Synthesis, crystal structure and second-order nonlinear optical properties of the trinuclear palladium orthometalated complex $[(\mu_3\text{-S})(\mu_3\text{-OH})\text{Pd}_3(\text{C}^\wedge\text{N})_3]$ (HC^N = p-(Bu$_2^n$N)–C$_6$H$_4$–CH=N–C$_6$H$_4$–NO$_2$-p)

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ABSTRACT

A smooth reaction of $[(\mu_2\text{-OH})_2\text{Pd}_2(\text{C}^\wedge\text{N})_2]$ (**3**) with CS$_2$·(HC^N = p-(Bu$_2^n$N)–C$_6$H$_4$–CH=N–C$_6$H$_4$–NO$_2$-p) provides $[(\mu_3\text{-S})(\mu_3\text{-OH})\text{Pd}_3(\text{C}^\wedge\text{N})_3]$ (**4**). The X-ray structures of **4** shows that the complex contains a $(\mu_3\text{-S})(\mu_3\text{-OH})\text{Pd}_3$ core which forces an all-cis arrangement of the three orthometalated ligands. The variation of the $\beta(0)$ value per imine moiety, on going from the free imine to the trinuclear complex (**4**) is negative: -17%. In contrast, for the dinuclear complexes $[(\mu_2\text{-SBu})(\mu_2\text{-OAc})\text{Pd}_2(\text{C}^\wedge\text{N})_2]$ (**5**) or $[(\mu_2\text{-SBu})(\mu_2\text{-Cl})\text{Pd}_2(\text{C}^\wedge\text{N})_2]$ (**6**), having also a cis-arrangement of the orthometallated imines, this variation is positive: $+14\%$ and $+30\%$, respectively. The $\beta(0)$ variation seems to be concordant with the trend of the molar extinction coefficients values.

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1. Introduction

Organometallic and coordination complexes with nonlinear optical (NLO) properties are currently of considerable interest [1]. Among the many systems studied so far, Schiff base complexes have received some attention [2]. Analogously to organic NLO chromophores, most of the NLO complexes follow a simple molecular scheme constituted by a donor–π conjugated bridge–acceptor structure (D–π–A), in which the metallorganic group can play the role of the donor, the bridging moiety, or the acceptor (Sketch 1) [3].

Reported Schiff base complexes correspond to the latter case and the complexation produces geometrically planar structures for the Schiff base moiety. This, consequently, improves the conjugation between the donor and the acceptor groups in the Schiff base, usually leading to an enhancement of optical nonlinearity, when compared to the parent free ligand.

Recently we discovered a new synthetic route that affords trinuclear orthopalladated complexes $[(\mu_3\text{-S})(\mu_3\text{-OH})\text{Pd}_3(\text{C}^\wedge\text{N})_3]\cdot$(HC^N = p-C$_nH_{2n+1}$O–C$_6H_4$–CH=N–C$_6H_4$–OC$_nH_{2n+1}$-p, n = 2, 10) by reaction of $[(\mu\text{-OH})_2\text{Pd}_2(\text{C}^\wedge\text{N})_2]$ with CS$_2$ [4], or to a mixture of a trinuclear complex, $[(\mu_3\text{-S})(\mu_3\text{-OH})\text{Pd}_3(\text{C}^\wedge\text{N})_3]$, and a tetranuclear non-polar one, $[(\mu_4\text{-S})\{\mu_2\text{-(OH)}\text{Pd}_2(\text{C}^\wedge\text{N})_2\}_2]$, when the imine used is HC^N = p-C$_2$H$_5$O–C$_6$H$_4$–CH=N–C$_6$H$_4$–C$_2$H$_5$-p [5]. In all cases, the asymmetric combination of (μ-S) and (μ-OH) bridges, with different trans influence, induces an all-cis arrangement of the three orthometalated fragments in the trinuclear complexes, as confirmed by X-ray diffraction methods. We considered that it might be interesting to study the NLO behavior of these unprecedented polar trinuclear compounds, which contain three parallel imine moieties, preparing a specially designed imine with appropriate donor and acceptor substituents. The results could then be compared with the free imine, and with previously prepared dinuclear Pd complexes containing two parallel imine moieties.

2. Results and discussion

The imine chosen to prepare the complexes in this work is HC^N = p-(Bu^{n}N)$_2$–C$_6$H$_4$–CH=N–C$_6$H$_4$–NO$_2$-p (**1**), with the dibutylamino and nitro groups in the aldehydic and the anilinic rings, respectively; the first hyperpolarizability value (β) is expected to be larger when the strong donor group (the amine) is located in the cyclometalated ring, and the acceptor is in the dangling aryl [6]. The reaction of $[(\mu\text{-OAc})_2\text{Pd}_2(\text{C}^\wedge\text{N})_2]$ (**2**) in CH$_2$Cl$_2$ with KOH in methanol (room temperature, 8 min) led to exchange of the bridging acetato ligands by hydroxo groups, affording **3** in ca. 74% yield (Scheme 1). Elemental analyses confirmed the proposed stoichiometry. The presence of the μ-OH ligand was supported by
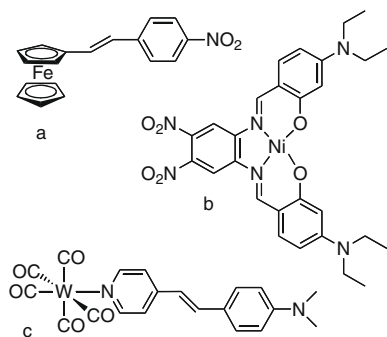
Sketch 1. Metallorganic groups playing the role of: (a) the donor; (b) the bridging moiety; (c) the acceptor.

the observation in the ^{1}H NMR spectrum of a singlet at −2.21 ppm in the expected range for μ-OH (e.g. −2.07 ppm for the similar dinuclear complex with HC^N = p-(RO–C$_6$H$_4$–CH=N–C$_6$H$_4$–OR-p) [7]). The resonances of the orthopalladated imine ligand indicated a planar structure of the complex and confirmed its isomeric purity, corresponding to a *trans* arrangement of the two imine moieties.

Complex **3** in CH$_2$Cl$_2$ reacted with CS$_2$ (molar ratio 1:10), at 25 °C for 5 h, affording the trinuclear complex **4**, which was obtained in 67% yield (Scheme 1). Its ^{1}H NMR spectrum shows just one set of ^{1}H signals for the orthopalladated imine ligands, proving the chemical equivalence of the imine ligands and the isomeric purity of the complex, and a singlet at −3.03 ppm, in the expected range for μ$_3$-OH (e.g. −2.55 ppm for the similar trinuclear complex with HC^N = p-(EtO–C$_6$H$_4$–CH=N–C$_6$H$_4$–Et-p) [5]), with intensity corresponding to one μ$_3$-OH group for three imines. A *trans* arrangement of the sulfide and the iminic nitrogens, expected for the thermodynamically preferred isomer [8], was unambiguously supported for **4** by a single-crystal X-ray diffraction determination (Fig. 1).

The molecule consists of three Pd(C^N) moieties linked by one μ$_3$-sulfide and one μ$_3$-hydroxo ligand. The cyclometalated carbon is coordinated *trans* to the oxygen atoms of the bridging hydroxo groups, and a *cis* arrangement of the three imine moieties is found. The three Pd atoms describe an isosceles triangle and the Pd–Pd distances (2.9327(18)–3.150(2) Å) (similar to 2.943(2)–3.137(2) Å found for the trinuclear complex with HC^N = p-(EtO–C$_6$H$_4$–CH=N–C$_6$H$_4$–Et-p) [5], and 3.047–3.387 Å for [Pd$_3$(μ$_3$-S)(μ$_3$-SC$_4$H$_9$)(C^N)$_3$] with HC^N = p-(EtO–C$_6$H$_4$–CH=N–C$_6$H$_4$–OEt-p) [4]) do not suggest significant intermetallic interaction. A similar distortion from the ideal equilateral triangle to isosceles was found
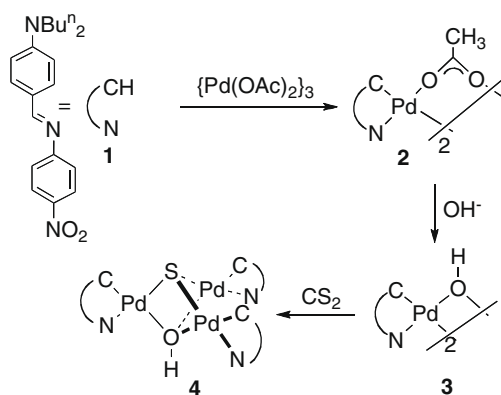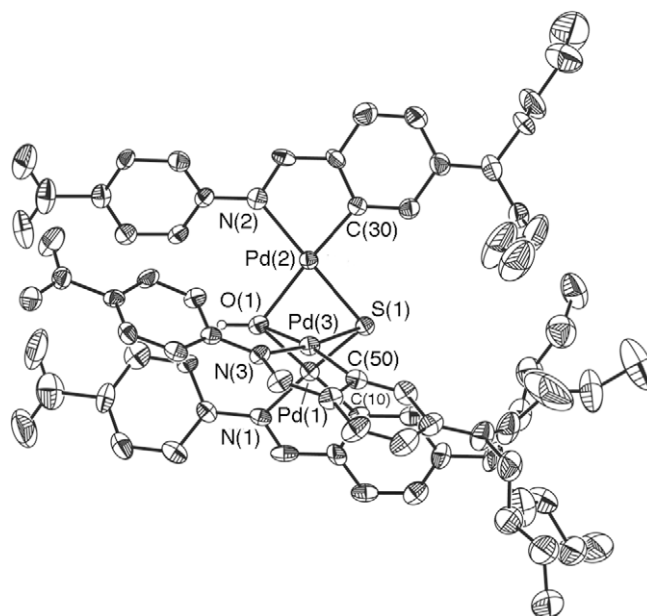

Fig. 1. Molecular structure of **4** with thermal ellipsoids (30% probability).

in related trinuclear palladium orthometalated complexes [5]. This geometry could be expected from a second-order Jahn–Teller effect [9], but it might simply be due to packing effects [10].

The linear and nonlinear optical properties of complex **4** are collected in Table 1, along with those of the free imine, and the previously reported dinuclear complexes [Pd$_2$(μ-SBu^n)(μ-X)(C^N)$_2$] (see Sketch 2: X = OAc, (**5**), Cl (**6**)) [6]. The hyperpolarizability (β) values in Table 1 were calculated from the experimental values of μβ (the projection of the hyperpolarizability on the dipole moment vector); the later product was directly measured in Electric Field Induced Second Harmonic Generation (EFISH) experiments, and the dipole moments (μ) were determined independently. EFISH experiments for the free imine and the dinuclear complexes were performed at 1.34 μm [6]. Here the trinuclear complex (**4**) as well as the free imine (**1**) have been measured at 1.907 μm. Static β(0) values, extrapolated using a simple two-level model [11], are also gathered in Table 1. A good agreement between β(0) values extrapolated from EFISH measurements at 1.34 and 1.907 μm have been obtained for compound **1**.

The dinuclear palladium complexes reported before induce a β(0) enhancement per imine moiety when compared to the free imine (+14% for **5** and +30% for **6**), whereas for the trinuclear complex (**4**) the β(0) contribution per imine decreases 17%. Although non linear behavior is influenced by several factors, we can get some qualitative insight into the trend of experimental β values by considering optical absorption spectra. The UV–Vis absorption maximum, which is indicative of the energy difference between HOMO and LUMO for the complexes, appears for compound **4** at lower frequency (is red shifted) than for the dinuclear complexes **5** and **6**. This should, in principle, correspond to a larger enhance-

Scheme 1.
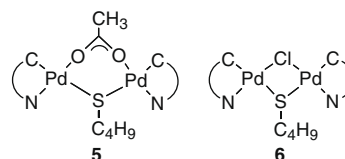
Sketch 2.

Table 1
Linear and NLO properties of the free imine and its dinuclear (**5**, **6**) and trinuclear (**4**) orthopalladated complexes.

Compound	λ_{max} (nm)	ε (L mol^{-1} cm^{-1})	μ (D)	β (10^{-30} cm^5 esu^{-1})	$\beta(0)$ (10^{-30} cm^5 esu^{-1})	Variation $\beta(0)$[c] (% per imine moiety)
1	416	34200	7.9	69 ± 6[a]	38 ± 3	
				52 ± 5[b]	40 ± 4	
4	473	59400	13.8	140 ± 20[b]	99 ± 14	−17
5	466	104200	13.1	192 ± 23[a]	87 ± 10	+14
6	464	153100	17.1	217 ± 45[a]	99 ± 10	+30

[a] From EFISH measurements in CHCl$_3$ at 1.34 μm [6].
[b] From EFISH measurements in CH$_2$Cl$_2$ at 1.9 μm.
[c] Variation of $\beta(0)$ refers to the change (%) of $\beta(0)$ per complexed imine moiety, as compared with the value of the free imine: Variation% = $100(\beta(0)_{complex} - n \times \beta(0)_{imine})/n \times \beta(0)_{imine}$; n = number of imine moieties in the complex.

ment of $\beta(0)$, in contrast with the experimental observation. However, the extent of overlap between these frontier orbitals is very different, being lower for the trinuclear complex, as can be deduced from the molar extinction coefficients values (ε), also collected in Table 1. The variation of the ε values is, in fact, much larger than the variation of the absorption maxima. The $\beta(0)$ variations shown in Table 1 seem to be concordant with the trend of the molar extinction coefficients, suggesting that the extent of overlap between HOMO and LUMO dominates the hyperpolarizability values in this family of complexes. A change of an ancillary ligand in the trinuclear complex, in order to allow for a better HOMO–LUMO overlap, might lead to an improvement in the value of the hyperpolarizability in trinuclear complexes.

3. Experimental

3.1. General procedures

C, H, N, analyses were carried out on a Perkin–Elmer 2400 microanalyzer. IR spectra were recorded on a Perkin–Elmer FT-1720X spectrometer using Nujol mulls between polyethylene plates. 1H NMR spectra were recorded on Bruker AC-300 or ARX-300 MHz spectrophotometers.

3.1.1. [(μ_2-OH)Pd$_2$(C^N)$_2$] (**3**)

To a solution of [(μ_2-OAc)$_2$Pd$_2$(C^N)$_2$] [6] (0.753 g, 0.727 mmol) in dichloromethane (35 mL) was added 2.15 mmol of KOH in methanol (5.8 mL of a solution 0.37 M) and the mixture was stirred for 8 min at room temperature. The solvent was evaporated off and the brown residue was extracted in 15 mL of dichloromethane. The solution was filtered through Kieselguhr and concentrated to dryness. The residue was crystallized in dichloromethane/diethyl ether 1/3. Yield 0.512 g (74%). *Anal.* Calc. for C$_{42}$H$_{54}$N$_6$O$_6$Pd$_2$: C, 53.00; H, 5.72; N, 8.83. Found: C, 52.68; H, 5.10; N, 8.70%. ^{1}H NMR (300 MHz, CDCl3): δ 7.82 (s, 1H); 8.22, 7.59 (AA'BB' system, 8.8 Hz, 4H); 7.21 (d, 8.8 Hz, 1H); 6.27 (dd, 8.8 Hz, 1H); 6.16 (s, 1H); 3.30 (t, 7.6 Hz, 2H); 1.52, 1.26 (m, 4H); 0.90 (t, 7.0, 3H); −2.21 (s, 1H).

3.1.2. [(μ_3-S)(μ_3-OH)Pd$_3$(C^N)$_3$] (**4**)

Complex **1** (0.050 g, 0.052 mmol) and CS$_2$ (33 μL, 0.55 mmol) in dichloromethane (20 mL) were stirred at 25 °C for 4 h. The solvent was then evaporated and the residue was washed with diethyl ether and was crystallized in dichloromethane/diethyl ether. Yield: 0.050 g (67%). *Anal.* Calc. for C$_{63}$H$_{79}$N$_9$O$_7$Pd$_3$S: C, 53.08; H, 5.59; N, 8.84. Found: C, 52.83; H, 5.34; N, 8.67%. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.91 (s, 1H); 7.62, 7.07 (AA'BB' system, 8.8 Hz, 4H); 7.20 (d, 8.6 Hz, 1H); 7.32 (d, 2.2 Hz); 6.23 (dd, 8.8 Hz, 2.2 Hz, 1H); 3.39 (t, 7.2 Hz, 2H); 1.38 (m, 4H); 0.93 (t, 7.2, 3H); −3.03 (s, 1H).

3.2. EFISH measurements

Measurements were carried out with a nonlinear optics spectrometer from SOPRA. The laser source was a Q-switched Nd:YAG laser (Quantel YG 781, 10 pps, 8 ns), operating at 1.064 μm, which pumped a hydrogen Raman shifter. The first Stokes peak at 1.907 μm was used as fundamental light. The vertically polarized excitation was focused onto the EFISH cell. The polarizing DC voltage (parallel to the light polarization) applied to the solutions was 5 kV and the separation between the electrodes in the sample cell was 2 mm. The output light from the cell was filtered to select the second harmonic light (0.954 μm), which was finally detected with a R642 photomultiplier from Hamamatsu.

The experiment was performed by using solutions containing compound **4** in CH$_2$Cl$_2$, at concentrations in the range 10^{-3}–5×10^{-3} M. Static $\beta(0)$ values were extrapolated from the experimental β values using a two-level dispersion model [11]. Under the same experimental conditions, $\mu\beta(0) = 480 \times 10^{-48}$ esu was obtained for azo dye Disperse Red 1. The ground state dipole moment μ was determined by the standard method of Guggenheim [12].

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.10.028. CCDC 714393 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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