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Jonathan Cisterna, Vincent Dorcet, Carolina Manzur, Isabelle Ledoux-Rak, Jean-René Hamon, et al.. Synthesis, spectral, electrochemical, crystal structures and nonlinear optical properties of unsymmetrical Ni(II) and Cu(II) Schiff base complexes. *Inorganica Chimica Acta*, 2015, 430, pp.82-90. 10.1016/j.ica.2015.02.030 . hal-01153264

**HAL Id: hal-01153264**

**<https://univ-rennes.hal.science/hal-01153264>**

Submitted on 19 May 2015

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Ms. Ref. No.: ICA-D-14-01012

Revised version

**Synthesis, spectral, electrochemical, crystal structures and nonlinear optical properties of unsymmetrical Ni(II) and Cu(II) Schiff base complexes**

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## Abstract

This paper explores the synthesis, spectroscopic and structural characterization, linear and nonlinear optical properties, as well as the electrochemical behavior of two series of robust neutral Ni(II)- and Cu(II)-centered organometallic macrocyclic salen-type Schiff base complexes, namely, the 5-nitrosubstituted derivatives  $M[\text{Fc}-\text{C}(\text{O})\text{CH}=\text{C}(\text{CH}_3)\text{N}-o\text{-C}_6\text{H}_4\text{-N}=\text{CH}-(2\text{-O},5\text{-NO}_2\text{-C}_6\text{H}_3)]$  ( $M = \text{Ni}$  (**2**),  $\text{Cu}$  (**3**)), and their 3,5-difluorosubstituted analogues  $M[\text{Fc}-\text{C}(\text{O})\text{CH}=\text{C}(\text{CH}_3)\text{N}-o\text{-C}_6\text{H}_4\text{-N}=\text{CH}-(2\text{-O},3,5\text{-F}_2\text{-C}_6\text{H}_2)]$  ( $M = \text{Ni}$  (**4**),  $\text{Cu}$  (**5**);  $\text{Fc} = \text{ferrocenyl} = (\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)$ ). Compounds **2-5** were synthesized in good yields (75-87%) in refluxing ethanol for 4 h, *via* template reaction by condensation of the tridentate half-unit metalloligand  $\text{Fc}-\text{C}(\text{O})\text{CH}=\text{C}(\text{CH}_3)\text{-N}(\text{H})\text{-}o\text{-C}_6\text{H}_4\text{NH}_2$  (**1**) with 5-nitrosalicylaldehyde and 3,5-difluorosalicylaldehyde, respectively, in the presence of hydrated Nickel(II) and Copper(II) acetate salts, respectively. Their composition and identity were inferred from elemental analysis, FT-IR, UV-vis, and multinuclear NMR spectroscopy. Single crystal X-ray diffraction analysis of the two 3,5-difluorosubstituted compounds **4** and **5** indicates a slightly bowed structure of the unsymmetrical Schiff base scaffold. Both  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  ions are tetraordinated in a distorted square planar environment, with two nitrogen atoms and two oxygen atoms as donors. The electrochemical behavior of the four binuclear complexes was investigated by cyclic voltammetry, showing greater anodic shifts of the reversible redox process ascribed to the  $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$  couple of the ferrocenyl donor fragment of the 5-nitrosubstituted derivatives compared to their 3,5-difluorosubstituted counterparts. Harmonic Light Scattering measurements showed that compounds **2-5** exhibited rather high second-order nonlinear responses, found between 200 and  $267 \times 10^{-30}$  esu, establishing a good correlation between redox potentials and the hyperpolarizability  $\beta_{1.91}$  values.

**Keywords:** Nickel; Copper;  $\text{N}_2\text{O}_2$ -ligand; Schiff base complexes; Crystal structure; Nonlinear optics

## 1. Introduction

Rational design and synthesis of cyclic or acyclic Schiff bases metal complexes are of continuing interest [1, 2], not only as synthetic intermediates but also as polytopic ligands in coordination chemistry [3]. Interests for these complexes is mainly due to their use in numerous fields of applications varying from catalysis [4] to pharmaceuticals [5], including new functional molecular-based materials [6, 7] with second-order nonlinear optical (NLO) properties [8]. In particular, tetradentate  $N_2O_2$  salen-type Schiff base complexes [9] that are well-established for all first-row transition metals have appeared to be a promising class of efficient chromophores exhibiting large NLO responses [8a, 10]. Among them, various unsymmetrical acyclic Schiff base complexes possessing strong electron donor (D) and electron acceptor (A) groups bound to a planar metal-containing  $\pi$ -conjugated Schiff base M(ONNO) framework have been extensively investigated [11-16]. Such D- $\pi$ -A systems, obtained by the 1:1:1 stepwise condensation of  $\beta$ -diketone, salicylaldehyde and a primary alkyl- or aryldiamine in the presence of a metal salt, have gained considerable attention for nonlinear optics due to their facile syntheses, thermal stability, and versatility in ligand design providing for the straightforward modulation of the sterics, electronics, and chirality at the central metal ion. In addition, coordination compounds that can be either neutral or ionic, exhibit low energy electronic charge transfer excitations tunable by virtue of the nature, oxidation state, and coordination sphere of the metal center and thus should be promising candidates as second-order NLO materials [8, 17].

Over the last decade, we designed and constructed novel neutral binuclear and ionic trinuclear three-dimensional Schiff base architectures featuring a planar metallo-salen framework that connects through its  $\pi$ -electron system a ferrocene donor unit and the cationic 12-electron  $[(\eta^5-C_5Me_5)Ru^+]$  acceptor moiety,  $\eta^6$ -coordinated to the salicylidene ring [18, 19]. Those organometallic donor-acceptor substituted unsymmetrical Ni(II)- and Cu(II)-centered Schiff base complexes exhibited large second-order NLO responses that increased with the nuclearity of the compounds [15, 16]. As an extension of this work and in order to further enhance the second-order NLO responses, we were interested in reacting the metalloligand  $Fc-C(=O)CH=C(CH_3)N(H)-o-C_6H_4-NH_2$  (1,  $Fc = (\eta^5-C_5H_5)Fe(\eta^5-C_5H_4)$ ) [20]

with strong electron-withdrawing salicylaldehydes bearing fluorine and nitro groups to generate, via template synthesis, new D- $\pi$ -A organometallic-inorganic hybrids and to study their electronic and NLO properties. Herein, we wish to report on the thorough investigation, including synthesis, analytical and spectroscopic characterization, and electrochemical behavior of a family of four neutral metal(II)-centered organometallic macrocyclic salen-type Schiff base complexes, namely, the binuclear 5-nitro derivatives  $M[\text{Fc-C}(\text{O})\text{CH}=\text{C}(\text{CH}_3)\text{N-}o\text{-C}_6\text{H}_4\text{-N}=\text{CH}-(2\text{-O},5\text{-NO}_2\text{-C}_6\text{H}_3)]$  (**2**:  $M = \text{Ni}$ , **3**:  $M = \text{Cu}$ ), and their 3,5-difluoro analogues  $M[\text{Fc-C}(\text{O})\text{CH}=\text{C}(\text{CH}_3)\text{N-}o\text{-C}_6\text{H}_4\text{-N}=\text{CH}-(2\text{-O-}3,5\text{-F}_2\text{-C}_6\text{H}_2)]$  (**4**:  $M = \text{Ni}$ , **5**:  $M = \text{Cu}$ ) (see formulas on Scheme 1). The X-ray crystal structures of these two latter difluorinated compounds **4** and **5** are also described. In addition, we disclose the first hyperpolarizability ( $\beta$ ) values of the neutral binuclear unsymmetrical Schiff base complexes **2-5** obtained in this work from Harmonic Light Scattering (HLS) experiments.

## 2. Experimental

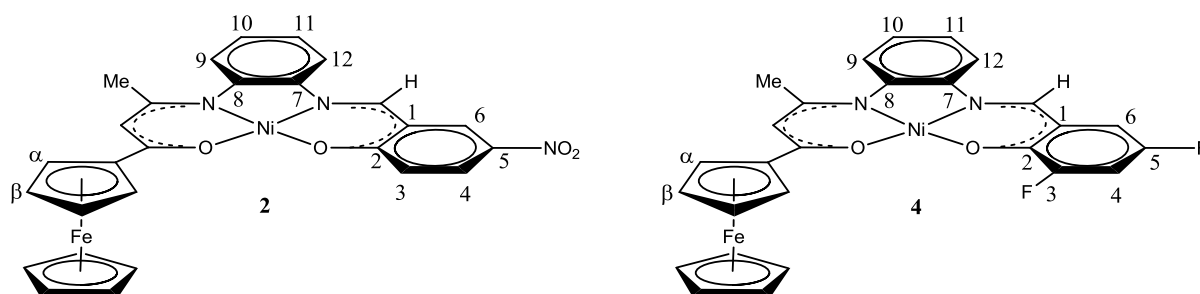
### 2.1. Materials and general procedures

Reactions were performed under dry nitrogen atmosphere using standard Schlenk techniques. Solvents were dried and distilled according to standard procedures [21]. 5-nitrosalicylaldehyde, 3,5-difluorosalicylaldehyde, nickel(II) acetate tetrahydrate, and copper(II) acetate monohydrate were purchased from Aldrich and used without further purification. The organometallic tridentate “half unit”  $\text{Fc-C}(\text{O})\text{CH}=\text{C}(\text{CH}_3)\text{N}(\text{H})\text{-}o\text{-C}_6\text{H}_4\text{NH}_2$  (**1**), was synthesized according to published procedure [20].

### 2.2. Characterization

Solid-state FT-IR spectra were recorded on a Perkin-Elmer Model 1600 FT-IR spectrophotometer with KBr disks in the 4000 to 450  $\text{cm}^{-1}$  range. Electronic spectra were obtained with a SHIMADZU UV-1800 spectrophotometer. NMR spectra were recorded with a Bruker Avance III 400 spectrometer. All NMR spectra are reported in parts per million (ppm,  $\delta$ ) relative to tetramethylsilane ( $\text{Me}_4\text{Si}$ ) for  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra, with the residual solvent proton and carbon resonances used as internal standards. Chemical shifts of  $^{19}\text{F}$  NMR spectra are referenced against external  $\text{CFCl}_3$ . Coupling constants ( $J$ ) are reported in Hertz (Hz), and integrations are reported as number of protons. The following abbreviations are used to describe peak patterns: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad.  $^1\text{H}$  and  $^{13}\text{C}$  NMR chemical shift assignments are supported by data obtained from  $^1\text{H}$ - $^1\text{H}$  COSY,  $^1\text{H}$ - $^{13}\text{C}$  HMQC, and  $^1\text{H}$ - $^{13}\text{C}$  HMBC NMR experiments, and are given according to the numbering scheme of Fig. 1. Elemental analyses were conducted on a Thermo-FINNIGAN

Flash EA 1112 CHNS/O analyzer by the Microanalytical Service of the Centre Regional de Mesures Physiques de l'Ouest (CRMPO) at the University of Rennes 1, France. Cyclic voltammetry (CV) measurements were performed using a Radiometer Analytical model PGZ 100 all-in one potentiostat, using a standard three-electrode setup with a vitreous carbon working electrode, platinum wire auxiliary electrode, and Ag/AgCl as the reference electrode. Dichloromethane solutions were 1.0 mM in the compound under study and 0.1 M in the supporting electrolyte  $n\text{-Bu}_4\text{N}^+\text{PF}_6^-$  with voltage scan rate = 100  $\text{mV s}^{-1}$ . The ferrocene/ferricenium redox couple ( $\text{Cp}_2\text{Fe}/\text{Cp}_2\text{Fe}^+$ ) was used as internal reference for the potential measurements. Melting points were determined in evacuated capillaries on a Kofler Bristoline melting point apparatus and were not corrected.



**Fig. 1** Labeling scheme used for NMR assignments

### 2.3. Synthesis of $\text{Ni}[\text{CpFe}(\eta^5\text{-C}_5\text{H}_4)\text{-C}(\text{O})\text{CH}=\text{C}(\text{CH}_3)\text{N-}o\text{-C}_6\text{H}_4\text{N}=\text{CH-(2-O,5-NO}_2\text{-C}_6\text{H}_3)]$ (**2**)

To a Schlenk tube containing 200 mg (0.55 mmol) of a solution of  $\text{CpFe}(\eta^5\text{-C}_5\text{H}_4)\text{C}(\text{O})\text{CH}=\text{C}(\text{CH}_3)\text{N}(\text{H})\text{-}o\text{-C}_6\text{H}_4\text{NH}_2$  (**1**) in 10 mL of ethanol, a solution of 93 mg (0.55 mmol) of 5-nitrosalicylaldehyde dissolved in 5 mL of ethanol, was added, under stirring. The resulting solution was refluxed for 15 min, cooled to room temperature and a solution of 207.2 mg (0.833 mmol) of nickel(II) acetate tetrahydrate dissolved in 5 mL of ethanol was added. The resulting mixture was refluxed for 4 h affording a dark red solid. The suspension was cooled at  $-30\text{ }^\circ\text{C}$  for 4 h. The dark red material was filtered off and washed with 3 x 4 mL portion of cold ethanol and 3 x 4 mL portion of diethyl ether. The solid was dried under vacuum for 2 h to give 245mg (78% yield) of **2** as a red powder. M. p. 296-298  $^\circ\text{C}$  (dec). Anal. calcd for  $\text{C}_{27}\text{H}_{21}\text{FeN}_3\text{NiO}_4 \cdot 0.5\text{H}_2\text{O}$  ( $574.03\text{ g mol}^{-1}$ ): C, 56.44; H, 3.86; N, 7.32. Found: C, 56.51; H, 3.68; N, 7.04. FT-IR (KBr pellet,  $\text{cm}^{-1}$ ): 3090 (vw), 3070 (vw)  $\nu(\text{C-H aryl})$ , 2968 (vw), 2925 (vw), 2855 (vw)  $\nu(\text{C-H alkyl})$ , 1606 (s)  $\nu(\text{C}=\text{O})$ ,  $\nu(\text{C}=\text{N})$  and/or  $\nu(\text{C}=\text{C})$ , 1544

(s), 1522 (s)  $\nu(\text{C-O})$ , 1377 (vs)  $\nu_{\text{asym}}(\text{NO}_2)$ , 1312 (vs)  $\nu_{\text{sym}}(\text{NO}_2)$ .  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ , 343 K): 2.47 (s, 3 H,  $\text{CH}_3$ ), 4.23 (s, 5 H,  $\text{C}_5\text{H}_5$ ), 4.48 (t,  $^3J_{\text{HH}} = 1.9$  Hz, 2 H,  $\text{H}_\beta$   $\text{C}_5\text{H}_4$ ), 4.78 (t,  $^3J_{\text{HH}} = 1.9$  Hz, 2 H,  $\text{H}_\alpha\text{C}_5\text{H}_4$ ), 5.81 (s, 1 H,  $\text{CH}=\text{C}$ ), 6.92 (d,  $^3J_{\text{HH}} = 9.4$  Hz, 1 H, H-3), 7.11 (td,  $^3J_{\text{HH}} = 8.2$  Hz,  $^4J_{\text{HH}} = 1.0$  Hz, 1 H, H-11), 7.22 (td,  $^3J_{\text{HH}} = 8.3$  Hz,  $^4J_{\text{HH}} = 1.0$  Hz, 1 H, H-10), 7.50 (dd,  $^3J_{\text{HH}} = 8.3$  Hz,  $^4J_{\text{HH}} = 1.0$  Hz, 1 H, H-9), 8.01 (dd,  $^3J_{\text{HH}} = 8.2$  Hz,  $^4J_{\text{HH}} = 1.0$  Hz, 1 H, H-12), 8.10 (dd,  $^3J_{\text{HH}} = 9.4$  Hz,  $^4J_{\text{HH}} = 3.0$  Hz, 1 H, H-4), 8.72 (d,  $^4J_{\text{HH}} = 3.0$  Hz, 1 H, H-6), 9.98 (br s, 1 H,  $\text{N}=\text{CH}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{DMSO-}d_6$ , 343 K): 26.22 ( $\text{CH}_3$ ), 68.52 ( $\text{C}_\alpha$   $\text{C}_5\text{H}_4$ ), 69.83 ( $\text{C}_5\text{H}_5$ ), 70.76 ( $\text{C}_\beta$   $\text{C}_5\text{H}_4$ ), 81.61 ( $\text{C}_{\text{ipso}}$   $\text{C}_5\text{H}_4$ ), 103.01 ( $\text{CH}=\text{C}$ ), 116.40 (C-12), 120.04 (C-1), 122.51 (C-9), 123.38 (C-11), 123.43 (C-3), 127.77 (C-10), 128.08 (C-4), 131.63 (C-6), 135.95 (C-5), 140.57 (C-7), 144.18 (C-8), 155.95 ( $\text{N}=\text{CH}$ ), 163.48 ( $\text{CH}=\text{C}$ ), 169.10 (C-2), 179.56 (C=O).

#### 2.4. Synthesis of $\text{Cu}[\text{CpFe}(\eta^5\text{-C}_5\text{H}_4)\text{-C}(\text{O})\text{CH}=\text{C}(\text{CH}_3)\text{N-}o\text{-C}_6\text{H}_4\text{N}=\text{CH-(2-O,5-NO}_2\text{-C}_6\text{H}_3)]$ (3)

The synthesis of this complex was carried out following a procedure similar to that described above for complex **2**, using in this case 200 mg (0.55 mmol) of the hemiligand **1** dissolved in 10 mL of ethanol, 93 mg (0.55 mmol) of 5-nitrosalicylaldehyde dissolved in 5 mL of ethanol and 166 mg (0.466 mmol) of copper(II) acetate monohydrate in 5 mL of ethanol. Yield: 238 mg (75%) of a dark orange powder. M. p. 266-269 °C (dec). Anal. calcd for  $\text{C}_{27}\text{H}_{21}\text{CuFeN}_3\text{O}_4$  (570.86 g mol<sup>-1</sup>): C, 56.81; H, 3.71; N, 7.36. Found: C, 56.45; H, 3.67; N, 7.08. FT-IR (KBr pellet, cm<sup>-1</sup>): 3089 (vw)  $\nu(\text{C-H aryl})$ , 2970 (vw), 2951 (vw), 2822 (vw)  $\nu(\text{C-H alkyl})$ , 1609 (s)  $\nu(\text{C}=\text{O})$ ,  $\nu(\text{C}=\text{N})$  and/or  $\nu(\text{C}=\text{C})$ , 1542 (s), 1515 (s)  $\nu(\text{C-O})$ , 1375 (vs)  $\nu_{\text{asym}}(\text{NO}_2)$ , 1318 (vs)  $\nu_{\text{sym}}(\text{NO}_2)$ .

#### 2.5. Synthesis of $\text{Ni}[\text{CpFe}(\eta^5\text{-C}_5\text{H}_4)\text{-C}(\text{O})\text{CH}=\text{C}(\text{CH}_3)\text{N-}o\text{-C}_6\text{H}_4\text{N}=\text{CH-(2-O,3,5-F}_2\text{-C}_6\text{H}_2)]$ (4)

The synthesis of this complex was carried out following a procedure similar to that described above for complex **2**, using in this case 200 mg (0.55 mmol) of the hemiligand **1** dissolved in 10 mL of ethanol, 88 mg (0.55 mmol) of 3,5-difluorosalicylaldehyde dissolved in 5 mL of ethanol and 207.2 mg (0.833 mmol) of nickel(II) acetate tetrahydrate in 5 mL of ethanol. Yield: 267 mg (87%) of a violet powder. Recrystallization by slow diffusion of pentane into a saturated dichloromethane of **4** deposited single crystals suitable for X-ray structure determination. M. p. 256–259 °C (dec). Anal calcd for  $\text{C}_{27}\text{H}_{20}\text{F}_2\text{FeN}_2\text{NiO}_2 \cdot 0.5\text{H}_2\text{O}$

(565.03 g mol<sup>-1</sup>): C, 57.34 ; H, 3.75; N, 4.96. Found: C, 57.14; H, 3.78; N, 4.76. FT-IR (KBr pellet, cm<sup>-1</sup>): 3078 (vw), 3001 (vw)  $\nu$ (C–H aryl), 2972 (vw), 2932 (vw), 2823 (vw)  $\nu$ (C–H alkyl), 1605 (s), 1547 (vs), 1521 (vs)  $\nu$ (C=O),  $\nu$ (C=N) and/or  $\nu$ (C=C), 1400 (s), 1377 (vs), 1365 (vs)  $\nu$ (C–F), 1288 (s), 1266 (s)  $\nu$ (C–O). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, 298 K): 2.47 (s, 3H, CH<sub>3</sub>), 4.22 (s, 5 H, C<sub>5</sub>H<sub>5</sub>), 4.46 (t, <sup>3</sup>J<sub>HH</sub> = 2.0 Hz, 2 H, H<sub>β</sub> C<sub>5</sub>H<sub>4</sub>), 4.77 (t, <sup>3</sup>J<sub>HH</sub> = 2.0 Hz, 2 H, H<sub>α</sub> C<sub>5</sub>H<sub>4</sub>), 5.86 (s, 1 H, CH=C), 7.09 (br ddd, <sup>3</sup>J<sub>HH</sub> = 7.4 and 8.3 Hz, <sup>4</sup>J<sub>HH</sub> = 1.0 Hz, 1 H, H-11), 7.18 (br ddd, <sup>3</sup>J<sub>HH</sub> = 7.4 and 8.3 Hz, <sup>4</sup>J<sub>HH</sub> = 1.0 Hz, 1 H, H-10), 7.26 (ddd, <sup>3</sup>J<sub>HF</sub> = 9.0 Hz, <sup>4</sup>J<sub>HH</sub> = 3.2 Hz, <sup>5</sup>J<sub>HF</sub> = 1.7 Hz, 1 H, H-6), 7.347 (ddd, <sup>3</sup>J<sub>HF</sub> = 9.0 and 11.3 Hz, <sup>4</sup>J<sub>HH</sub> = 3.2 Hz, 1 H, H-4), 7.51 (dd, <sup>3</sup>J<sub>HH</sub> = 8.3 Hz, <sup>4</sup>J<sub>HH</sub> = 1.0 Hz, 1 H, H-9), 7.98 (dd, <sup>3</sup>J<sub>HH</sub> = 8.3 Hz, <sup>4</sup>J<sub>HH</sub> = 1.0 Hz, 1 H, H-12), 9.05 (br s, 1 H, N=CH). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, DMSO-*d*<sub>6</sub>, 298 K): 24.80 (CH<sub>3</sub>), 68.33 (C<sub>α</sub> C<sub>5</sub>H<sub>4</sub>), 69.81 (C<sub>5</sub>H<sub>5</sub>), 70.69 (C<sub>β</sub> C<sub>5</sub>H<sub>4</sub>), 79.72 (C<sub>ipso</sub> C<sub>5</sub>H<sub>4</sub>), 102.58 (CH=C), 108.66 (dd, <sup>2</sup>J<sub>CF</sub> = 22.1 and 29.2 Hz, C-4), 111.40 (dd, <sup>2</sup>J<sub>CF</sub> = 22.1 Hz, <sup>4</sup>J<sub>CF</sub> = 4.0 Hz, C-6), 115.88 (C-12), 120.22 (dd, <sup>3</sup>J<sub>CF</sub> = 5.0 and 10.0 Hz, C-1), 121.98 (C-9), 123.19 (C-11), 127.21 (C-10), 141.32 (C-7), 144.43 (C-8), 149.68 (dd, <sup>1</sup>J<sub>CF</sub> = 231.0 Hz, <sup>3</sup>J<sub>CF</sub> = 11.0 Hz, C-3), 150.48 (d, <sup>2</sup>J<sub>CF</sub> = 13.0 Hz, C-2), 153.07 (dd, <sup>1</sup>J<sub>CF</sub> = 247.0 Hz, <sup>3</sup>J<sub>CF</sub> = 12.0 Hz, C-5), 154.41 (N=CH), 163.25 (CH=C), 179.26 (C=O). <sup>19</sup>F NMR (376.5 MHz, DMSO-*d*<sub>6</sub>, 298 K): -128.26 (t, <sup>3</sup>J<sub>HF</sub> = 9.0 Hz, F-5), -129.81 (d, <sup>3</sup>J<sub>HF</sub> = 11.3 Hz, F-3).

## 2.6. Synthesis of Cu[CpFe(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>)-C(O)CH=C(CH<sub>3</sub>)N-*o*-C<sub>6</sub>H<sub>4</sub>N=CH-(2-O,3,5-F<sub>2</sub>-C<sub>6</sub>H<sub>2</sub>)] (5)

The synthesis of this complex was carried out following a procedure similar to that described above for complex **4**, using in this case a solution of 88 mg (0.55 mmol) of 3,5-difluorosalicylaldehyde in 5 mL of ethanol and 166 mg (0.466 mmol) of copper(II) acetate monohydrate in 5 mL of ethanol. Yield: 253 mg (81.2%) of a brown powder. Single crystals of **5** suitable for X-ray structure determination were grown by slow diffusion of pentane into a saturated dichloromethane solution of the compound. m. p.: 254–257 °C (dec). Anal. calcd for C<sub>27</sub>H<sub>21</sub>CuF<sub>2</sub>FeN<sub>2</sub>O<sub>2</sub> (561.85 g mol<sup>-1</sup>): C, 57.72; H, 3.59; N, 4.99. Found: C, 57.27; H, 3.58; N, 4.72. FT-IR (KBr pellet, cm<sup>-1</sup>): 3080 (vw), 3008 (vw)  $\nu$ (C–H aryl), 2969 (vw), 2923 (vw), 2853 (vw)  $\nu$ (C–H alkyl), 1608 (s), 1545 (vs), 1510 (vs)  $\nu$ (C=O)  $\nu$ (C=N) and/or  $\nu$ (C=C), 1397 (s), 1374 (vs)  $\nu$ (C–F), 1284 (s), 1256 (s)  $\nu$ (C–O).

## 2.7. X-ray Crystal Structure Determinations



Well-shaped black single crystals of complexes **4** and **5** of suitable dimensions were coated in Paratone-N oil, mounted on a Kaptan loop and transferred to the cold gas stream of the cooling device. Intensity data were collected at  $T = 150(2)$  K on a APEXII, Bruker-AXS diffractometer, Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å), equipped with a bidimensional CCD detector and were corrected for absorption effects using multiscanned reflections. The two structures were solved by direct methods using the *SIR97* program [22], and then refined with full-matrix least-square methods based on  $F^2$  (*SHELXL-97*) [23], with the aid of *WINGX* program [24]. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. All the hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms. A summary of the details about crystal data, collection parameters and refinement are documented in Table 1, and additional crystallographic details are in the CIF files. ORTEP views were drawn using *Olex2* software [25].

**Table 1** Crystal data, data collection, structure refinement parameters for **4** and **5**

	<b>4</b>	<b>5</b>
Empirical formula	C <sub>27</sub> H <sub>20</sub> F <sub>2</sub> FeN <sub>2</sub> NiO <sub>2</sub>	C <sub>27</sub> H <sub>20</sub> CuF <sub>2</sub> FeN <sub>2</sub> O <sub>2</sub>
Molecular weight (gmol <sup>-1</sup> )	557,01	561,84
Collection T (K)	150(2)	150(2)
Crystal system	Monoclinic	Monoclinic
Space group	P2 <sub>1</sub> /a	P2 <sub>1</sub> /a
a (Å)	9.4978(3)	9.6180(4)
b (Å)	19.5254(5)	19.2339(9)
c (Å)	11.6027(5)	11.6989(6)
$\beta$ (deg)	93.893(2)	95.096(2)
V (Å <sup>3</sup> )	2146.74(14)	2155.64(17)
Z	4	4
D <sub>calcd</sub> (g cm <sup>-3</sup> )	1.723	1.731
Crystal size (mm)	0.6 x 0.15 x 0.05	0.6 x 0.19 x 0.03
F(000)	1136	1140
Absorption coefficient (mm <sup>-1</sup> )	1.601	1.707
$\theta$ range (°)	3.00 to 27.47	3.00 to 27.48
Range h, k, l,	-8/12, -24/25, -15/15	-12/9, -23/24, -14/15
No. total refl.	18522	18397
No. unique refl.	4910	4904
Comp. to $\theta_{\max}$ (%)	99.8	99.3
Max/min transmission	0.923/0.779	0.950/0.788
Data/restraints/parameters	4910/0/317	4904/0/317

Final R indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0362$	$R_1 = 0.0361$
	$wR_2 = 0.0763$	$wR_2 = 0.0762$
R indexes (all data)	$R_1 = 0.0523$	$R_1 = 0.0554$
	$wR_2 = 0.0822$	$wR_2 = 0.0825$
GoF/ $F^2$	1.038	1.052
Largest diff. peak and hole ( $e \text{ \AA}^{-3}$ )	0.449 and -0.412	0.348 and -0.518

## 2.8. Harmonic Light Scattering (HLS) measurements

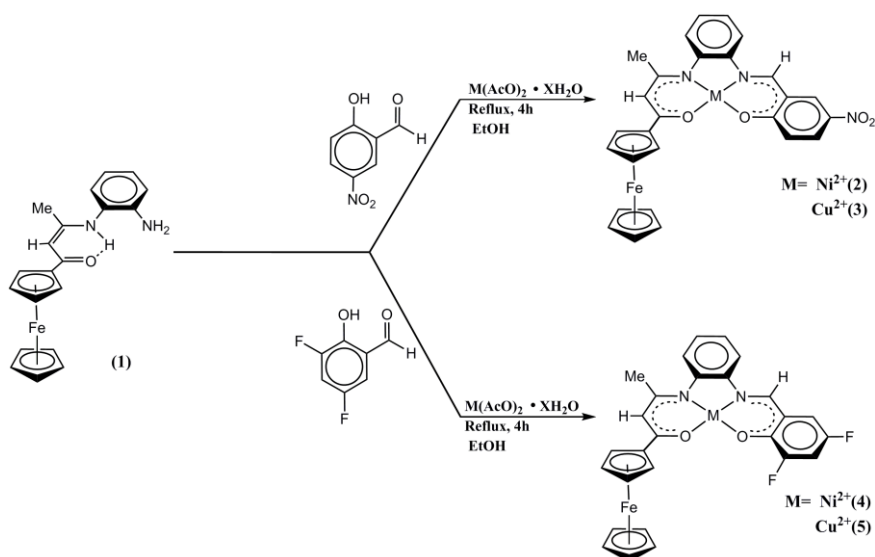
The HLS technique [26] at 1.91  $\mu\text{m}$  was employed to measure the first order hyperpolarizabilities  $\beta_{1.91}$  of compounds **2-5**. The 1.91  $\mu\text{m}$  fundamental beam was emitted by a high-pressure (30 bar), 50 cm long Raman cell pumped by a  $\text{Nd}^{3+}$ :YAG laser operating at 1.06  $\mu\text{m}$  and providing pulses of 15 ns duration at a 10 Hz repetition rate. The backscattered 1.91  $\mu\text{m}$  Raman emission was collected at a  $45^\circ$  incidence angle by mean of a dichroic mirror, to eliminate most of the residual 1.06  $\mu\text{m}$  pump photons. Choosing the 1.91  $\mu\text{m}$  wavelength, whose harmonics at 955 nm is far from any resonance of the molecules to be investigated, prevents the contribution of possible two-photon fluorescence emission to the HLS signal. We have evidenced the absence of any wide-band two-photon fluorescence by checking that no HLS signal can be detected for wavelengths different from 955 nm. Our reference sample was a concentrated ( $10^{-2}$  M) solution of ethyl violet, its octupolar  $\beta$  value being  $170 \times 10^{-30}$  esu at 1.91  $\mu\text{m}$  [27]. Dimethylformamide (DMF) was used as solvent to solubilize the species. DMF appears to be transparent at 1.91  $\mu\text{m}$ . The HLS photons at 955 nm were focused onto a Hamamatsu R632-01 photomultiplier tube using two collecting lenses. The detected signal was then sampled and averaged using a boxcar, and processed by a computer. The reference beam was collected at a  $45^\circ$  incidence angle by a glass plate, and focused onto a highly nonlinear N-4-nitrophenyl-prolinol (NPP) powder [28], which was used as the frequency doubler. The variation of the scattered second harmonic intensity from the solution was recorded on the computer as a function of the reference second harmonic signal provided by the NPP powder, both signals scaling as the square of the incoming fundamental intensity. Values for  $\beta_{1.91}$  were then inferred from the slopes of the resulting lines [29].

## 3. Results and discussion

### 3.1. Synthesis and characterization

The neutral binuclear unsymmetrical Schiff base complexes **2-5** were synthesized following a one-pot template reaction, by refluxing for 4 h in ethanol, the hemi-ligand Fc-

$C(O)CH=C(CH_3)N(H)-o-C_6H_4NH_2$  (**1**) with equimolar amounts of the desired 5-nitro or 3,5-difluoro substituted salicylaldehyde, and an slight excess (1.5 equiv) of the appropriate metal(II) acetate, as outlined in Scheme 1). Compounds **2** and **3** were isolated in similar yields (78 and 75%) as red wine and dark orange powders, respectively, while **4** and **5** were obtained as violet and dark brown microcrystalline solids in 87 and 81% yields, respectively. The four new complexes show a great thermal stability and are moisture insensitive both in solution and in the solid phase. They are slightly soluble in dichloromethane, exhibit good solubility in common organic solvents, and are all insoluble in diethyl ether, hydrocarbons and water. Composition and identity of the four new compounds were deduced from satisfactory elemental analysis, FT-IR, multinuclear and multidimensional NMR, and UV-vis spectroscopy. Additionally, the crystal and molecular structures of **4** and **5** were determined by single crystal X-ray diffraction analysis (see section 3.4).



**Scheme 1** Templated synthesis of complexes **2–5**

### 3.2. FT-IR spectroscopy

The solid-state FT-IR spectra of compounds **2–5** are similar to those we have previously described [15, 18, 19], and present the characteristic set of medium to strong intensity bands about  $1600\text{ cm}^{-1}$  attributed to the  $\nu(C\equiv C)$ ,  $\nu(C\equiv N)$  and  $\nu(C=O)$  stretching vibrations of the organic Schiff base skeleton (see Experimental for details). In addition, compounds **2** and **3** exhibit two bands around  $1560\text{ cm}^{-1}$  and  $1400\text{ cm}^{-1}$ , respectively, which have been attributed to the  $\nu_{\text{asym}}$  and  $\nu_{\text{sym}}$  ( $NO_2$ ) modes, respectively [30]. The strong band observed near  $1380\text{ cm}^{-1}$  in the spectra of **4** and **5** was assigned to the  $\nu(C-F)$  stretching

vibration of the doubly substituted salicylaldehyde fragment. Finally, a medium intensity band attributable to the  $\nu(\text{C}=\text{O})$  stretching mode was also observed about  $1260\text{ cm}^{-1}$

### 3.3. NMR spectroscopy

The  $^1\text{H}$  NMR spectra of the two diamagnetic compounds recorded in  $\text{DMSO-}d_6$ , at 343 K for **2** and at 298 K for **4**, exhibit the expected resonance patterns consistent with the proposed structures, with the presence of the  $\text{N}=\text{CH}$  azomethine proton resonating as the most downfield shifted signals of the spectra at 9.98 and 9.05 ppm, respectively, indicating the assembly of the quadridentate Schiff base ligands. The ferrocenyl enaminketonate entity is clearly identified by its three sharp singlet resonances at 2.47/2.47, 4.23/4.22 and 5.81/5.86 ppm (integral ratio 3:5:1), respectively, due to the methyl, the free cyclopentadienyl ring and the *pseudo*-aromatic methine protons. The asymmetry of the compounds is clearly reflected by the four distinct resonances of the *o*-phenylene bridge, in agreement with four magnetically non-equivalent protons. They appear as double doublet (H-9 and H-12) and as triple doublet or broad double doublet (H-10 and H-11) signal pattern in the ranges 7.09-8.01 ppm.

In compound **2**, the H-3, H-4 and H-6 protons of the 5-nitrosalicylidene ring (see Fig. 1 for labelling scheme) resonate with the characteristic doublet-double doublet-doublet multiplicity pattern observed for 5-substituted salicylidene ring [15, 18b], at 6.92, 8.10 and 8.72 ppm (integral ratio 1:1:1), respectively. In compound **4**, the H-4 and H-6 protons of the 3,5-difluorosalicylidene ring give rise to more complex resonances at 7.34 and 7.26 ppm, respectively. Both protons show up as double doublet of doublets due to coupling with two magnetically non-equivalent fluorine nuclei ( $^3J_{\text{H-F}} = 9.0$  and  $11.3\text{ Hz}$ ,  $^5J_{\text{H-F}} = 1.7\text{ Hz}$ ). Only the  $^3J_{\text{H-F}}$  coupling constants are observable in the  $^{19}\text{F}$  NMR spectrum that presents a triplet at -128.26 ppm attributed to F-5 and a doublet at -129.81 ppm assigned to F-3.

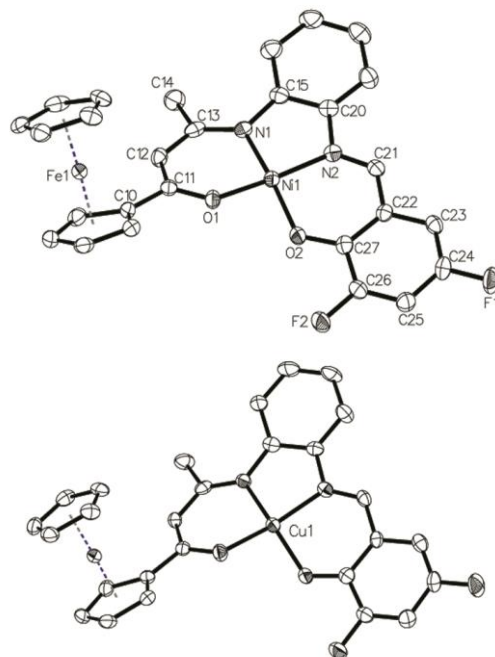
It is worth noting that the strong electron withdrawing ability of the nitro group, and to a lesser extent that of the two fluorines, is nicely illustrated by dramatic downfield shifts,  $> 2.5$  ppm in some instance, of the azomethine, salicylidene ring and even the *pseudo*-aromatic methyne protons compared to related chemical shifts measured in R-substituted

unsymmetrical binuclear Schiff base complexes (R = H [18a], Br [18b], OH [15, 19b], OC<sub>3</sub>H<sub>5</sub> [19a], CO<sub>2</sub>H [16]). This clearly shows the electronic influence of a powerful accepting group through the conjugated Ni(ONNO) bridge [31, 32]. Here, this strong acceptor ability of the 5-nitro group compared to that of the 3,5-difluoro substituents manifests itself also with a downfield shift  $\Delta\delta$  of +0.93 ppm of the azomethine NH proton signal.

The proton decoupled <sup>13</sup>C NMR spectra of **2** and **4** fully supports the interpretation outlined above, the unsymmetrical nature of both compounds being confirmed by the 25 resonances observed in their respective spectrum (see Experimental for complete assignments). Specifically, in **2** the signal of the C-5 carbon bearing the nitro group appeared at 135.95 ppm, whereas in **4**, the C-3 and C-5 carbons attached to the fluorine substituents showed up as double doublets at 149.68 and 153.07 ppm with <sup>1</sup>J<sub>C-F</sub> and <sup>3</sup>J<sub>C-F</sub> coupling constants of 231/247 and 11/12 Hz, respectively.

### 3.4. X-ray crystallographic studies

Perspective views of the two binuclear Schiff base complexes **4** and **5** are shown in Fig. 2, with selected bond distances and angles listed in Tables 2 and 3, respectively. Both **4** and **5** crystallize in the monoclinic centrosymmetric space groups P2<sub>1</sub>/a with one binuclear entity per asymmetric unit. The two compounds consist of a ferrocenyl fragment linked to a M(II)-centered unsymmetrical macroacyclic Schiff base complex (M = Ni: **4**, Cu: **5**) forming monomeric entities that are separated by normal van der Waals distances. In each compound, the ferrocenyl unit features a typical linear η<sup>5</sup>-Fe-η<sup>5</sup> sandwich structure, with cyclopentadienyl rings slightly staggered with twist angles of 15.50° for **4** and 13.13° for **5**. The ring centroid-iron-ring centroid angle is of 177.02° in **4** and 177.74° in **5**. The ring centroid-iron distances of 1.652, 1.651 Å and 1.652, 1.650 Å for the ring with and without the side chain, respectively, indicate that there is a Fe(II) oxidation state in the metallocenyl units [33].



**Fig. 2** Molecular structures of **4** (top), and **5** (bottom) with partial atom numbering schemes. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at 60% probability.

**Table 2** Selected bond distances (Å) and angles (°) for compound **4**

Bond distances			
Ni(1)-O(1)	1.8471(15)	Ni(1)-O(2)	1.8528(16)
Ni(1)-N(1)	1.8779(19)	Ni(1)-N(2)	1.8495(19)
O(1)-C(11)	1.284(3)	O(2)-C(27)	1.304(3)
N(1)-C(13)	1.343(3)	N(1)-C(15)	1.416(3)
N(2)-C(20)	1.428(3)	N(2)-C(21)	1.306(3)
C(10)-C(11)	1.478(3)	C(11)-C(12)	1.388(3)
C(12)-C(13)	1.403(3)	C(15)-C(20)	1.402(3)
C(24)-F(1)	1.373(3)	C(26)-F(2)	1.359(3)
Fe(1)-C(Cp) avg	2.044(3)	Fe(1)-C(Cp') avg	2.048(2)
Bond angles			
O(1)-Ni(1)-O(2)	84.20(7)	O(1)-Ni(1)-N(1)	96.17(8)
O(2)-Ni(1)-N(2)	94.91(8)	N(1)-Ni(1)-N(2)	86.69(8)
O(1)-Ni(1)-N(2)	169.21(8)	O(2)-Ni(1)-N(1)	169.40(8)
Ni(1)-O(1)-C(11)	125.20(15)	Ni(1)-O(2)-C(27)	126.65(15)
Ni(1)-N(1)-C(13)	122.52(16)	Ni(1)-N(1)-C(15)	112.11(15)
Ni(1)-N(2)-C(20)	112.68(15)	Ni(1)-N(2)-C(21)	125.85(16)
C(11)-C(12)-C(13)	125.8(2)	C(21)-C(22)-C(27)	120.8(2)

Abbreviations: Cp = C<sub>5</sub>H<sub>5</sub>, Cp' = C<sub>5</sub>H<sub>4</sub>

**Table 3** Selected bond distances (Å) and angles (°) for compound **5**

Bond distances			
Cu(1)-O(1)	1.9068(16)	Cu(1)-O(2)	1.9085(17)
Cu(1)-N(1)	1.946(2)	Cu(1)-N(2)	1.9319(19)
O(1)-C(11)	1.284(3)	O(2)-C(27)	1.301(3)
N(1)-C(13)	1.329(3)	N(1)-C(15)	1.419(3)
N(2)-C(20)	1.423(3)	N(2)-C(21)	1.294(3)
C(10)-C(11)	1.481(3)	C(11)-C(12)	1.396(3)
C(12)-C(13)	1.412(3)	C(15)-C(20)	1.403(3)
C(24)-F(1)	1.368(3)	C(26)-F(2)	1.360(3)
Fe(1)-C(Cp) avg	2.043(3)	Fe(1)-C(Cp') avg	2.046(3)
Bond angles			
O(1)-Cu(1)-O(2)	89.36(7)	O(1)-Cu(1)-N(1)	95.29(8)
O(2)-Cu(1)-N(2)	93.70(8)	N(1)-Cu(1)-N(2)	85.38(8)
O(1)-Cu(1)-N(2)	167.18(8)	O(2)-Cu(1)-N(1)	162.97(8)
Cu(1)-O(1)-C(11)	123.15(16)	Cu(1)-O(2)-C(27)	125.27(16)
Cu(1)-N(1)-C(13)	121.75(17)	Cu(1)-N(1)-C(15)	111.23(16)
Cu(1)-N(2)-C(20)	111.41(15)	Cu(1)-N(2)-C(21)	125.15(18)
C(11)-C(12)-C(13)	127.4(2)	C(21)-C(22)-C(27)	122.1(2)

Abbreviations: Cp = C<sub>5</sub>H<sub>5</sub>, Cp' = C<sub>5</sub>H<sub>4</sub>

The crystal structures of **4** and **5** reveal that the unsymmetrical Schiff base ligand coordinates to the metal(II) center as a doubly deprotonated form in a tetradentate fashion with a N<sub>2</sub>O<sub>2</sub> *cis*-configuration, as previously observed for such binuclear species [15, 16, 18, 19a]. This leads to the formation of a six-, five-, six-membered chelate ring arrangement around the central metal ion. In each compound, the Ni(II)- and Cu(II)-centered ions adopt a distorted square planar geometry as reflected by the deviations from the idealized values of 360 and 180° expected for the sum of the bond angles involving the metal, two O and two N atoms, and the two diagonal O-M-N angles. Those values are of 361.97°, 169.21(8) and 169.40(8)° for the Ni(II)-containing compound **4**, and of 363.72°, 162.97(8) and 167.18(8)° for the Cu(II) derivative **5**. This distortion towards a tetrahedral environment should presumably arise from an electronic effect of the 3,5-difluorosalicylidene ring, as in all the other structurally characterized unsymmetrical Schiff base complexes substituted with Br, OH, CO<sub>2</sub>H, or the cationic organometallic moiety [(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)Ru<sup>+</sup>], such a tetrahedral distortion has never been observed [15, 16, 18, 19a]. However, in solution the binuclear compounds must adopt a square planar geometry because the NMR spectra of both **2** and **4** were free from line broadening (see section 3.3).

Moreover, as a consequence of this tetrahedral distortion, the plane of [O(1)C(11)C(12)C(13)N(1)] subunit makes a dihedral angle of 21.56° in **4** and of 18.08° in **5**,

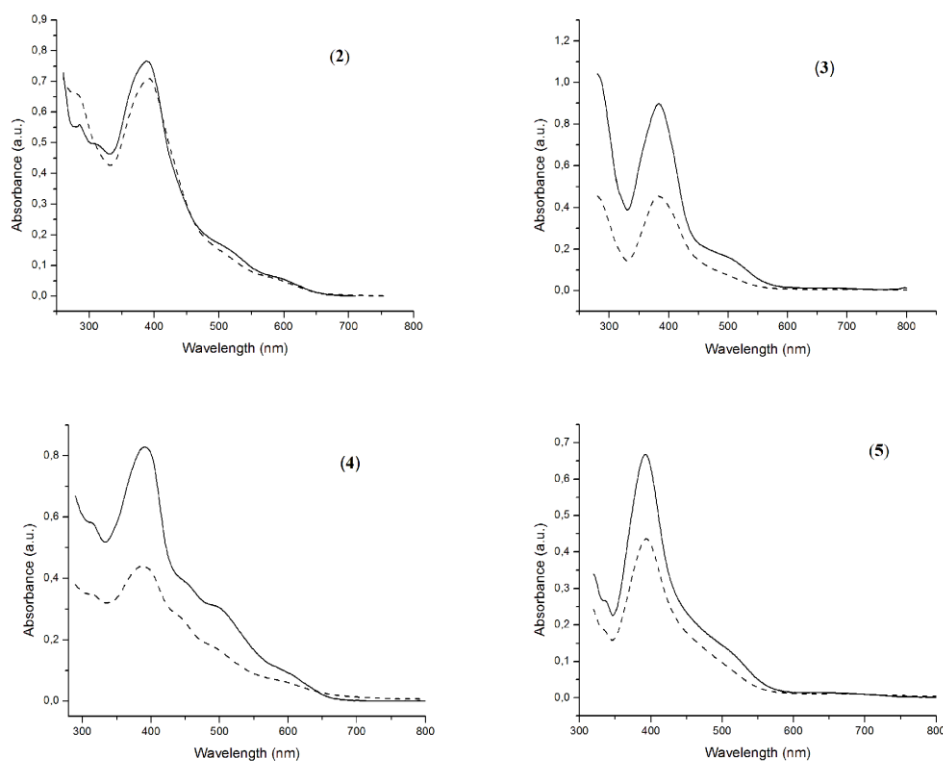
with the substituted cyclopentadienyl ring, and are greater than those measured previously (~ 5-10°) for analogous binuclear Schiff base complexes [15, 16, 18, 19a]. The six-membered metallacycles are held together by the five-membered diazametallacycle in which the N-C-C-N torsion angles are negligible (-0.5(3) and 1.5(3)°, respectively). A peculiar feature of such unsymmetrical Schiff base derivatives [18], is that in **4** and **5** the Werner-type coordination M(N<sub>2</sub>O<sub>2</sub>) core is also part of a bowed chelate Schiff base scaffold with angles of 174.4(5) and 173.2(5)°, respectively, formed by the two central carbons of the 6-membered chelate rings, C(12) and C(22), and the metal center.

The metal-heteroatom bond lengths range from 1.8471(15) and 1.8779(19) Å in **4** (Table 2) and from 1.9068(16) and 1.947(2) Å in **5** (Table 3). They are unexceptional and are in agreement with those reported in the literature [15, 16, 18, 19a, 34, 35]. The O-C, C-C and C-N bond lengths range between measured values for single and double bonds (Tables 2 and 3) [36], being indicative of a substantial delocalization of the electron density throughout the entire  $\pi$ -conjugated system.

### 3.5. Electronic absorption spectra

The electronic absorption spectra in the UV-visible region of the binuclear Schiff base complexes **2-5** were measured in CH<sub>2</sub>Cl<sub>2</sub> and in DMSO (see Fig. 3), and the spectral data are collected in Table 4. In the 350-430 nm region, the spectra exhibit a broad strong absorption band, while in the 450-650 nm range, these absorption spectra give rise to a set of two and three absorption bands for the closed-shell Ni(II) derivatives **2** and **4**, respectively, and one absorption band for the open-shell Cu(II) analogues **3** and **5**. Based on our previous computational TDDFT-assisted assignments [15,37], the high energy band is attributed to  $\pi$ - $\pi^*$  intraligand charge transfer transitions (ILCT), and the low energy bands are assumed to involve metal-to-ligand and ligand-to-metal charge transfer transitions. In addition, on passing from CH<sub>2</sub>Cl<sub>2</sub> ( $\epsilon = 8.90$ ) to the more polar DMSO solvent ( $\epsilon = 47.6$ ), the low-energy absorption bands exhibit significant blue shifts (Table 4), indicative of a negative change in the dipole moment between the excited and the ground states [15,16]. Such a hypsochromic behavior in solvents of higher polarity has already been observed and appears to be a general trend for NLO active push-pull salicylaldiminato Schiff base complexes [10], as well as for dipolar organometallic donor-acceptor substituted unsymmetrical Schiff base chromophores [15,16].





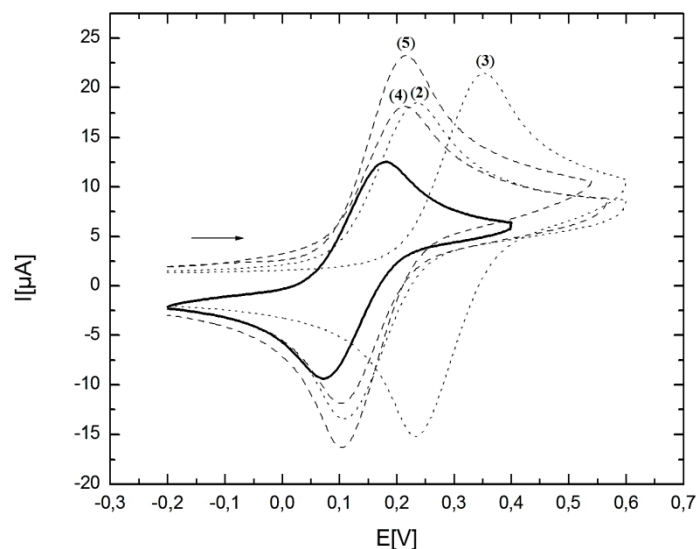
**Fig. 3** Electronic absorption spectra of complexes **2-5** recorded in  $\text{CH}_2\text{Cl}_2$  (solid line) and in DMSO (dashed line).

**Table 4** UV-vis absorption data for the binuclear Schiff base complexes **2-5**

Compd.	$\lambda/\text{nm}$ ( $\log \epsilon$ )/ $\text{m}^{-1}\text{cm}^{-1}$		Solvent shift/ $\text{cm}^{-1}$
	( $\text{CH}_2\text{Cl}_2$ )	(DMSO)	
<b>2</b>	386(4.86)	387(4.82)	+66
	485(4.26)	504(3.93)	+778
	596(3.61)	567(3.78)	-858
<b>3</b>	380(4.94)	383(4.56)	+206
	478(4.25)	434(4.10)	-2120
<b>4</b>	391(4.89)	390(4.53)	-66
	454(4.17)	448(4.10)	-295
	491(4.42)	497(3.80)	+246
	563(4.08)	506(3.97)	-2001
<b>5</b>	390(4.78)	391(4.59)	+66
	501(4.03)	467(4.04)	-1453

### 3.6. Cyclic voltammetry

In order to get a deeper insight into the mutual donor-acceptor electronic influence and to determine the electronic effects of the 5-NO<sub>2</sub> and 3,5-F<sub>2</sub> substituents on the electrochemical behavior of the bimetallic Schiff base complexes **2-5**, cyclic voltammetry (CV) experiments were performed in methylene chloride solution containing 0.1 M *n*Bu<sub>4</sub>N<sup>+</sup>PF<sub>6</sub><sup>-</sup> as supporting electrolyte, at room temperature. The cyclovoltammograms of the ferrocenyl unit of the four compounds are depicted on Fig. 4 and their respective formal electrode potentials  $E_{1/2}$  (vs. ferrocene/ferricenium redox couple) are listed in Table 5. These redox processes arising from the monoelectronic oxidation of the ferrocenyl moiety [38], are chemically reversible with current ratio  $i_{pa}/i_{pc}$  equals to unity. The anodic to cathodic peak-to-peak separations  $\Delta E_p$  (see Table 5), albeit slightly larger, remain close to the 103 mV value measured for the internal ferrocene standard under the same electrochemical conditions. They are, however, significantly greater than the ideal value of 60 mV for a fully reversible one-electron process. This may be ascribed to a combination of uncompensated solution resistance and slightly slow electron-transfer kinetics [39]. The increased difficulty to oxidize the Fe(II) center with respect to free ferrocene features the electron withdrawing ability of the substituted neutral Schiff base side chain. The CV data obtained here are in accordance with our previous observations within this family of binuclear macrocyclic unsymmetrical Schiff base complexes [15,16,18,19b].



**Fig. 4** Cyclic voltammograms of the ferrocenyl unit of the nitro derivatives **2** and **3** (dotted line), and of the difluoro derivatives **4** and **5** (dashed line), recorded in CH<sub>2</sub>Cl<sub>2</sub>/0.1 M *n*-Bu<sub>4</sub>N<sup>+</sup>PF<sub>6</sub><sup>-</sup> at 293 K  $v = 100 \text{ mV s}^{-1}$ , reference electrode Ag/Ag<sup>+</sup>, internal reference Cp<sub>2</sub>Fe<sup>0/+</sup> (solid line).

**Table 5** Electrochemical data<sup>a</sup> for compounds **2-5**

Compd	$E_{1/2}$ (V) <sup>b</sup>	$\Delta E_p$ (mV)
<b>2</b>	48	130
<b>3</b>	168	110
<b>4</b>	33	120
<b>5</b>	33	120

<sup>a</sup> Recorded at 293 K in CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 M *n*-Bu<sub>4</sub>N<sup>+</sup>PF<sub>6</sub><sup>-</sup> as supporting electrolyte, at a vitreous carbon working electrode, with scan rate of 100 mV s<sup>-1</sup>. <sup>b</sup> all potentials are vs. Cp<sub>2</sub>Fe<sup>0/+</sup> redox couple.

From data of Table 5, it can be concluded that the nitro substituent ( $\sigma_p=0.778$ ) [32] is a better electron-withdrawing group than the two fluorine substituents ( $\sigma_o = 0.24$ ,  $\sigma_p$  0.062), as for both nickel and copper Schiff base complexes the anodic shifts are greater for the nitro derivatives **2** and **3** than for their difluoro analogues **4** and **5**, with  $\Delta E_{1/2}$  values of +15 and +135 mV, respectively. Moreover, it is worth nothing that the copper-containing complex **3** is much more anodically shifted than its nickel-containing counterpart **2** ( $\Delta E_{1/2} = +120$  mV), indicating that the electron-accepting ability of the 5-NO<sub>2</sub> substituent through the  $\pi$ -conjugated open-shell d<sup>9</sup> Cu(II) N<sub>2</sub>O<sub>2</sub>-bridge is somewhat stronger than that with the closed-shell d<sup>8</sup> Ni(II) N<sub>2</sub>O<sub>2</sub>-bridge. This clearly suggests that there is a stronger interaction between the donor ferrocenyl moiety and the acceptor NO<sub>2</sub> substituent group, resulting from a better electron delocalization in the Schiff base framework mediated by the open-shell configuration of the central copper(II) ion [18b]. Such a difference between Ni and Cu complexes is not observed for the difluorinated species **4** and **5** (Table 5). Interestingly, the electrochemical behavior can be correlated with the NLO properties, the greater anodic shift the greater first hyperpolarizability  $\beta$  (see Section 3.7).

### 3.7. Quadratic NLO Studies

The quadratic nonlinear response of the new push-pull N<sub>2</sub>O<sub>2</sub> Schiff base complexes **2-5** have been determined at a 1.91  $\mu$ m incident wavelength using the HLS technique (see section 2.7). For solubility reasons and in order to allow comparison with previously determined second-order NLO responses, the HLS measurements were carried out in DMF ( $\epsilon = 36.7$ ), and the experimental values of the multipolar first hyperpolarizability  $\beta$  values are presented in Table 6. The rather high  $\beta_{1,91}$  values ranging between 200 and 267  $\times 10^{-30}$  esu are quite similar and in agreement with the  $\beta_{1,91}$  values determined previously under the same experimental conditions for unsymmetrical binuclear Schiff base chromophores [15, 16].

Interestingly, the nature of the electronic distribution of the metal centers (closed-shell vs. open-shell) in the square-planar geometry of complexes **2** and **3** manifests itself by a higher  $\beta_{1.91}$  value for the copper derivative **3** than for its nickel counterpart **2** (see Table 6), following the same trend as that observed by cyclic voltammetry, thus confirming the improved electronic delocalization in the Schiff-base open-shell complex with respect to a closed-shell one. In contrast, the almost identical  $\beta_{1.91}$  values reported for **4** and **5** confirm the CV behavior in the case of fluorine derivatives (see section 3.6), where the open-shell structure does not seem to play any role when using fluorine atoms as electron acceptors.

**Table 6** HLS  $\beta$  values determined at  $\lambda_{\text{inc}}$  1.91  $\mu\text{m}$  for compounds **2-5**

Compd <sup>a</sup>	$\beta$ ( $10^{-30}$ esu) <sup>b</sup>
<b>2</b>	214
<b>3</b>	267
<b>4</b>	213
<b>5</b>	200

<sup>a</sup> as  $10^{-2}$  M DMF solutions

#### 4. Conclusions

In this contribution, we have synthesized and fully characterized two series of robust neutral binuclear unsymmetrical salen-type complexes, and their electrochemical, linear and second order nonlinear optical properties have been thoroughly investigated. All the organometallic-inorganic D- $\pi$ -A conjugated hybrids investigated in this work contain the ferrocenyl donor group and the M(ONNO) unit (M = Ni(II), Cu(II)), the salicylidene ring of the acyclic tetradentate Schiff base chelate being substituted by 5-nitro or 3,5-difluoro electron withdrawing groups. Single crystal X-ray diffraction analyses of the two difluorosubstituted compounds **4** and **5** show a strongly distorted square pyramidal geometry of both the Ni- and Cu(ONNO) cores inserted into a bowed unsymmetrical Schiff base scaffold, and reveal the partial delocalization of bonding electron density throughout the metal Schiff base framework. This is further supported by UV-vis and electrochemical data that clearly indicate a mutual donor-acceptor electronic influence between the electron releasing organometallic unit and the M(ONNO) coordination core. HLS measurements show that the four  $\pi$ -conjugated push-pull chromophores exhibit rather high second-order nonlinear responses, and emphasize the better electron withdrawing ability of the 5-nitro with respect to

the 3,5-difluoro substitution, in agreement with CV data. They also confirm the interest of using open-shell complexes to improve their nonlinear optical properties, as already reported in earlier studies [40], the nature of the electron withdrawing group playing a significant role. Further investigations, including structural and computational studies, have to be performed in order to understand the peculiar electrochemical and NLO behavior of the 5-nitrosubstituted copper complex **3**.

### **Acknowledgments**

The authors thank Dr S. Sinbandhit (CRMPO, Rennes) and Prof. P. Grez (PUC Valparaiso) for helpful assistance with NMR experiments and stimulating discussion of the electrochemical data, respectively. This research has been performed as part of the Chilean-French International Associated Laboratory for "Inorganic Functional Materials" (LIAMIF-CNRS N°836). Financial support from the Fondo Nacional de Desarrollo Científico y Tecnológico [FONDECYT (Chile), grant no. 1130105 (D.C., C.M. and M.F.), the Vicerrectoría de Investigación y Estudios Avanzados, Pontificia Universidad Católica de Valparaíso, Chile (D.C., C.M. and M.F.), the CNRS and the Université de Rennes 1 is gratefully acknowledged. J. C. thanks the CONICYT (Chile) for support of a graduate fellowship.

### **Appendix. Supplementary material**

CCDC-1035237 (for **4**) and 1035238 (for **5**) contain 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](http://www.ccdc.cam.ac.uk/data_request/cif).

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