

# Organometallic nickel(II) complexes with substituted benzonitrile ligands. Synthesis, electrochemical studies and non-linear optical properties. The X-ray crystal structure of $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)\{\text{P}(\text{C}_6\text{H}_5)_3\}(\text{NCC}_6\text{H}_4\text{NH}_2)]\text{[PF}_6\text{]}$

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## Abstract

A new family of organometallic Ni(II) benzonitrile derivatives bearing strong donor substituents of general formula  $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)\{\text{P}(\text{C}_6\text{H}_5)_3\}\text{NCC}_6\text{H}_4\text{R}]\text{[PF}_6\text{]}$  (R = NH<sub>2</sub>, N(CH<sub>3</sub>)<sub>2</sub>, C<sub>6</sub>H<sub>5</sub>, OCH<sub>3</sub>, H, F) has been synthesized. A structural study by X-ray diffraction of the compound with R = NH<sub>2</sub> showed crystallization on the centrosymmetric monoclinic space group,  $P2_1/n$ , with a quasi planar structure of the coordinated nitrile. First and second hyperpolarizabilities evaluated by hyper-Rayleigh scattering and Maker fringe techniques showed essentially the same values for the complexes and the uncoordinated chromophores. Theoretical studies by the extended Hückel method found a small amount of  $\pi$  delocalization due to the cancelling effects on the interaction of the metal fragment orbitals with  $\pi$  and  $\pi^*$  nitrile orbitals. © 1998 Elsevier Science S.A.

**Keywords:** Organometallic Ni; Delocalization; Nitrile orbitals

## 1. Introduction

In the field of organometallic chemistry, much interest is currently devoted to the synthesis of new materials possessing large second-order nonlinearities, especially because of their potential use in the area of integrated optics [1]. In particular, after the 1987 report of Green et al. [2] on the second harmonic generation efficiency of *cis*-[1-ferrocenyl-2-(4-nitrophenyl)ethylene] the related research [3–8] in this area has increased constantly.

Non-linear optical (NLO) properties have been associated, in organic and in organometallic materials, with highly polarized  $\pi$ -electronic systems which form under an applied electric field associated with a laser beam. Under this perspective, molecules possessing conjugated donor-acceptor systems, are seen as potentially good candidates for the manifestation of the properties. Recently, we published some results on the chemistry and NLO properties, namely SHG efficiencies, of compounds formed by the unit  $\text{M}(\eta^5\text{-C}_5\text{H}_5)(\text{P}\cdots\text{P})$  (M = Fe(II), Ru(II)) and *p*-substituted benzonitriles containing ligands [9,10]. Also, we reported on the optical third-harmonic generation (THG) of Ru(II) compounds [11]. This work has been motivated by the reports on the relatively high second harmonic generated signals for some *para*-substituted benzonitriles such as *p*-MeOC<sub>6</sub>H<sub>4</sub>CN, *p*-H<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CN [12] and *p*-

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