm region, absent in the absorption spectrum of the free ligand, involving both the ligand and metal center. Moreover, the band at 414 nm ($\epsilon = 6900$ in $CHCl_3$ solution) exhibits a solvatochromic shift, characteristic of a large dipole moment change ($\Delta\mu$) between the ground and the excited state, and frequently suggestive of a large hyperpolarizability.[1,2] Importantly, a negative solvatochromism, i.e., a hypsochromic (blue) shift with increasing solvent polarity, is observed, thus indicating a reduction of the dipole moment upon electronic excitation.[21] Finally, a weak feature ($\epsilon \approx 100$) assigned to "d–d" transitions,[20] is present in the 500–600-nm region. ZINDO-SOS calculations[22] account well for the experimental linear optical spectroscopic features, and satisfactory agreement between calculated and observed transitions energies is found (Table 1). In particular, the charge-transfer (CT) band at 414 nm may be characterized as principally $\pi \rightarrow \pi^*$ (HOMO → LUMO) in character, essentially involving the metal $d_{xz} + O_{2p}$ and the C=N orbitals, and is mainly responsible for the second-order NLO response (vide infra). Moreover, the calculated negative $\Delta\mu_{ge}$ (−4.1 D) value associated with this transition is in good agreement with that determined from the negative solvatochromism (−3.4 D).[23]

Table 1. Comparison of ZINDO-Derived[a] and Experimental Transition Energies[b] of Ni(salen)

exc state	sym	λ^{calc}	$f^{calc\ c}$	$\lambda_{max}{}^{expt}$	$f^{expt\ c}$	main character
S1	B_1	422	0.008	540	0.00	$d_{z^2} \rightarrow d_{xy}$
S2	B_2	368	0.043	446	0.03	$d_{xz} \rightarrow d_{xy}$
S3	B_1	364	0.029			$d_{xz}, O_{2p} \rightarrow C{=}N$
S4	A_1	360	0.257	414	0.07	$d_{xz}, O_{2p} \rightarrow C{=}N$
S5	A_2	342	0.005	392 (sh)		$d_{yz} \rightarrow d_{xy}$
S8	B_1	293	0.508	332	0.15	$\pi \rightarrow \pi^*$
S12	B_1	277	0.180			$\pi \rightarrow \pi^*$

[a] Singlet excited states (S). [b] Transition energies (λ_{max}) in nm. [c] Oscillator strength.

Solution-phase hyperpolarizabilities (β_{vec})[24] were measured using electric field induced second harmonic generation (EFISH) techniques described previously (Table 2).[25–28] The β_{vec} values are rather large for coordination complexes,[3–6] ranging from $\sim -10 \times 10^{-30}$ cm^5 esu^{-1} ($\hbar\omega$ = 0.92 eV), similar to that of the classic organic chromophore *p*-nitroaniline,[14] to $\sim -55 \times 10^{-30}$ cm^5 esu^{-1} ($\hbar\omega$ = 0.92 eV),[30] rivalling β_{vec} values reported for efficient, thermally robust second-order organic chromophores such as 4,4′-donor–acceptor substituted stilbenes.[14,29] For example, $\mu\beta_{1300}$(**5**) = -546×10^{-48} esu vs 662×10^{-48} esu for 4-(*N*,*N*-dimethylamino)-4′-nitrostilbene.[29] The present computationally derived[22] hyperpolarizability parameters compare well with experimental data (Table 2). The EFISH measurements on the H_2salen and H_2salophen free ligands indicate very small ($<1 \times 10^{-30}$ cm^5 esu^{-1}) β_{vec} values,[27] illustrating the efficacy of metal complexation in "switching on" NLO response. Thus, the calculated β_{vec} value for the H_2salophen ligand is 3.11×10^{-30} cm^5 esu^{-1} ($\hbar\omega$ = 0.92 eV) even assuming an idealized cis structure,[18] i.e., ~5× smaller than that calculated for the related Ni(II) complex (see Table 2).

A detailed analysis of the computational results indicates that the second-order response of the present Ni(salen) complexes is dominated in all instances by the intense,

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(19) UV–vis spectra were recorded with an HP 8452A diode array spectrophotometer.

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(21) Representative λ_{max} (solvent) data for **1** in nm: 423 (toluene), 414 chloroform, 410 (acetone), 406 (acetonitrile), 400 (methanol).

(22) (a) Metrical parameters used for the calculations were taken from crystal structure data[15,17] or reasonable estimations.[22b] Standard ZINDO transition-metal parameters were employed,[5] and the sum-over-state (SOS) monoexcited configuration interaction (MECI) method,[5,14] including the 160 lowest energy transitions, was used to compute the elements of the β tensor. (b) Kanis, D. R.; Marks, T. J.; Ratner, M. A. *Int. J. Quantum Chem.* **1992**, *43*, 61.

(23) (a) Determined from the solvatochromism of the absorption band in twelve different solvents by means of the Lippert-Mataga equation.[23b] (b) Mataga, N.; Kubota, T. *Molecular Interactions and Electronic Spectra*; Marcel Dekker: New York, 1970; p 371.

(24) Vector component along the dipole moment direction.[1,5]

(25) EFISH measurements[26] were performed using a Q-switched Nd:YAG laser operating at 1.34 μm ($\hbar\omega$ = 0.92 eV) and delivering 60-ns pulses. Details of the EFISH measurements will be reported elsewhere.[27] Since EFISH gives the scalar product $\mu_g\beta$, ground-state dipole moments were measured independently by standard methods.[28]

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(30) This β_{vec} value refers to that obtained from the calculated dipole moment.

(31) The calculations at zero frequency indicate that the dispersive enhancement of β_{vec} for compounds **4** and **5** is no greater than a factor of 2 and is negligible for compounds **1**–**3**.

Table 2. Comparison of ZINDO-Derived and Experimental Linear Optical Spectroscopic[a] and Nonlinear Optical Properties[b] of Bis(salicylaldiminato)nickel(II) Complexes

compd	λ_{max}^{expt} ($\epsilon \times 10^{-3}$)	λ^{calc}	f^{calc} [c]	μ^{expt} [d]	μ^{calc} [d]	$\Delta\mu_{ge}^{calc}$ [e]	β_t^{calc} [e]	β_{vec}^{calc}	β_{vec}^{expt}	$\mu\beta_{vec}^{expt}$	$\mu\beta_{vec}^{calc}$
1	414 (6.9)[f]	360	0.26	8.9[f]	8.4	−4.1	−4.8	−10.1	−9.3[f]	−85	−85
2	398 (8.6)[f]	352	0.31	8.6[f]	8.4	−3.7	−4.0	−12.9	−9.6[f]	−108	−83
3	480 (9.0)[f]	387	0.44	7.0[f]	8.5	−5.3	−17.4	−17.3	−20.5[f]	−147	−144
4	570 (9.3)[g]	485	0.18	*h*	7.7	−12.5	−36.8	−38.7	−43[g,i]	−298[g]	−331
5	570 (13.1)[g]	491	0.18	*h*	9.9	−11.6	−47.3	−55.2	−55[g,i]	−546[g]	−545

[a] Transition energies (λ_{max}) in nanometers. [b] All hyperpolarizability data are in units of 10^{-30} cm^5 esu^{-1}; estimated uncertainties are ±10%; $\hbar\omega$ = 0.92 eV. [c] Oscillator strength. [d] Ground-state dipole moment in debye; estimated uncertainties are ±0.3 D. [e] See eq 1. [f] Chloroform solution. [g] Acetone solution. [h] Complex insufficiently soluble for accurate measurement. [i] Estimated using calculated dipole moment.

low-energy HOMO → LUMO CT excitation mentioned above. In such cases, the quadratic hyperpolarizability can be related to the two-state contribution[1,26c] (eq 1).

$$\beta_t = \frac{3e^2}{2} \frac{\hbar\omega_{ge} f \Delta\mu_{ge}}{[(\hbar\omega_{ge})^2 - (\hbar\omega)^2][(\hbar\omega_{ge})^2 - (2\hbar\omega)^2]} \qquad (1)$$

Here $\hbar\omega$ is the incident (laser) radiation frequency, $\Delta\mu_{ge}$ is the dipole moment change between the excited and ground state, $\hbar\omega_{ge}$ is the energy, and f is the oscillator strength of the optical transition involved in the two-state process. Therefore, the increasing β_{vec} values on passing from **1** to **5** can be related directly to the increasing CT character, hence greater $\Delta\mu_{ge}$ values, and to the bathochromic shift of the β-determining CT transition (Table 2). This is a direct consequence of the partially acquired donor (4-OMe) and/or acceptor (3-NO$_2$-ophen) character of the two states involved.

In conclusion, this contribution illustrates a synthetic strategy for obtaining thermally stable noncentrosymmetric coordination complexes having sizable second-order NLO responses, tunable by the metal center. The present Ni(II) complexes possess appreciable microscopic nonlinearities, and represent a new class of second-order NLO transition-metal chromophores. Our results again illustrate the power of semiempirical computational formalisms in targeting structures with high second-order responses and in understanding their properties. Finally, the thermal stability of these molecules renders them intriguing candidates for NLO investigations in glassy polymer matrices. Further work in this direction is in progress.

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Supplementary Material Available: Analytical data (EI and FAB MS, ^{1}H NMR, elemental analysis) of compounds **1–5** (1 page). Ordering information is given on any current masthead page.