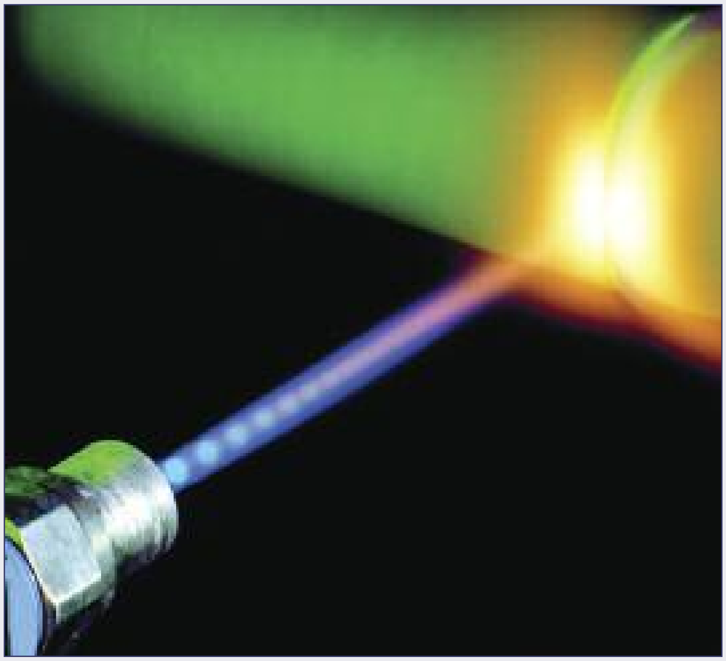

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SCHIFF BASE METAL COMPLEXES FOR SECOND ORDER NONLINEAR OPTICS

The research in the development of new materials suitable for NLO purposes has increased in the last few decades. Coordination metal complexes with tetradentate Schiff base ligands are a good target to aim to, since they are robust, chemically and physically stable, and the degrees of variability that can lead to an enhancement of the NLO responses are great. All the chemical variations on the molecular structures (changes of the ligand skeleton and metals) studied are here reported, without going into details, in order to underline the fundamental role of the metal centre in the NLO properties and all the possible developments in the research in this specific field.

Nonlinear optics (NLO) is the study of all the phenomena that occur from the interaction of intense light with matter [1, 2]. The interaction with a nonlinear optical material causes a modification of the optical properties of the system, and the next photon that arrives sees a different material. Typically only laser light is sufficiently intense to generate NLO phenomena; therefore the beginning of this research field is often taken to be the discovery of second-harmonic generation by Franken *et al.* in 1961 [3], the year after the construction of the first laser by Maiman [4].

NLO interactions cause changing in frequency, phase, polarization or path of incident light, and are ‘nonlinear’ because the response of a system to the applied optical field depends in a nonlinear manner upon the strength of the optical field. The chemist’s goal is to develop materials that control this interaction in order to modulate or combine photons (wave mixing), fine tuning both the magnitude and response time of the optical process.

The electric field of light, **E**, interacts with a molecule producing a force that displaces the electron density away from the nucleus, resulting in a charge separation, *i.e.* an induced polarization **p**. For small fields the charge displacement from the equilibrium position is proportional to the strength of the applied field through the equation

$$\mathbf{p} = \alpha\mathbf{E} \qquad (1)$$

where α is the linear polarization coefficient.

Application of a symmetric electric field **E** can lead to an asymmetric polarization response, when the restoring force on the electrons within the molecule is not linearly proportional to its displacement during the polarization process (nonlinear phenomenon). The polarization wave can show diminished maxima in one direction and accentuated maxima in the opposite direction. This asymmetric polarization **p** can be decomposed into a DC polarization component and other ones at the fundamental and the second harmonic frequencies (Fig. 1). These second-order NLO effects can only be induced by molecules and materials lacking a centre of symmetry (in order to allow an asymmetric restoring force), usually with dipolar D–π–A structure, where D and A are electron acceptor and electron donor groups, respectively, and π is a conjugated system (bridge).

The common mathematical approximation of the nonlinear molecular polarization **p** is given by a Taylor series expansion:

$$\mathbf{p} = \alpha\mathbf{E} + \beta\, \mathbf{E}\bullet\mathbf{E} + \gamma\, \mathbf{E}\bullet\mathbf{E}\bullet\mathbf{E} + \dots \qquad (2)$$

The light-induced dipole moment $\boldsymbol{\mu}$ of the molecule is given by the sum of the static dipole $\boldsymbol{\mu}_g$ in the absence of an electric field and the polarization **p**

$$\boldsymbol{\mu} = \boldsymbol{\mu}_g + \mathbf{p} = \boldsymbol{\mu}_g + \alpha\,\mathbf{E} + \beta\,\mathbf{E}\bullet\mathbf{E} + \gamma\,\mathbf{E}\bullet\mathbf{E}\bullet\mathbf{E} + \dots \qquad (3)$$

The terms beyond $\alpha\mathbf{E}$ are not linear in **E**: they are referred to as the nonlinear polarization and give rise to nonlinear optical effects. β and γ are the first and second hyperpolarizabilities, respectively.

The observed bulk nonlinear polarization **P** is given by an expression analogous to equation (3):

$$\mathbf{P} = \mathbf{P}_0 + \chi^{(1)}\,E + \chi^{(2)}\,\mathbf{E}\bullet\mathbf{E} + \chi^{(3)}\,\mathbf{E}\bullet\mathbf{E}\bullet\mathbf{E} + \dots \qquad (4)$$

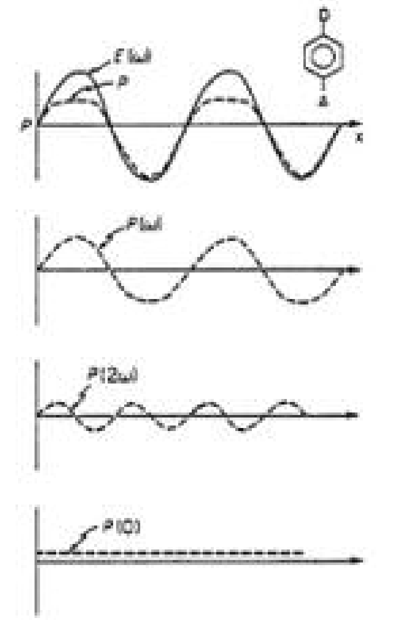


Fig. 1 - Polarization p of the prototype dipolar molecule D-π-A along the x axis, caused by the electric field E(ω), and its Fourier components at 0, ω and 2ω frequencies

where $\mathbf{P}_0$ is the built-in static dipole of the bulk sample.

$\chi^{(i)}$ are the susceptibility coefficients of *i* order. The relation between the microscopic α, β, γ, etc. hyperpolarizabilities and the macroscopic $\chi^{(1)}$, $\chi^{(2)}$, $\chi^{(3)}$, etc. susceptibilities has been done by the number of molecules in the volumetric unit N_m and local field factors f_ω, that depend from the laser frequency.

In 1977 [5], Oudar proposed a simplified approach for studying the electronic state of the polarized molecules in which only the first molecular excited state is taken into account, and assuming that only one tensor component (β_{iii}) dominates the NLO response (case of a unidirectional charge-transfer CT transition). This so called 'two-state' model is a very good approximation for estimating the frequency-dependent (dynamic) first hyperpolarizability for most of the NLO chromophores, when a single CT state dominates the NLO response. It implies that frequency doubling will be enhanced near resonance, that is, when the input (laser) frequency or the second harmonic approaches the frequency of the lowest optical CT transition. This model is of great value to chemists because it allows a simple, direct analysis of β-determining parameters and, hence, a chemical interpretation of molecular NLO properties through easily accessible optical spectra.

The charge-transfer contribution to hyperpolarizability, β_{CT}, within the Oudar's "two-state" model is given by this equation:

$$\beta_{CT} = 3(\Delta E^2_{eg}\mu^2_{eg}\Delta\mu_{eg})/2[(\Delta E^2_{eg}-E^2_L)(\Delta E^2_{eg}-4E^2_L)] \qquad (5)$$

where ΔE_{eg} is the transition energy, μ_{eg} is the transition dipole moment, $\Delta\mu_{eg}$ is the dipole moment variation between the ground and the excited state, and E_L is the energy of the laser used, for example, for EFISH measurements (see below). It is also possible to isolate the $\beta_{0,static}$ value from the dependence on E_L, reprocessing the former equation in the following formula [6, 7]:

$$\beta_{CT} = \beta_{0,static}F(\omega) =$$
$$= [(3\mu^2_{eg}\Delta\mu_{eg})/2\Delta E^2_{eg}]\{\Delta E^4_{eg}/[(\Delta E^2_{eg}-E^2_L)(\Delta E^2_{eg}-4E^2_L)]\} \qquad (6)$$

where the second term is the dispersion factor F(ω). As said before, all the quantities occurring in the expression of β_{CT} can be determined by simple UV-visible spectroscopic measurements [8-12]. The most used instrumental technique to evaluate the first hyperpolarizability β is the Electric Field Induced Second Harmonic generation (EFISH) [13], in which the dipolar molecules are aligned along the $\boldsymbol{\mu}_g$ direction and a laser at frequency ω induces the electronic transition, with the following generation of the light at double frequency 2ω.

The current intense research activity in second-order nonlinear optical (NLO) molecule-based materials has produced a wide variety of new chromophores [2, 14, 15]. Among them, molecules with D–π–A structure have been studied in great details, and in particular organic compounds [16]. These molecules are polarizable non-centrosymmetric systems in which an electron donor, D, and an electron acceptor, A, group are linked through delocalized π systems, which provide the polarizable electrons.

More recently, organometallic and coordination complexes have represented an emerging and growing class of materials [17]. Compared to organic molecules, they offer not only a larger variety of molecular and bulk structures, but also the possibility of high environmental stability and a diversity of electronic properties by virtue of the coordinated metal centre. Since 1987, when Green *et al* reported a good second-harmonic generation (SHG) efficiency by a ferrocenyl derivative [18], attention has been paid to metal complexes as potential second-order NLO materials, in which the donor and/or the acceptor, or the bridge moieties, are selectively replaced by an organometallic fragment.

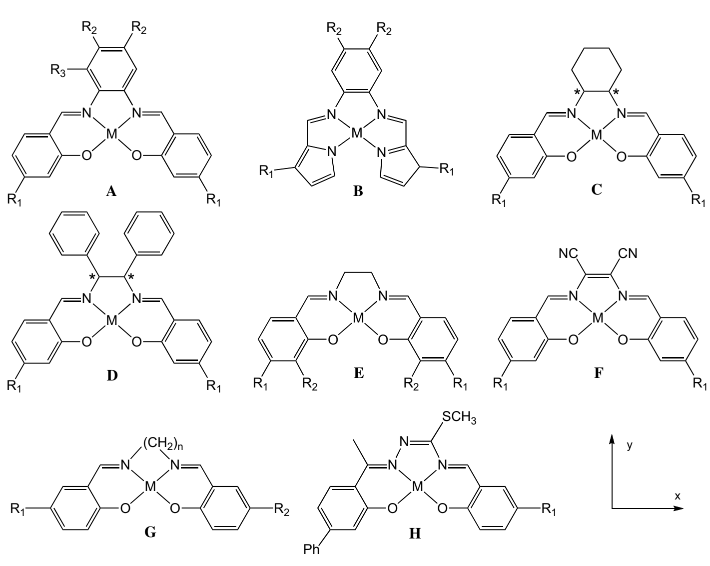
Schiff Base Metal Complexes for Nonlinear Optics

Salen-type Schiff base complexes have been quite extensively studied for the past years with respect to their application in such a field. The first publication appeared in 1991 [19], where [M^{III}(salen)]$^+$ (M = Cr, Mn, Fe) moieties were part of an inorganic coordination polymer through py-NHCH$_2$-X$^-$ (-X$^-$ = -COO$^-$, -SO$_3^-$) linkages. However, in these systems the metal-salen core was just used to enhance the NLO response of the apical substituted pyridine, and not directly involved. Santo Di Bella, Pascal Lacroix, Isabelle Ledoux and Tobin Marks started in 1994 [20] a systematic approach at a molecular point of view to the study of this class of coordination compounds as potentially applicable NLO materials.

One of the main reasons to choose tetradentate Schiff base metal complexes is their great thermal stability: almost all of them don't decompose up to 250 °C and this is an important feature for NLO materials, in order to use strong laser sources with very high local temperatures and energies, without causing damages and loss of efficiency. Also, the degree of variability in such systems is great, considering all the different substitution positions (use of different diamines and carbonyl derivatives) and the variety of metals that give stable and handle compounds with these ligands. The latter feature is very important because the metal centre has a powerful active role, due to the opportunity to change its oxidation state and therefore d configuration, leading to a different activity of the metal in the electronic system of the complex (the metal can act as donor, acceptor or electronic bridging group lowering charge transfer transitions in energy).

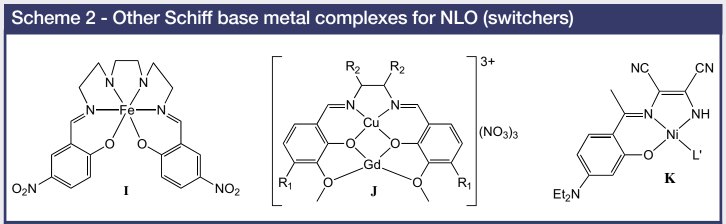
Schemes 1 and 2 show the salen-type Schiff base compounds studied in the last decades, and in 2001 two reviews were written on this topic by Lacroix [6] and Di Bella [7]. All the NLO values available are listed in Tab. 1. Almost all the ligands derive from the condensation of differently substituted salicylaldehydes (compounds **A**, **C**, **D**, **E**, **F**, **G**, **I**, **J**) and different

Scheme 1 - Tetradentate Schiff base metal complexes studied for NLO applications



Comp.	R$_1$	R$_2$	R$_3$	M (+2)	Ref.
A1	H	H	H	Co	[9,23,28]
A2	H	H	H	Cu	[9,23,28]
A3	H	H	H	Ni	[9,20,23,24,28]
A4	H	H	NO$_2$	Ni	[20,24,28]
A5	OMe	H	H	Ni	[24,28]
A6	OMe	H	NO$_2$	Ni	[20,23,24,28]
A7	OMe	H	NO$_2$	Co	[23]
A8	NEt$_2$	H	H	Ni	[31]
A9	NEt$_2$	NO$_2$	H	Ni	[26,28,31]
A10	OH	Cl	H	Ni	[28]
A11	NEt$_2$	Cl	H	Ni	[28,30,31]
B1	H	H	–	Ni	[33]
B2	H	Cl	–	Ni	[33]
B3	OMe	Cl	–	Ni	[33]
C1	NEt$_2$	–	–	Ni	[25,26,27]
C2	NEt$_2$	–	–	MnCl	[25]
D1	NEt$_2$	–	–	Ni	[27]
E1	H	H	–	Ni	[20,24,28]
E2	OMe	H	–	Ni	[20,24,28]
E3	H	H	–	Fe(X)(4-Y-py)	[21]
E4	OMe	OMe	–	Cu	[32]
E5	OMe	OMe	–	Ni	[32]
F1	NEt$_2$	–	–	Ni	[22,26,28]
F2	NEt$_2$	–	–	Cu	[22,28]
F3	NEt$_2$	–	–	Zn	[22]
G1 (n=2)	H	H	–	Cu	[12]
G2	H	Me	–	Cu	[12]
G3	H	OMe	–	Cu	[12]
G4	H	NMe$_2$	–	Cu	[12]
G5	NO$_2$	H	–	Cu	[12]
G6	NO$_2$	Me	–	Cu	[12]
G7	NO$_2$	OMe	–	Cu	[12]
G8	NO$_2$	NMe$_2$	–	Cu	[12]
G9 (n=3)	H	H	–	Cu	[12]
G10	H	Me	–	Cu	[12]
G11	H	OMe	–	Cu	[12]
G12	H	NMe$_2$	–	Cu	[12]
G13	NO$_2$	H	–	Cu	[12]
G14	NO$_2$	Me	–	Cu	[12]
G15	NO$_2$	OMe	–	Cu	[12]
G16	NO$_2$	NMe$_2$	–	Cu	[12]
H1	H	–	–	Ni	[35]
H2	N=NPh	–	–	Ni	[35]
H3	H	–	–	Cu	[35]
H4	N=NPh	–	–	Cu	[35]
H5	H	–	–	Zn	[35]
H6	N=NPh	–	–	Zn	[35]
H7	H	–	–	VO	[35]
H8	N=NPh	–	–	VO	[35]

Scheme 2 - Other Schiff base metal complexes for NLO (switchers)



Compound	R_1	R_2	L'	Ref
I1	–	–	–	[29]
J1	H	H	–	[32]
J2	OMe	H	–	[32]
J3	OMe	Ph (1R,2R)	–	[32]
K1	–	–	$MePhCHNH_2$	[36]
K2	–	–	$^iPrNH_2$	[36]
K3	–	–	py	[36]
K4	–	–	PPh_3	[36]

aliphatic, aromatic or chiral primary diamines (with the exception of **I1**, where triethylentetramine is used); only very few cases have been studied with different carbonyl derivatives (compounds **B**, **H** and **K**). One of the most studied metals has been nickel. In its +2 oxidation state, nickel has a d^8 electronic configuration, and needs 4 electron donating pairs to reach the stable 16-electron, square planar geometry. Tetradentate bis-anionic Schiff bases are perfect ligands to suit this metal, giving neutral, very stable and resistant complexes, as already remarked above.

The largest number of complexes studied is derived from [M(salophen)] (compounds **A**), with different metal centres (but in particular Ni) and varied substitutions on the three aromatic rings. Importantly, it has been proven by theoretical analysis that the NLO response of [Ni(salophen)] complexes is dominated by the HOMO → LUMO (CT) transition, in which the nickel atom acts as a donor. Without going into details, the NLO properties of these compounds are enhanced with dipolar D–π–A structure, where the presence of donating D groups in position 4 of salicylaldehydes and withdrawing A groups on the diamine phenyl bridge increases the charge asymmetry along the *y*-axis of the [M(salophen)] basic structure and shifts the charge transfer bands at lower energies (red shift), enhancing the efficiency. In particular, NO_2 is the best acceptor group and NEt_2 the best donor group (compound **A9**, with a β_{vec} value of 198 10^{-30} cm^5 esu^{-1} [26, 28, 31]) in such systems. CN groups as acceptors are also very efficient in enhancing the NLO responses (compounds **F** and **K**). In all these cases, once the metal atom is introduced in the ligand skeleton, there is an enhancement of the intramolecular charge transfer, leaving unvaried its direction along the *y*-axis. Positive values are due to the increase of the dipole moment from the ground to the excited state, whereas negative figures mean a diminishing of the charge separation.

Chiral complexes with enantiomerically pure 1,2-diaminocyclohexane and 1,2-diphenyl-diaminoethane have been synthesised in order to obtain asymmetric crystals suitable for NLO measurements in the solid state. With the Kurtz powder technique [34], the NLO efficiency of a material is tested with respect to the reference compound urea (whose second harmonic generation – SHG – is equal to 1), and the values are relative to it. The research in this direction is however very limited for the moment, but this means that the possibilities of new discovers are huge.

Our group started in 2006 a systematic research on new unsymmetrically substituted tetradentate Schiff base metal complexes [12]. The first metal used was Cu, and the synthesised compounds **G** have a push-pull substitution along the *x*-axis. This kind of ligands with a D–π–A charge asymmetry leads to a first LMCT (ligand-to-metal charge transfer) band at low

Tab. 1 - Second order NLO values for Schiff base metal complexes (see Schemes 1 and 2)

Compound	$\mu_g\ \beta_{vec}\ 10^{-30}$ ($D\ cm^5\ esu^{-1}$) [#]	μ_g (D)	$\beta_{vec}\ 10^{-30}$ ($cm^5\ esu^{-1}$) [#]	SHG (urea) [§]
A1	–1340 [b]	7.7 [d]	–170	–
A2	–350 [b]	7.0	–50.0	–
A3	–147 [b]	7.0	–20.5	–
A4	–331 [b]	7.7 [d]	–43	–
A5	–126 [b]	5.5	–23	–
A6	–546 [b]	6.9 [d]	–79	–
A8	–	3.2 [d]	37.2 [d]	–
A9	1530 [c]	7.7 [d]	198	–
A11	157 [b]	3.3 [d]	47	–
B1	–	–	–	1.2 [a]
C1	–	–	–	0.3 [a], < 0.25 [c]
C2	–	–	–	0.5 [a], 8 [c]
D1	–	–	–	13 [a]
E1	–85 [b]	8.9	–9.3	–
E2	–108 [b]	8.6	–9.6	–
E3	–	–	–	2.00 ($X=N_3^-$,Y=H) [a]
E4	–	6.0	–6.5 [a]	–
E5	–	6.0	–10.5 [a]	–
F1	1457 [b], 800 [c]	6.2	235 [b], 129 [c]	–
F2	1360 [b]	6.8	200	–
F3	–	6.5	400 [b]	–
G1	108 [c]	5.8 (6.1 [d])	18	–
G2	268 [c]	5.8 (6.0 [d])	45	–
G3	205 [c]	4.9 [d]	42	–
G4	–	6.2 [d]	–	–
G5	540 [c]	9.2 (9.8 [d])	55	–
G6	–	10.1 [d]	–	–
G7	493 [c]	9.6 [d]	51	–
G8	672 [c]	10.9 [d]	62	–
G9	310 [c]	5.9 [d]	53	–
G10	–	5.7 [d]	–	–
G11	479 [c]	4.6 [d]	104	–
G12	498 [c]	5.6 [d]	106	–
G13	540 [c]	10.1 (10.3 [d])	58	–
G14	–	10.6 [d]	–	–
G15	–	9.8 (9.9 [d])	–	–
G16	560 [c]	10.6 (11.2 [d])	50	–
H2	–176 [c]	2.4	–73	–
H4	–538 [c]	2.3	–234	–
H5	–340 [c]	3.9	–87	–
H6	–1650 [c]	5.9	–280	–
H8	–200 [c]	2.4	–83	–
J3	–	–	–	0.3 [a]
K1	–	11	17.5 [c]	–

[#] EFISH technique [13]; [§] Kurtz powder technique [34]; [a] at 1.064 μm (1.17 eV); [b] at 1.34 μm (0.92 eV); [c] at 1.907 μm (0.65 eV); [d] theoretical values energy from the donating moiety to copper, followed by a stronger CT band toward the acceptor A fragment. The use of different D and A groups yields to fine tune of the electronic properties of these complexes, in which the directions of μ_g and β are tilted and not coincident (especially when the NO_2 group is present), as confirmed by theoretical calculations.

Further studies on the use of different metals and different ligands are ongoing. A similar approach has been used recently by Gradinaru *et al* [35], with unsymmetrical Schiff base metal complexes of semicarbazide derivatives (compounds **H**), where the effect of different metals has been tested.

On the other hand, compounds **I** and **J** have been studied as potential switchers, due to the presence of magnetically active metal centres (Fe, Cu and Gd) and the possibility of modulating their NLO properties changing the magnetic state of the compound. Costes *et al.* [36] in 2005 synthesised new Schiff base nickel complexes, bearing a tridentate dianionic ligand (compounds **K** in Scheme 2), with a fourth ancillary ligand L'. In this class of compounds the NLO response is limited, but the possibility of switching the direction of the β vector by simple protonation of the coordinated amido group is very important.

References

[1] R.W. Boyd, Nonlinear Optics, Second Edition, Academic Press, 2003.

[2] S.R. Marder *et al.,* Materials for Nonlinear Optics, Chemical Perspectives, ACS Symposium Series 455, American Chemical Society, Washington DC, 1991.

[3] P.A. Franken *et al., Phys. Rev. Letters*, 1961, **7**(4), 118.

[4] a) T.H. Maiman, *Nature*, 1960, **187**, 493; b) R.J. Collins *et al., Phys. Rev. Letters*, 1960, **5**(7), 303.

[5] J.L. Oudar, *J. Chem. Phys.*, 1977, **67**(2), 446.

[6] P.G. Lacroix, *Eur. J. Inorg. Chem.*, 2001, 339.

[7] S. Di Bella, *New. J. Chem.*, 2002, **26**, 495.

[8] a) C. Bosshard *et al., J. Appl. Phys.*, 1992, **71**, 1594; b) M.S. Paley, J.M. Harris, *J. Org. Chem.*, 1989, **54**, 3774.

[9] S. Di Bella *et al., J. Am. Chem. Soc.*, 1995, **117**, 9481.

[10] E.G. McRae, *J. Phys. Chem.* 1957, **61**, 562.

[11] S. Bruni *et al., Spectrochim. Acta, Part A*, 2001, **57**, 1417.

[12] L. Rigamonti *et al., Inorg. Chem.*, 2006, **45**, 10976.

[13] a) B.F. Levine, C.G. Bethea, *Appl. Phys. Lett.*, 1974, **24**, 445; b) K.D. Singer, A.F. Garito, *J. Chem. Phys.*, 1981, **75**, 3572; c) I. Ledoux, J. Zyss, *J. Chem. Phys.*, 1982, **73**, 203.

[14] N.P. Prasad, D.J. Williams, Introduction to Nonlinear Optical Effects in Molecules and Polymers, Wiley, New York, 1991.

[15] H.S. Nalwa, S. Miyata, Nonlinear Optics of Organic Molecules and Polymers, CRC Press, Boca Raton, FL, 1997.

[16] a) S.R. Marder, *Chem. Commun.*, 2006, 131; b) N. Leclerc *et al., Chem. Mater.*, 2005, **17**, 502; c) J.M. Cole, S. Kreiling, *Cryst. Eng. Comm.*, 2002, **4**, 232; d) V. Ostroverkhov *et al., Chem. Phys. Lett.*, 2001, **340**, 109; e) D.R. Kanis *et al., Chem. Rev.*, 1994, **94**, 195; f) W. Nie, *Adv. Mater.*, 1993, **5**, 520.

[17] a) H.S. Nalwa, *Appl. Organomet. Chem.*, 1991, **5**, 349; b) S.R. Marder *et al.,* Inorganic Materials, Wiley, New York, 1992, p. 116; c) N.J. Long, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 21; d) I.R. Whittall *et al., Adv. Organomet. Chem.*, 1998, **42**, 291; e) S. Di Bella, *Chem. Soc. Rev.*, 2001, **30**, 355; f) B.J. Coe, N.R.M. Curati, *Comments Inorg. Chem.*, 2004, **25**, 147; g) H. Le Bozec, T. Renouard, *Eur. J. Inorg. Chem.*, 2000, 229; h) J. Heck *et al., Coord. Chem. Rev.*, 1999, **190-192**, 1217.

[18] M.L.H. Green *et al., Nature*, 1987, **330**, 360.

[19] W. Chiang *et al., Spec. Publ. R. Soc. Chem.*, 1991, **91**, 210.

[20] S. Di Bella *et al., Chem Mater.*, 1994, **6**, 881.

[21] W. Chiang, *et al., Polyhedron*, 1996, **15**(14), 2369.

[22] P. G. Lacroix *et al., Chem. Mater.*, 1996, **8**, 541.

[23] S. Di Bella *et al., J. Am. Chem. Soc.*, 1996, **118**, 12747.

[24] S. Di Bella *et al., J. Am. Chem. Soc.*, 1997, **119**, 9550.

[25] G. Lenoble *et al., Inorg. Chem.*, 1998, **37**, 2158.

[26] F. Averseng *et al., Chem. Mater.*, 1999, **11**, 995.

[27] F. Aversene *et al., J. Mater. Chem.*, 2000, **10**, 1013.

[28] S. Di Bella, I. Fragalà, *Synthetic Metals*, 2000, **115**, 191.

[29] F. Averseng *et al., Chem. Mater.*, 2000, **12**, 2225.

[30] S. Di Bella *et al., Chem. Eur. J.*, 2001, **7**(17), 3738.

[31] S. Di Bella, I. Fragalà, *New. J. Chem.*, 2002, **26**, 285.

[32] O. Margeat *et al., Inorg. Chem.*, 2004, **43**, 4743.

[33] S. Di Bella *et al., Inorg. Chim. Acta*, 2004, **357**, 1161.

[34] a) S.K. Kurtz, T.T. Perry, *J. Appl. Phys.*, 1968, **39**, 3798; b) J.P. Dougherty, S.K. Kurtz, *J. Appl. Crystallogr.*, 1976, **9**, 145.

[35] J. Gradinaru *et al., Inorg. Chem.*, 2007, **46**, 884.

[36] J.P. Costes *et al., Inorg. Chem.*, 2005, **44**, 1973.

RIASSUNTO

Complessi metallici con basi di Schiff per l'ottica non lineare del secondo ordine

La ricerca e lo sviluppo di nuovi materiali adatti ad applicazioni nel campo dell'ottica non lineare è aumentato negli ultimi anni, tra cui composti di coordinazione metallici con leganti tetradentati tipo basi di Schiff. Questi sono un ottimo target, poiché sono chimicamente e fisicamente stabili, e presentano un grado di variabilità nello scheletro dei leganti di questi complessi elevato, che può portare ad un incremento della risposta NLO. Tutte le variazioni chimiche finora studiate sono riportate e spiegate non in modo dettagliato, al fine di mettere in luce il ruolo fondamentale del centro metallico nella risposta NLO e tutti i possibili sviluppi in questo campo di ricerca.