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Inorganica Chimica Acta 357 (2004) 548–556

Inorganica Chimica Acta

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New NLO active cyclopalladated chromophores in main-chain polymers ☆

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Received 24 July 2003; accepted 2 August 2003

Abstract

Four new OH-functionalized orthopalladated complexes bearing an electron-donor and an acceptor group in a *trans*-like arrangement with respect to the metal have been prepared and characterized. The ligands are Schiff bases, bound as C,N- or N,O-chelating moieties. Four new polyesters were obtained by polycondensation from the monomeric complexes and pentyloxyterephthaloyl chloride. Two "model" complexes, each one related to one monomer, were also synthetized, in order to obtain further and more detailed characterization data, and in particular to perform measurements of $\mu\beta$.

Keywords: Cyclopalladated complexes; Nonlinear optics; Main-chain polymers

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1. Introduction

A significant part of the research in the field of nonlinear optics is being focused on the design of new chromophoric coordination compounds [1–3]. Metal complexes can possess a large NLO response due to the attainment of low-energy excited states with dipole moment significantly different from the ground-state dipole moment. Most of these excited states are involved in metal-to-ligand and/or ligand-to-metal charge-transfer and have large oscillator strengths. In these cases, charge transfer is expected to provide a substantial contribution to the second order molecular hyperpolarizability [3].

The NLO properties of several types of transition metal complexes have been previously examined by the authors [4–6]. In particular, a series of cyclopalladated derivatives of Schiff bases was prepared, developing a synthetic strategy to obtain thermally stable and soluble non-centrosymmetric coordination compounds, with fair second order NLO response. Variation in molecular design of cyclopalladated complexes was used to obtain information on the correlations between structure and NLO properties. In this work, we describe further developments in this area.

Four metal complexes with the general formula reported in Scheme 1 have been prepared, characterized and successively used as monomers in the preparation of a series of polyesters.

It is to note that the above complexes are organometal derivatives. Organometallics can form polymers or can be included in polymers, just as simple organic molecules, and the use of NLO active monomers is expected to produce NLO active materials. The synthesis of Pd(II) based organometal side-chain NLO active polyacrylates has already been described [4]. A variety of examples of metallic main-chain polymers, with the second order NLO active units in the polymeric backbone, have been reported in the literature, but most of them contain non-organometal coordinated groups, as in the case of bis(salicylaldiminate) derivatives of copper, nickel and cobalt [8] or zinc [9]. Very few examples

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☆ Supplementary data associated with this article can be found, in the online version, at doi:10.1016/S0020-1693(03)00495-X.

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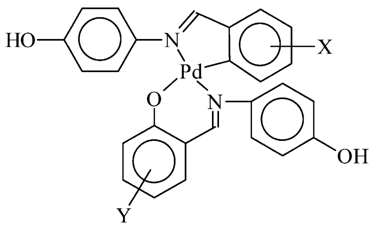
doi:10.1016/S0020-1693(03)00495-X



Scheme 1. General formulas of the monomeric complexes.

of main-chain polymers with metal–carbon complexes as chromophores are known, such as metallocene or metal-containing acetylene polymers for third-order NLO activities [2]. This could be ascribed to the higher stability displayed by "classical" coordination monomers with respect to organometallic species in the conditions required for polycondensation. A modification of a synthetic route leading to stable and soluble materials previously [10] followed by us in order to get interfacial polycondensation of cyclopalladated monomers was used in this work to prepare four main-chain polymers. Direct polycondensation of OH-functionalized cyclopalladated NLO active monomers with pentyloxyterephthaloyl chloride was achieved. In all the monomeric metal complexes, one Schiff base acts as C,N-chelate and a second one as N,O-chelate. These bases contain an electron-donor group or an electron-acceptor group and the final complexes contain both an electron-donor and an acceptor group in a *trans*-like arrangement with respect to the metal. More particularly, one group is in *para* or *meta* position with respect to the Pd–C bond, while the other one is in *para* or *meta* position with respect to the Pd–O bond. Two models (**Mod$_{1\text{–}2}$**, Scheme 4) of the monomers, in which the OH functions are protected, have also been synthetized in order to obtain further and more detailed characterization data, especially of structural type, and $\mu\beta$ measured by electric field induced second harmonic (EFISH) technique. The new models **Mod$_{3\text{–}4}$** correspond to the complexes with the donor and acceptor groups in *para* position. Herein their features are compared with those of **Mod$_{1\text{–}2}$** which have been reported previously [7] and have the donor and acceptor groups in *meta* position.

2. Experimental

2.1. Methods

Optical observations on low molecular weight species and polymers were performed by use of a Zeiss polarizing microscope equipped with a Mettler FP5 microfurnace. Phase transition temperatures and enthalpies were measured with a Perkin–Elmer DSC-7 apparatus at a scanning rate of 10 K min^{-1}, under a dry nitrogen flow. Thermogravimetric analysis was performed using a Mettler TG50 apparatus to evaluate the palladium content of complexes and polymers and their decomposition temperature. X-ray diffraction patterns were recorded at room temperature by a flat film camera using Ni-filtered CuKα radiation on polymer samples. Single crystal X-ray data were collected on a Nonius MACH3 automated single crystal diffractometer using graphite monochromated MoKα radiation ($\lambda = 0.71069$ Å). ^{1}H NMR spectra were recorded in $CDCl_3$, Me_2SO–d_6 (DMSO) or acetone–d_6 at 200 MHz using a Varian Gemini 200 spectrometer. Inherent viscosities (η_{inh}) were measured in 1,1,2,2,-tetrachloroethane or in dichloromethane solutions at 25.0 °C using a Ubbelohde viscometer. UV–Vis absorption spectra were recorded at room temperature utilizing a Perkin–Elmer Lambda 7 spectrometer. Infrared spectra were recorded on a JASCO FT-IR 430 spectrometer in chloroform solutions.

2.2. Materials

The reagents 4-aminophenol, 4-(dimethylamino) benzaldehyde, 4-nitrobenzaldheyde, 2-hydroxy-4-(diethylamino)benzaldehyde, 3-nitrobenzaldheyde, 3-(dimethylamino)benzaldehyde, 4-nitroaniline, anisidine, salicylaldehyde, and 2-hydroxy-5-nitrobenzaldehyde were commercially available (Aldrich). The compound 4-nitrosalicylaldehyde was obtained by adaptation of literature methods [11]. The compound 2-hydroxy-5-[(4-nitrophenyl)azo]benzaldehyde, though commercially available, was obtained from 4-nitroaniline and salicylaldehyde by standard methods [12]. The compound 4-aminophenyl benzoate was synthetized according to the literature [13].

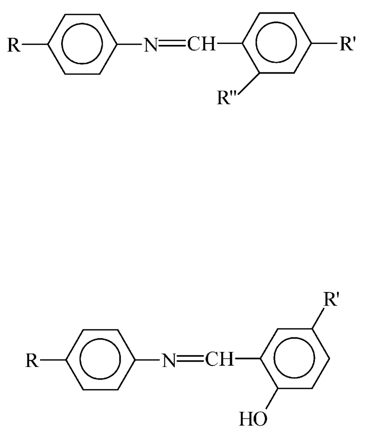
The imines **I$_1$**, **I$_2$**, **I$_5$**, **I$_6$** and **I$_{6m}$** (see formulas in Scheme 2), though commercially available, were synthetized from the correspondent amines and aldehydes, by standard methods [12].

The imine **I$_{7m}$** in Scheme 2 was obtained from stoichiometric amounts of 2-hydroxy-5-[(4-nitrophenyl)azo] benzaldehyde and anisidine in boiling dimethyl sulfoxide. Pentyloxyterephthaloyl chloride was synthetized from hydroxyterephthalic acid by standard methods [12].

2.3. Synthesis of 3-(dimethylamino)benzaldehyde

The compound was obtained by a reductive methylation, adapting a procedure reported in the literature [14].

To 7.50 g (0.050 mol) of 3-nitrobenzaldehyde dissolved in 120 ml of ethanol 33 ml of aqueous solution of formaldehyde (40% by weight) and 10 ml of Nickel Raney suspension (containing about 4 g of Nickel) were added. The suspension was stirred for 5 h under hydrogen pressure (at about 2 atm). After this time, the suspension was filtered, concentrated in vacuum, and the crude product



R= OH; R'= $N(CH_3)_2$; R''= H **I_1**

R= OH; R'= NO_2; R''= H **I_2**

R= OH; R'= H; R''= $N(CH_3)_2$ **I_3**

R= (C_6H_5)-*p*COO; R'= H; R''= $N(CH_3)_2$ **I_{3m}**

R= OH; R'= NO_2; R''= OH **I_4**

R= OH; R'= $N(CH_2CH_3)_2$; R''= OH **I_5**

R = OH; R' = NO_2 **I_6**

R = OH; R' = N=N-*p*(C_6H_4)-*p*NO_2 **I_7**

R = CH_3O; R' = NO_2 **I_{6m}**

R = CH_3O; R' = N=N-*p*(C_6H_4)-*p*NO_2 **I_{7m}**

Scheme 2. Formulas of the organic ligands.

was purified by distillation ($T = 100$ °C, $P = 1.5$ mmHg). Yield = 60%.

^{1}H NMR ($CDCl_3$): δ 3.0 (6H, s); δ 6.7 (1H, m); δ 6.9 (1H, d); δ 7.1 (1H, s); δ 7.3 (1H, d); δ 9.9 (1H, s).

2.4. Synthesis of Schiff bases (see formulas in Scheme 2)

The imines **I_3** and **I_{3m}** were obtained in about 10 min from stoichiometric amounts of 3-(dimethylamino)benzaldehyde and, respectively, 4-aminophenol or 4-aminophenyl benzoate in boiling ethanol. **I_{3m}** was recrystallized from boiling petroleum benzin. M.p. = 184 °C, yield = 80% (**I_3**). M.p. = 95.3 °C; yield = 45% (**I_{3m}**).

^{1}H NMR (DMSO) for **I_3**: δ 3.0 (6H, s); δ 6.7 (2H, d); δ 6.8 (1H, dd); δ 7.2 (5H, m); δ 8.5 (1H, s); δ 9.4 (1H, s).

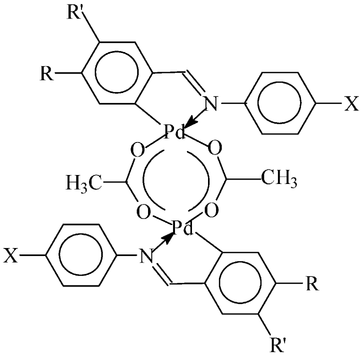
^{1}H NMR (DMSO) for **I_{3m}**: δ 2.9 (6H, s); δ 6.8 (1H, dd); δ 7.3 (6H, m); δ 7.6 (2H, m); δ 7.7 (1H, m); δ 8.1 (2H, d); δ 8.6 (1H, s).

The imine **I_4** was produced in situ in the synthesis of **M_4**. On a sample obtained for characterization from 2-hydroxy-4-nitrobenzaldehyde in ethanol, it was found: m.p. = 251 °C, yield = 68%. ^{1}H NMR (DMSO): δ 7.0 (2H, d); δ 7.2 (2H, d); δ 7.7 (3H, m); δ 9.0 (1H, s); δ 9.9 (1H, s); δ 13.9 (1H, s);

The imine **I_7** was synthetized by the reaction of stoichiometric amounts of 2-hydroxy-5-[(4-nitrophenyl)azo] benzaldehyde and 4-aminophenol in boiling *N*,*N*-dimethylformamide for about 10 min. M.p. = 297.8 °C; yield = 91%;. ^{1}H NMR (DMSO) for **I_7**: δ 6.9 (2H, d); δ 7.1 (1H, d); δ 7.4 (2H, d); δ 8.0 (4H, d); δ 8.3 (1 H, s); δ 8.4 (2H, d); δ 9.2 (1H, s); δ 9.9 (1H, s);

2.5. Synthesis of the dinuclear complexes

The dinuclear complexes **D_{1-3}** and **D_{3m}** (see Scheme 3 for the formulas) were obtained by reaction of palladium(II) acetate with the appropriate ligands following a previously described general procedure [15].



R=$N(CH_3)_2$; R'= H; X= OH **D_1**

R=NO_2; R'= H; X= OH **D_2**

R= H; R'= $N(CH_3)_2$; X= OH **D_3**

R= H; R'=$N(CH_3)_2$; X= *p*-$OCO(C_6H_5)$ **D_{3m}**

Scheme 3. Formulas of the dinuclear complexes.

The complexes **D_{1-3}** were obtained, respectively, from **I_{1-3}**, and **D_{3m}** was obtained from **I_{3m}**. As an example, the preparation of **D_1** is described.

A mixture of 0.53 g (2.18 mmol) of **I_1** and 0.49 g of palladium (II) acetate (2.18 mmol) in 20 ml of acetic acid was gently boiled under nitrogen for ca. 30 min. On cooling at room temperature a green-yellow microcrystalline solid precipitated. The solid was recovered by filtration and washed with ethanol. In the case of **D_2** the reaction mixture was kept at reflux for 3 h. Yields: **D_1** = 62; **D_2** = 75; **D_3** = 42; **D_{3m}** = 44%.

The dinuclear species were employed as crude products in the further reactions. Palladium contents calculated by

TGA measurements and thermodynamic data are reported in Table 1 ^{1}H NMR data gave evidence of the fairly high purity of the products.

^{1}H NMR (DMSO): for $\mathbf{D_1}$: δ 2.1 (3H, s); δ 2.9 (6H, s); δ 5.7 (1H, d); δ 6.3 (1H, d); δ 6.5 (4H, dd); δ 7.1 (1H, d); δ 7.5 (1H, s); δ 9.5 (1H, s). For $\mathbf{D_2}$: δ 1.9 (3H, s); δ 6.4 (2H, d); δ 6.6 (2H, d); δ 7.0 (1H, s); δ 7.5 (1 H, d); δ 7.9 (1H, dd); δ 8.2 (1H, s); δ 9.7 (1H, s). For $\mathbf{D_3}$: δ 1.9 (3H, s); δ 2.9 (6H, s); δ 6.6 (2H, d); δ 6.8 (2H, dd); δ 7.2 (2H, m); δ 7.4 (1H, s); δ 8.3 (1H, s); δ 9.6 (1H, s). For $\mathbf{D_{3m}}$: δ 1.8 (3H, s); δ 2.9 (6H, s); δ 6.4 (1H, d);δ 6.5 (1H, d); δ 6.7 (1H, d); δ 6.9 (1 H, s); δ 7.0 (2H, dd); δ 7.4 (2H, dd); δ 7.6 (2H, m); δ 7.7 (1H, d); δ 8.1 (2H, d).

2.6. Synthesis of the mononuclear complexes

The preparation of the four mononuclear complexes $\mathbf{M_{1–4}}$ (formulas in Scheme 4) was carried out by the same general procedure.

The monomers $\mathbf{M_1}$ and $\mathbf{M_2}$ were obtained, respectively, from the dinuclear complex $\mathbf{D_1}$ by reaction with the O,N-ligand $\mathbf{I_4}$ and from $\mathbf{D_2}$ by reaction with $\mathbf{I_5}$. The monomers $\mathbf{M_3}$ and $\mathbf{M_4}$ were obtained from the same dinuclear complex $\mathbf{D_3}$ by reaction, respectively, with the O,N-ligands $\mathbf{I_6}$ and $\mathbf{I_7}$.

In a typical preparation of $\mathbf{M_3}$ 1.10 g (4.0 mmol) of $\mathbf{I_6}$ was dissolved in 20 ml of *N*,*N*-dimethylformamide (only in this case of $\mathbf{M_1}$ the O,N-ligand was synthetized in situ). To this solution were added 1.5 g of sodium acetate, 1.0 g of potassium carbonate and finally 2.00 g of $\mathbf{D_3}$ (2.0 mmol). The suspension was stirred for about 30 min at 40 °C, while the color faded. After this time the mixture was filtered and poured in about 100 ml of ethanol/water (1:3) with 0.5 g of sodium acetate. A red precipitate was obtained, which was washed with water and dried at 120 °C. For $\mathbf{M_1}$ the reaction time was about 1 h at room temperature.

The monomer $\mathbf{M_2}$ was obtained by the same general procedure, but employing ethanol/dichloromethane (1:3) as the solvent and stirring the reaction mixture at room temperature for 2 h. After this time, the mixture was filtered and the solution was concentrated in vacuo until a brown-red solid precipitated.

Table 1
Thermodynamic data and Pd content (%) of dinuclear, monomeric and model complexes

	T_d (°C)^a	T_m (°C)	ΔH_m (J/g)	%Pd$_{calc}$^{b}	%Pd$_{exp}$^{c}
$\mathbf{D_1}$	275			26.29	28.19
$\mathbf{D_2}$	312			26.14	25.78
$\mathbf{D_3}$	207			26.20	26.79
$\mathbf{D_{3m}}$	210			20.92	20.84
$\mathbf{M_1}$	283			17.60	17.18
$\mathbf{M_2}$	275			16.68	16.48
$\mathbf{M_3}$	220			17.65	17.83
$\mathbf{M_4}$	226			15.05	15.17
$\mathbf{Mod_3}$	285	241	32	14.80	15.06
$\mathbf{Mod_4}$	290	142	42	12.90	12.75

[a] Decomposition temperature, calculated at 5% by weight loss.
[b] Calculated palladium content.
[c] Experimental palladium content.

Yields: $\mathbf{M_1} = 67$; $\mathbf{M_2} = 63$; $\mathbf{M_3} = 52$; $\mathbf{M_4} = 45\%$.

Thermodynamic data and Pd content (%) for the mononuclear species are reported in Table 1. ^{1}H NMR data confirm a good purity degree.

^{1}H NMR (acetone): for $\mathbf{M_1}$: δ 2.6 (6H, s); δ 5.4 (1H, d); δ 6.2 (1H, dd); δ 6.9 (4H, m); δ 7.2 (3H, m); δ 7.3 (2H, d); δ 7.6 (3H, m); δ 8.0 (1H, s); δ 8.4 (1H, s);δ 8.5 (1H, s); δ 8.7 (1H, d). For $\mathbf{M_2}$ (DMSO): δ 1.2 (3H, t);δ 3.4 (4H, dd); δ 5.8 (1H, d); δ 6.1 (1H, dd); δ 6.8 (3H, m); δ 6.9 (2H, d); δ 7.1 (2H, d); δ 7.4 (5H, m); δ 7.5 (1H, d); δ 7.7 (1H, d); δ 7.8 (1H, s); δ 8.6 (2H, s). For $\mathbf{M_3}$ (DMSO): δ 2.7 (6H, s); δ 5.5 (1H, d); δ 6.1 (1H, d); δ 6.3 (1H, d); δ 6.8 (4H, m); δ 7.2 (3H, m); δ 7.5 (2H, d); δ 8.0 (1H, dd); δ 8.2 (1H, s);δ 8.4 (1H, s); δ 8.5 (1H, d); δ 9.7 (2H, s). For $\mathbf{M_4}$ (DMSO): δ 2.9 (6H, s); δ 5.6 (1H, d); δ 6.1 (1H, d); δ 6.5 (1H, d); δ 6.9 (5H, m); δ 7.3 (2H, d); δ 7.6 (2H, d); δ 7.9 (3H, m); δ 8.3 (5H, m); δ 9.7 (2H, s).

2.7. Synthesis of the model complexes

The model complexes $\mathbf{Mod_{3–4}}$ (see formulas in Scheme 4) were synthetized by the same general procedure. Here is given a typical preparation of $\mathbf{Mod_3}$.

To a solution of $\mathbf{I_{6m}}$, 0.11 g (0.4 mmol) in 8 ml of *N*,*N*-dimethylformamide were added 0.15 g of sodium acetate, 0.10 g of potassium carbonate and finally 0.20 g of $\mathbf{D_{3m}}$ (0.2 mmol). The suspension was stirred at room temperature for about 20 min, while the color faded. After this time the product was precipitated by addition of ethanol (2–3 ml). It was recrystallized from dichloromethane/petroleum benzin, obtaining red crystals. Yield 50%.

$\mathbf{Mod_4}$ was obtained by reaction of $\mathbf{D_{3m}}$ with $\mathbf{I_{7m}}$ and crystallized from dichloromethane/petroleum benzin, obtaining dark red crystals with 52% yield.

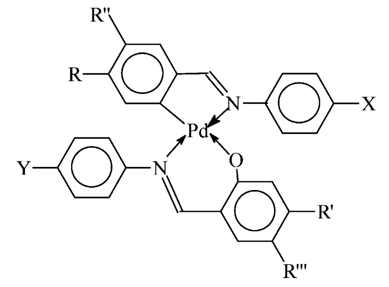
Thermodynamic data and Pd content (%) for the model complexes are reported in Table 1.

^{1}H NMR data confirm a very good purity degree.

^{1}H NMR For $\mathbf{Mod_3}$ ($CDCl_3$): δ 2.8 (6H, s);δ 3.9 (3H, s); δ 5.5 (1H, d); δ 6.2 (1H, dd); δ 6.5 (1H, d); δ 6.8 (1H, d); δ 6.9 (2H, d); δ 7.2 (1H, s); δ 7.4 (2H, d); δ 7.5 (4H, m); δ 7.7 (2H, d); δ 8.0 (1H, d); δ 8.1 (2H, t); δ 8.2 (1H, d); δ 8.3 (2H, m). For $\mathbf{Mod_4}$: δ 2.9 (6H, s); δ 3.9 (3H, s); δ 5.5 (1H, d); δ 6.2 (1H, dd); δ 6.6 (1H, d); δ 6.8 (1H, d); δ 7.0 (4H, m); δ 7.2 (4H, m); δ 7.3 (2H, d); δ 7.5 (2H, d); δ 7.9 (5H, m); δ 8.0 (1H, s); δ 8.1 (1H, s); δ 8.3 (2H, d).

2.8. Synthesis of the polymers

The synthesis of the four polymers $\mathbf{P_{1–4}}$ (formulas in Scheme 5) was performed by a modification of the already used procedure [10] from $\mathbf{M_{1–4}}$ and pentyloxyterephthaloyl chloride.



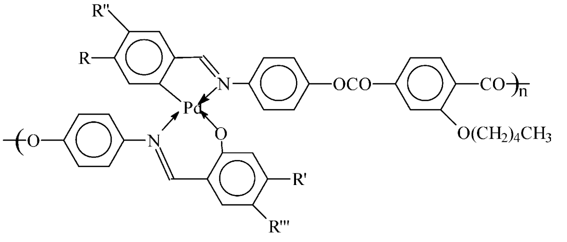
R=N(CH$_3$)$_2$; R'=NO$_2$; R''= R'''= H; X= Y= OH	**M$_1$**
R=NO$_2$; R'=N(CH$_2$CH$_3$)$_2$; R''= R'''= H; X= Y= OH	**M$_2$**
R= R'= H; R''= N(CH$_3$)$_2$; R'''=NO$_2$; X= Y= OH	**M$_3$**
R= R'= H; R''=N(CH$_3$)$_2$; R'''= N=N-*p*(C$_6$H$_4$)-*p*NO$_2$; X= Y= OH	**M$_4$**
R=N(CH$_3$)$_2$; R'=NO$_2$; R''= R'''= H; X= Y= OCH$_3$	**Mod$_1$**
R=NO$_2$; R'=N(CH$_2$CH$_3$)$_2$; R''= R'''= H; X= Y= OCH$_3$	**Mod$_2$**
R= R'= H; R''= N(CH$_3$)$_2$; R'''=NO$_2$; X= OCO-*p*(C$_6$H$_5$); Y= OCH$_3$	**Mod$_3$**
R= R'= H; R''=N(CH$_3$)$_2$; R'''= N=N-*p*(C$_6$H$_4$)-*p*NO$_2$; X= OCO-*p*(C$_6$H$_5$); Y= OCH$_3$	**Mod$_4$**

Scheme 4. Formulas of the monomeric and model complexes.

The synthesis of **P$_1$** is reported as an example. In 60 ml of water solution containing 0.292 g of KOH and 0.2 g of tetrabutylammonium hydrogen sulfate 1.017 g (1.69 mmol) of **M$_1$** were dispersed. To this mixture was added 30 ml of chloroform (dried by treatment with basic alumina) containing 0.488 g (1.69 mmol) of pentyloxyterephthaloyl chloride, under vigorous stirring. The reaction proceeded under stirring for about 8 min. About 100 ml of heptane were added to the mixture to precipitate the polymer. This was recovered by filtration and washed first with water, then in the order with: ethanol; twice with chloroform/heptane (1:2); ethanol containing a small amount of sodium acetate, water, and ethanol.

Finally, the polymer was dissolved in 1,1,2,2-tetrachloroethane at 70 °C (about 30% by weight of the crude material did not dissolve and was filtered off) and precipitated in heptane. It was recovered by filtration, washed with hexane, and dried at 80 °C. Yield = 69%.

For **P$_{2–4}$** yields are, respectively, 61, 60, and 65%. Thermodynamic data and Pd content (%) of the polymers are reported in Table 2.



R=N(CH$_3$)$_2$; R'=NO$_2$; R''= R'''= H	**P$_1$**
R=NO$_2$; R'=N(CH$_2$CH$_3$)$_2$; R''= R'''= H	**P$_2$**
R= R'= H; R''= N(CH$_3$)$_2$; R'''=NO$_2$	**P$_3$**
R= R'= H; R''=N(CH$_3$)$_2$; R'''= N=N-*p*(C$_6$H$_4$)-*p*NO$_2$	**P$_4$**

Scheme 5. Formulas of the polymers.

Table 2
Thermodynamic data and Pd content (%) of the polymers

	T_g (°C)	T_d (°C)[a]	η_{inh} (dL/g)[b]	%Pd$_{calc}$[c]	%Pd$_{sper}$[d]
P$_1$	178	291	0.17*	13.01	13.60
P$_2$	180	287	0.20*	12.56	13.34
P$_3$	161	260	0.10**	13.00	13.71
P$_4$	187	266	0.17***	11.50	11.79

[a] Calculated at 5% by weight loss.

[b] Measured at 25.0 °C at 0.50 g/dl concentration using as solvent: *: 1,1,2,2-tetrachloroethane; **: *N,N*-dimethylformamide; ***: *N*-methylpyrrolidone.

[c] Calculated palladium content.

[d] Experimental palladium content estimated by TGA measurements in air.

2.9. X-ray analysis of the model complexes

Single crystals of **Mod_3** and **Mod_4**, suitable for single crystal analysis, were obtained by evaporation from a chloroform and chloroform/toluene solution, respectively, both in the form of well-developed elongated prisms. Absorption effects were corrected using DIFABS [16]; the structures were solved by direct methods (SHELXS program of SHELX-97 package [17]), completed by difference Fourier methods and refined by the full matrix method (SHELXL program of the same package). Refinement was on F^2 against all independent measured reflections; sigma weights were introduced in the last refinement cycles. Largest peak and hole in the last difference Fourier were 0.85, −0.50 e Å^{-3} for **Mod_3** and 0.78, −0.50 e Å^{-3} for **Mod_4**. In both the structures C, N, O, Pd atoms were given anisotropic displacement parameters. H atoms were placed in calculated positions and refined by the riding model ($U_{iso} = U_{eq}$ of the carrier atom). Solvent is present in both structures, a chloroform molecule in **Mod_3** and a toluene molecule in **Mod_4**, and this occurrence seems to be correlated to the presence of voids in the crystal packing owing to the peculiar shape of the molecules. Some crystal, collection and refinement data are given in Tables 3 and 4.

2.10. NLO measurements

The molecular quadratic optical nonlinearities were experimentally determinated on a sample of **Mod_3** and **Mod_4** by using the EFISH technique. The set-up allows for the determination of the scalar $\mu\beta$ product where μ is the dipole moment and β the vector part of the quadratic hyperpolarizability tensor. The measurements were carried out in chloroform solutions at a fundamental wavelength of 1.907 μm, using a Q-switched, mode locked Nd^{3+}-YAG laser with pulse durations of 15 ns at 10 Hz repetition rate, whose 1.064 μm initial wavelength was shifted by stimulated Raman scattering in a high-pressure hydrogen cell. EFISH measurements data are summarized in Table 5 that also reports data for **Mod_{1-2}** taken from [10] for better comparison.

Table 3
Crystal, collection and refinement data for **Mod_3** and **Mod_4**

	Mod_3	**Mod_4**
Chemical formula	$C_{36}H_{30}N_4O_6Pd\cdot CHCl_3$	$C_{42}H_{34}N_6O_6Pd\cdot C_7H_8$
Formula weight	840.41	917.29
Temperature (K)	293	293
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a (Å)	9.418(4)	21.74(2)
b (Å)	13.933(8)	6.407(7)
c (Å)	14.832(8)	31.26(3)
α (°)	68.20(4)	90
β (°)	80.27(4)	98.6(1)
γ (°)	83.37(5)	90
V (Å^3)	1778(2)	4306(7)
Z, D_x (g/cm^3)	2, 1.570	4, 1.415
μ (mm^{-1})	0.800	0.489
Data/parameters	6242/460	7557/524
$R1$ on F ($I > 3\sigma(I)$)	0.0680	0.0659

$R1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$.

Table 4
Selected bond lengths (Å) and angles (°) for **Mod_3** and **Mod_4**

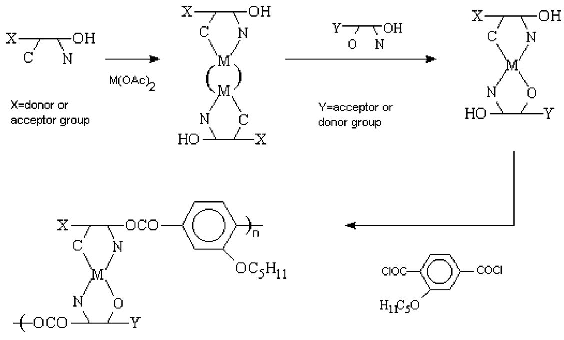
	Mod_3	**Mod_4**
Pd1–N2	2.04(1)	2.02(1)
Pd1–N3	2.036(9)	2.05(1)
Pd1–O4	2.059(8)	2.04(1)
Pd1–C6	2.02(1)	2.03(1)
N1–C3	1.40(2)	1.38(2)
N2–C9	1.29(2)	1.26(2)
N2–Pd1–C6	81.6(5)	80.0(6)
N2–Pd1–O4	87.5(4)	87.8(5)
N2–Pd1–N3	174.7(5)	176.9(5)
N3–Pd1–C6	101.7(4)	103.1(6)
N3–Pd1–O4	89.3(4)	89.1(5)
O4–Pd1–C6	16.7(4)	167.2(7)
C1–N1–C3	120(1)	118(2)
C2–N1–C3	118(1)	120(2)
C1–N1–C2	113(1)	114(2)
C9–N2–C10	119(1)	121(1)
C7–C9–N2	11(1)	118(2)
C27–N3–C30	115(1)	114(1)
N2–Pd1–O4–C32	−179(1)	162(1)
C6–Pd1–N3–C30	171(1)	−166(1)
Pd1–N3–C30–C31	3(2)	−9(3)
Pd1–O4–C32–C31	−2(2)	7(3)
C9–N2–C10–C11	−53(2)	−66(2)
C30–N3–C27–C28	−67(1)	65(2)
C12–C13–O2–C16	−70(1)	66(2)
C36–C35–N4–N5		176(2)
N4–N5–C42–C38		175(2)

Table 5
EFISH measurements data of the model complexes

	$\mu\beta$ (esu)
Mod_1	$120\cdot 10^{-48}$
Mod_2	$75\cdot 10^{-48}$
Mod_3	$35\cdot 10^{-48}$
Mod_4	$790\cdot 10^{-48}$

3. Results and discussion

The synthetic route adopted for the preparation of the polymers in summarized in Scheme 6, where the groups involved in coordination, those deputed to electron donation or withdrawal, and the hydroxylic functions are schematically shown.



Scheme 6. The synthetic route adopted for the preparation of the polymers.

3.1. Ligands and dinuclear complexes

Seven ligands ($\mathbf{I}_{1-7}$) (see Scheme 2) bearing a phenolic group apt to afford copolymerization by condensation were synthetized. $\mathbf{I}_{1-3}$ were suited for C,N-chelation and $\mathbf{I}_{4-7}$ for N,O-chelation. On the ground of the two-level model [18] these ligands are not expected to display very significant NLO activity. In fact, no one of them shows the typical structure of the nonlinear optically active compounds, where both an electron-donor and an acceptor group are conjugated by a delocalized π-electron system.

For the ligands (as well as for the dinuclear and mononuclear complexes, see below) some derivatives were prepared, in which the phenolic function was substituted by an ether group. The reason for the preparation of these "model" complexes is their easier purification and characterization, which in turn completes and makes easier the characterization of the phenolic species. Characterization data for the Schiff base ligands are reported in Table 1. The ^{1}H NMR data are in good agreement with the expected patterns.

The dinuclear complexes reported in Scheme 3, are intermediates in the preparation of the complexes used as monomers in the successive polymerizations. They include two phenolic functions and two equal groups capable of strong electron inductive effect (two donor groups in $\mathbf{D}_{1-2}$ and two withdrawing groups in $\mathbf{D}_3$ and $\mathbf{D}_{3m}$) and are centrosymmetric. All are microcrystalline solids which do not show melting before decomposition, as shown in Table 1.

3.2. Monomeric and model complexes

All the mononuclear complexes $\mathbf{M}_{1-4}$ include two phenolic groups and bear one electron-donor and one withdrawing group: one on the C,N-chelate, the other one on the N,O-chelate. On comparing $\mathbf{M}_1$ and $\mathbf{M}_2$ it is observed that the two compounds are substantially isomers, making allowance that in this context $N(CH_3)_2$ can be considered equivalent to $N(CH_2CH_3)_2$, and that in $\mathbf{M}_1$ the electron donor group is in the N,O-chelate and the acceptor in the C,N-chelate (both in *meta* positions), while this arrangement is reversed in $\mathbf{M}_2$.

In the four complexes the two polarizing groups are in *trans*-like position with reference to the square planar environment of the metal. In absence of NLO suited features for the ligands, this arrangement should be responsible of the chromophoric activity, as expected both for the complexes and for the polymers because of the active role of the metal linking the electron-donor to the acceptor group.

Within the above general arrangement some variation has been introduced, in order to get some information on the corresponding changes in NLO activity. First, in $\mathbf{M}_{3-4}$ one of the polarizing groups is in *para* position with respect to the metal-bonded carbon and the other in *para* to the coordinated oxygen, at variance with the analogous complexes $\mathbf{M}_{1-2}$, where the corresponding *meta* positions are involved. A different NLO behavior is expected for the two arrangements. In fact, a more extended and therefore more active [18] dipolar system should be involved in the first case. Another variation has been introduced by increasing the extension of the electron delocalization in $\mathbf{M}_4$ with respect to $\mathbf{M}_3$, where a shorter conjugated withdrawing system is present.

The molecular structure of the two new model compounds $\mathbf{Mod}_3$ and $\mathbf{Mod}_4$ is reported in Figs. 1 and 2.

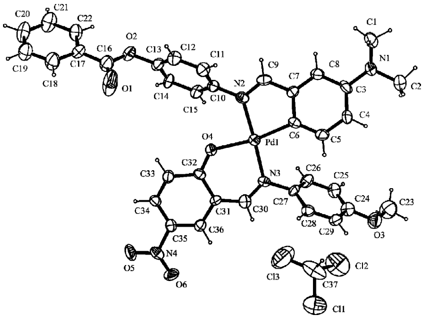


Fig. 1. Ortep view of $\mathbf{Mod}_3$. Anisotropic displacement ellipsoids are drawn at 30% probability level.

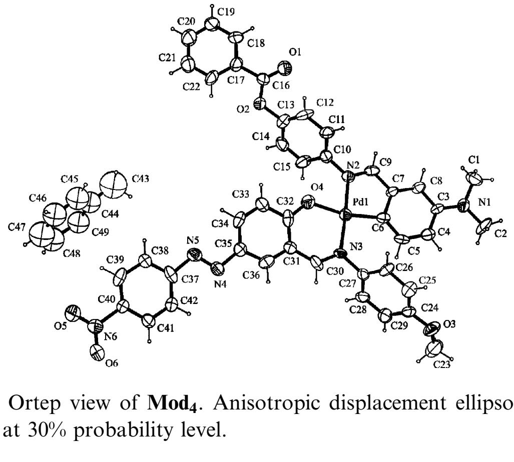


Fig. 2. Ortep view of $\mathbf{Mod}_4$. Anisotropic displacement ellipsoids are drawn at 30% probability level.

Selected bond lengths and angles are reported in Table 3. In both compounds, the coordination around Pd atom is substantially square planar, with standard values for the distances from metal to coordinated atoms [19]. The Pd atom is shared between a cyclo-palladated (five membered) planar ring and a salicylaldiminate (six membered) ring, the latter being substantially planar, at variance with the analogous compounds we have already studied [7]. The whole molecular part comprised between the dimethylamino donor group and the nitro acceptor takes a full planar conformation which is a required condition [18] for a significant charge transfer and, therefore, for relevant second order NLO activity. The geometry around the iminic N atom is planar trigonal in both compounds, indicating an sp^2 hybridization that should favor electron donation to the adjacent phenyl ring. In both compounds, the phenyl rings of the imine groups are tilted with respect to the planar push–pull core of the molecule by rotation around N3–C27 and N2–C10 and O2–C13, reasonably in order to release intramolecular steric interactions.

As for NLO activity, it can be noted from Table 5 that the $\mu\beta$ value of **Mod$_4$** is the largest one. It must be noted that the $\mu\beta$ value of **Mod$_4$** is comparable or even greater in some cases than those reported for some bis(salicylaldiminato) Ni(II) or Cu(II) coordination complexes [20–22]. Moreover, its $\mu\beta$ value is also higher than the value reported for Disperse Red ($\mu\beta$ is $580 \cdot 10^{-48}$ esu [18]), the typical organic NLO chromophore based on the 4-nitroazobenzene moiety. The higher $\mu\beta$ value for **Mod$_4$** could be explained on the basis of a larger extension of the π-electron delocalization. If so, the result gives evidence of the role of coordinated metal in the charge transfer. The $\mu\beta$ value for **Mod$_1$** and **Mod$_2$** is a little higher than for **Mod$_3$**. **Mod$_1$** and **Mod$_3$** display the same push–pull grouping, but in different positions in the metal environment. Substantially, the same observation holds if **Mod$_2$** is compared to **Mod$_3$**.

All the model compounds show an appreciable and comparable solvatochromic effect, measured on chloroform and *o*-dichlorobenzene solutions. A hypsochromic (blue) effect, with shift values of about 10 nm for a difference of 1.5 D between the dipole moment of the solvents used was also observed.

3.3. Polymers

Four polyesters **P$_{1–4}$** were obtained from the NLO active monomeric metal complexes. The use of NLO active monomers seems to be a convenient strategy to produce NLO active main-chain organometallic polymers. In fact, rigid rod-like polymers substituted with flexible side-chains can represent a suitable approach to processable NLO materials [23]. Thus, insertion of alkoxy side chains in the rigid structure of the main chain can ensure solubility and amorphism to the polymers. NLO active chromophores are directly linked to the rigid rod main-chain, while the alkoxy groups are pendants of the macromolecular backbone. So, we expect that the poling process of the polymers should involve rotation of the entire polymer backbone, with the motion of the chromophores substantially decoupled from those of the alkoxy side chain. Long thermal stability of the polar alignment can be expected [24] due to the restricted mobility of the chromophores below the glass transition.

The ^{1}H NMR spectra are in good agreement with the expected patterns. In particular, the comparison of the intensity of the signals related to the alkoxy protons (due only to the comonomer) with the intensity of the aromatic protons (due to both the comonomer and the organometallic monomer) confirms the stoichiometry. The IR spectra show the strong band characteristic for ester group centered at 1730 cm^{-1}. The polymers are soluble, and stable for several days at room temperature in solvents such as *N*,*N*-dimethylformamide, *N*-methylpirrolidone and 1,1,2,2-tetrachloroethane. Some relevant thermodynamic data are presented in Table 3. The palladium content of all the polymers is always close to the content calculated on the basis of stoichiometry. The UV–Vis transmittance spectrum was measured on thin film samples (obtained by evaporation of *N*-methylpirrolidone polymer solutions on glass slides, at about 80 °C). In Fig. 3, the transmittance spectra of the four polymers are shown.

As expected, the values of the maximum of transmittance of the polymers match very well the values of absorbance of the model complexes. Only the polymer containing an azobenzene group, **P$_4$**, shows absorption above 500 nm. The other ones show a large range absorption free centered around 532 nm, where it can be recorded as the second harmonic by employing a Nd^{3+}-YAG laser.

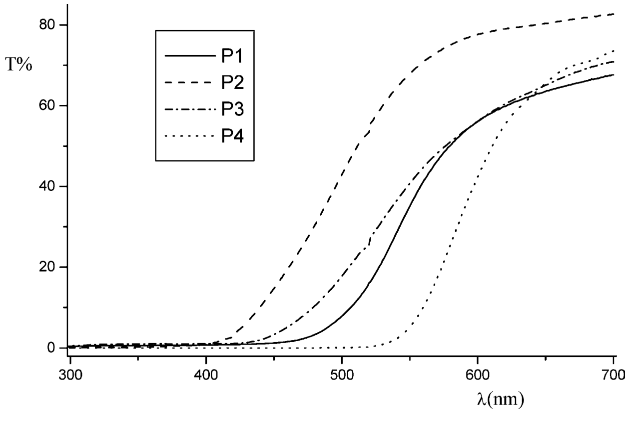


Fig. 3. UV–Vis transmittance spectra of thin film samples of the polymers.

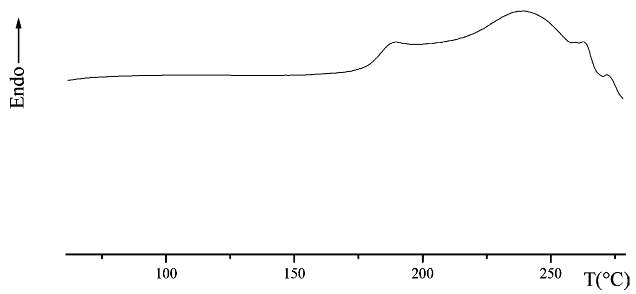


Fig. 4. DSC curve for a sample of $\mathbf{P_4}$.

Thin films of the polymers, obtained by spin-coating of 1,1,2,2-tetrachloroethane polymer solutions, are amorphous, also after annealing for 30 min at 10 °C below the glass transition. Optical observation, RX spectra and DSC analysis (the only signal detected is the one related to the glass transition, as can be seen from Fig. 4) confirmed the absence of crystallinity.

Moreover, preliminary experiments show that second harmonic intensity measured 10 °C above T_g on thin films of $\mathbf{P_1}$ and $\mathbf{P_4}$ is higher than that for $\mathbf{P_2}$ and $\mathbf{P_3}$, as suggested by the NLO responses of the model compounds $\mathbf{Mod_{1-4}}$. The good thermochemical stability of all the polymers is remarkable: as indicated by TGA measurements in nitrogen, there is a large temperature range, in which the materials can be poled, from the glass transition until decomposition.

4. Conclusions

The synthesis of four main-chain polyesters, containing Schiff bases cyclopalladated mononuclear complexes, has been achieved. The polymers are amorphous, display good chemical and thermal stability, and are fairly soluble in standard solvents. On the basis of the NLO responses performed on model complexes we can expect NLO activity for the polymers [24]. In particular, the large value of $\mu\beta$ (comparable with those recorded for some bis-salicylaldiminato complexes [22]) measured for $\mathbf{Mod_4}$ establishes the potentiality of the correspondent polymer, with the only requirement of a laser operating at wavelength over 1200 nm for the poling process.

Acknowledgements

The research has been supported by MIUR of Italy. NMR spectra and X-ray data were recorded at Centro Interdipartimentale di Metodologie Chimico-Fisiche of the Università di Napoli "Federico II".

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