



Synthesis, characterization and X-ray crystal structure of an allyloxo functionalized nonsymmetric nickel coordination complex based on N₂O₂ chelating ferrocenyl ligand

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ABSTRACT

The synthesis of the new air and thermally stable orange neutral dinuclear iron–nickel unsymmetrical Schiff base complex, [8-(2-oxo,5-allyloxo-phenyl)-4,7-diaza-3-methyl-1-ferrocenyl-1-one-octa-1,3,7-trienato]nickel(II) (**2**), was achieved via the Williamson coupling reaction between the 2-oxo,5-hydroxy-phenyl precursor **1** and allyl chloride in the presence of base. Complex **2** was isolated in 68% yield and characterized by IR, UV–Vis, ¹H and ¹³C NMR spectroscopy, HRMS and authenticated by a single crystal X-ray diffraction analysis. The organometallic/inorganic hybrid complex **2** consists in a ferrocenyl fragment linked to a classical Werner-type complex made of an unsymmetrical quadridentate N₂O₂ Schiff base ligand with a pendant allyl ether functionality as a potential anchoring group. The Ni(II) center displays a square-planar geometry with the nitrogen and oxygen atoms occupying mutually *trans* positions. The structure of **2** · H₂O shows that the water crystallization molecule interacts through two distinct intermolecular hydrogen bonds with the two oxygen atoms of the tetradentate N₂O₂ acyclic chelating ligand, forming in the solid state, a distorted six-membered ring.

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1. Introduction

The design and synthesis of tetradentate Schiff bases derived from the 1:1:1 stepwise condensation of β-diketone, with alkyl or aryl diamines and a wide range of carbonyl precursors, as well as their transition metal complexes have long been of interest due to their preparative accessibility, their structural variability and their tunable electronic properties allowing to carry out systematic reactivity studies based on ancillary ligand modifications [1–4]. For instance, unsymmetrical Schiff base complexes are used as multipurpose molecules because they can be employed as homogeneous and supported catalysts [5,6], chromophores for photochemical processes such as non-linear optics (NLO) [7], chelating substrates to incorporate metal ions into macromolecules and polymers [8], for extraction purposes [9], scaffolds for dendritic and amino acid superstructures [10], and building blocks for the construction of supramolecular assemblies [11]. However,

in all the aforementioned work, organic groups have always been used to structurally and electronically modify the properties of the Schiff base frameworks. Organotransition metal complexes offer many exciting possibilities due to their diverse structural, electronic, magnetic and optical properties and are, therefore, expected to possess physical properties significantly different from their organic counterparts [12].

Over the last few years, we have been designing an unprecedented class of organometallic–inorganic hybrid complexes in which the ubiquitous ferrocenyl subunit, [CpFe(η⁵-C₅H₄)] where Cp = η⁵-C₅H₅, was introduced in the construction of the unsymmetrical acyclic Schiff base backbones [13,14] (Fig. 1). A series of binuclear compounds M[8-(2-oxo,5-R-phenyl)-4,7-diaza-3-methyl-1-ferrocenyl-1-one-octa-1,3,7-trienato] (M = Ni, Cu) was synthesized following an efficient, straightforward and inexpensive one-pot procedure, using the appropriate 1-ferrocenyl-enamnone [13–15], 2-OH,5-R-benzaldehyde, and metal(II) acetate. We thought that further addition of a peripheral functional group to such electroactive complexes would be of great interest in that, for instance, it could allow their transformation into precursors using covalent coupling, to obtain robust molecular arrays on a substrate [16,17]. In this contribution, we report on our first attempt with the synthesis of the functionalized heterobinuclear Schiff base complex, Ni[CpFe(η⁵-C₅H₄)-C(O)CH=C(CH₃)NCH₂CH₂N

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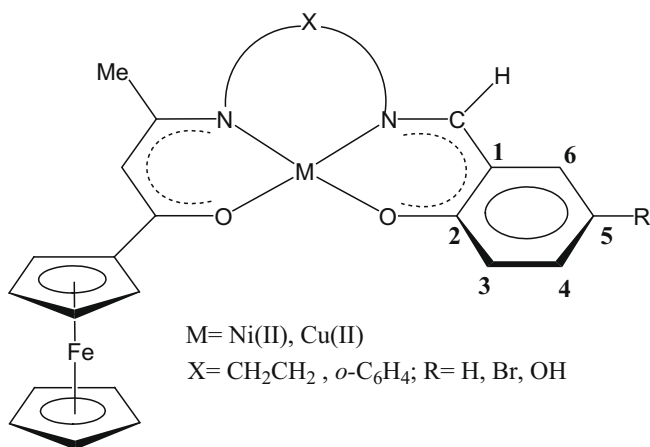


Fig. 1. Generic binuclear unsymmetrical Schiff base complexes.

=CH-(2-O,5-OCH₂CH=CH₂-C₆H₃)] (**2**) containing the pendant 5-allyloxy functionality, the full spectroscopic characterization (IR, UV-Vis, ¹H and ¹³C NMR) including mass spectrometry, and the crystal and molecular structure of **2**.

2. Experimental

2.1. General procedures

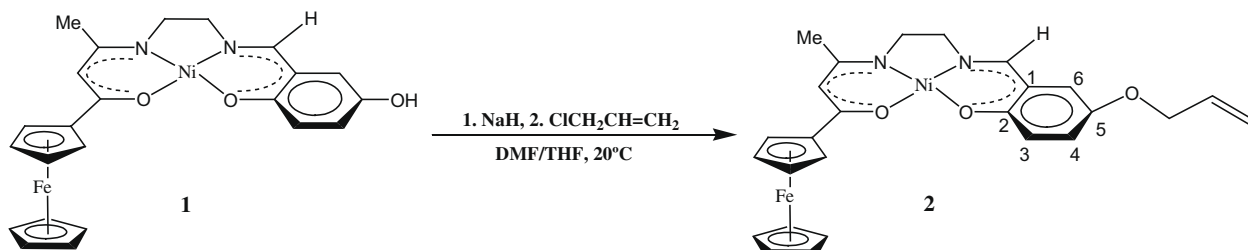
All operations were performed under inert atmosphere using standard vacuum/dinitrogen line (Schlenk) techniques. Solvents were dried and distilled under dinitrogen by standard methods prior to use. The hydroxo starting material **1** (see formula in Scheme 1) was synthesized following the published procedure [14]. Other reagents were purchased from commercial suppliers and used without further purification. IR spectra were obtained as KBr disks on a Perkin-Elmer model 1600 FT-IR spectrophotometer, in the range 4000–450 cm⁻¹. Electronic spectra were recorded with a Spectronic, Genesys 2 spectrophotometer. ¹H and ¹³C NMR spectra were recorded on Bruker AC 400 and Avance 500 Instruments. All NMR spectra are reported in ppm (δ) relative to tetramethylsilane (Me₄Si), with the residual solvent proton resonance and carbon resonances used as internal standards. 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: br = broad, s = singlet, d = doublet, t = triplet, m = multiplet. ¹H and ¹³C NMR chemical shift assignments are supported by data obtained from ¹H–¹H COSY, ¹H–¹³C HMQC, and ¹H–¹³C HMBC NMR experiments, and are given according to the numbering scheme depicted in Scheme 1. Mass spectrometric measurements (ESI⁺) were performed at the CRMPO (Rennes) on a high-resolution ZabSpec TOF VG Analytical spectrometer. Melting points were determined in evacuated capillaries and were not corrected.

2.2. Synthesis of Ni[CpFe(η⁵-C₅H₄)-C(O)CH=C(CH₃)NCH₂CH₂N=CH-(2-O,5-OCH₂CH=CH₂-C₆H₃)] (**2**)

A solution of compound **1** (215 mg, 0.405 mmol) in DMF (10 mL)/THF (5 mL) mixture was added dropwise to a 60% suspension of sodium hydride in mineral oil (10 mg, 0.405 mmol), and the resulting mixture was stirred for 30 min. Allyl chloride (30 μL, 3.60 mmol) was then added and the reaction medium was stirred for 12 additional hours at room temperature. The solution was filtered and concentrated until the formation of an oily residue, which was washed with ethanol (5 × 10 mL) to remove the remaining DMF. The oily residue was dissolved in dichloromethane (10 mL) and addition of diethyl ether (20 mL) caused the formation of an orange precipitate. It was collected by filtration, washed with diethyl ether (2 × 5 mL) and dried under vacuum. Recrystallization from CH₂Cl₂ gave single crystals suitable for X-ray analysis. Yield 145.8 mg, 68%. M.p. 202–205 °C. ESI MS (*m/z*), calcd for C₂₆H₂₆N₂O₃⁵⁶Fe⁵⁸Ni: 528.06463, found: 528.0653 [M]. IR (KBr, cm⁻¹): 3084(vw) ν(C-H arom); 2999(w), 2917 (w), 2853(w) ν(C-H aliph); 1631(m), 1577(m), 1535(m) ν(C···O), ν(C···C) and/or ν(C···N), 1260(w) ν(C-O). UV-Vis (λ_{max}, nm (log ε)): (CH₂Cl₂) 245(4.7), 307(4.1), 344(3.9), 383(3.8), 436(2.7), 465(3.7); (DMSO): 242(4.5), 305(3.9), 337(3.9), 390(3.7), 435(2.8), 458(3.5). ¹H NMR (400 MHz, CD₂Cl₂): δ 1.97 (s, 3H, CH₃), 3.04 (t, ³J_{HH} = 6.5 Hz, 2H, CH₂NCCH₃), 3.36 (t, ³J_{HH} = 6.4 Hz, 2H, CH₂NCH), 4.16 (s, 5H, Cp), 4.27 (s, 2H, H_β C₅H₄), 4.43 (d, ³J_{HH} = 5.3 Hz, 2H, -OCH₂CH=CH₂), 4.59 (s, 2H, H_α C₅H₄), 5.26 (d, ³J_{HH} = 10.3 Hz, 1H, -OCH₂CH=CH₂), 5.35 (s, 1H, CH=C), 5.39 (br s, 1H, -OCH₂CH=CH₂), 6.03 (m, 1H, -OCH₂CH=CH₂), 6.59 (d, ³J_{HH} = 2.7 Hz, 1H, H-6), 6.79 (d, ³J_{HH} = 9.2 Hz, 1H, H-3), 6.91 (dd, ³J_{HH} = 9.2 Hz, ⁴J_{HH} = 2.7 Hz, 1H, H-4), 7.41 (s, 1H, N=CH). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 21.77 (CH₃), 51.43 (CH₂NCCH₃), 60.26 (CH₂N=CH), 68.17 (C_α, C₅H₄), 69.57 (C_β, C₅H₄), 69.85 (Cp), 69.93 (OCH₂), 81.32 (C_{ipso} C₅H₄), 97.30 (CH=C), 113.73 (C-6), 117.37 (CH=CH₂), 118.80 (C-1), 122.41 (C-3), 124.52 (C-4), 133.79 (CH=CH₂), 147.96 (C-5), 160.57 (N=CH), 160.69 (C-2), 163.99 (CH=C), 176.06 (C=O).

2.3. X-ray crystal structure determination of **2** · H₂O

A X-ray quality crystal (0.35 × 0.20 × 0.03 mm) of compounds **2** · H₂O obtained as noted above, was mounted on the tip of a glass fiber in a random orientation. Intensity data were collected at *T* = 150(2) K on a Bruker Smart Apex diffractometer equipped with a bidimensional CCD detector using graphite monochromated Mo Kα radiation (λ = 0.71073 Å). Semi-empirical corrections, via *T*-scans, were applied for absorption. The diffraction frames were integrated using the SAINT package [18], and corrected for absorption with SADABS [19]. The structures was solved using XS in SHELXTL-PC [20], by direct methods and completed (non-H atoms) by difference Fourier techniques. Refinement was performed by the full-matrix least-squares method based on *F*². All non-hydrogen atoms were anisotropically refined. The positions of the hydrogen atoms at the water molecule was determined from the electron



Scheme 1. The synthesis of **2** with the labeling scheme used for the NMR assignments.

difference map, and isotropically refined. The remaining hydrogen atoms were geometrically positioned and treated as riding on the carbon atoms. ORTEP views were generated with XP in SHELXTL-PC [19].

Crystallographic data for 2 · H₂O: C₂₆H₂₆FeN₂NiO₃ · H₂O, Mr = 547.06 g mol⁻¹, monoclinic, P2₁/c, unit cell dimensions: *a* = 16.0602(11), *b* = 13.0482(9), *c* = 11.2587(8) Å, β = 102.3030(10)°, *V* = 2305.2(3) Å³, *Z* = 4, *D*_{calcd.} = 1.576 g cm⁻³, μ = 1.483 mm⁻¹, *F*(000) = 1136, data/restraints/parameters: 4587/0/316, *R*/*R*_w (*I* > 2σ(*I*)) = 0.0527/0.1106, *R*/*R*_w (all data) = 0.0757/0.1230, GOF = 1.062, [Δρ]_{min}/[Δρ]_{max}: -0.350/0.620.

3. Results and discussion

3.1. Synthesis and characterization

The allyl functionality was attached to precursor **1** by a Williamson coupling reaction [21], taking advantage of the acidic phenolic proton located in the 5-position of the salicylidene ring, outside the chelation motif of the ligand. Thus, a solution of **1** in DMF/THF (2/1) was added dropwise at room temperature to a dispersion of 60% sodium hydride in mineral oil and the resulting solution stirred for 30 min. An excess (9 equiv.) of allyl chloride was then added and the mixture stirred at room temperature for 12 h (Scheme 1). Upon work up, the target complex **2** was precipitated with diethyl ether as an orange powder and was recovered by filtration. Analytically pure **2** was obtained by recrystallisation from slow evaporation of a dichloromethane solution as orange microcrystals in a yield of 68%.

Compound **2** displays good thermal stability in air, both in solution and in the solid state, and exhibits a good solubility in common polar organic solvents but is insoluble in diethylether, hydrocarbons and water. Its structure was inferred from ¹H and ¹³C NMR, IR and UV–Vis spectroscopy, and by a X-ray diffraction analysis (see Section 3.2). In addition, high-resolution ESI MS gave an exact mass of *m/z* = 528.06463 for [M⁺] that matched the calculated value of 528.0653 and the expected isotopic distribution of peaks.

The more salient feature of the solid-state IR spectrum is the presence of a set of three medium intensity bands at 1631, 1577, and 1535 cm⁻¹ which can be assigned to the ν(C···C), ν(C···N) and/or ν(C···O) stretching modes of the organic Schiff base skeleton [13]. A weak intensity band attributable to the ν(CO) stretching mode was also observed at 1260 cm⁻¹.

The ¹H NMR spectrum of compound **2** exhibits all the expected resonance pattern consistent with the proposed structure (Fig. 2). The asymmetry of the complex is, indeed, clearly reflected in: (i) the ethylenediamine region which exhibits two distinct triplet resonances at 3.04 and 3.36 ppm, (ii) the ferrocenyl enaminketonate entity which is identified by its three sharp singlet resonances at 1.97, 4.16, and 5.35 ppm (integral ratio 3:5:1) due to the methyl, the unsubstituted cyclopentadienyl ring and the *pseudo*-aromatic methine protons, respectively, and (iii) the 5-substituted salicylidene ring showing a characteristic doublet, doublet, double-doublet multiplicity pattern attributed to H-6, H-3, and H-4 protons (integral ratio 1:1:1), respectively (see Scheme 1 for labelling scheme). As expected, the allyl group shows up as four resonances: a doublet at 4.43 ppm, a doublet and a broad singlet at 5.26 and 5.39 ppm,

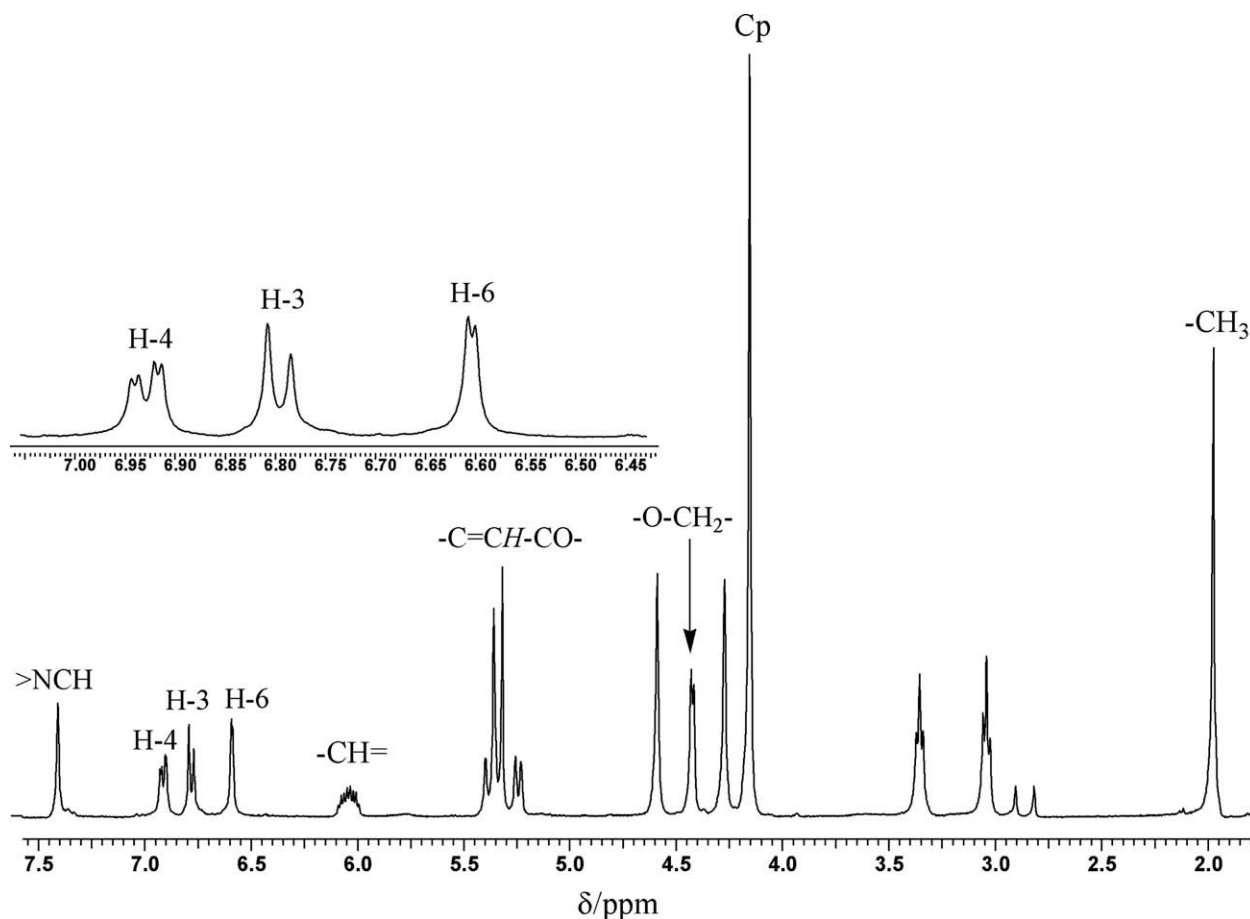


Fig. 2. The ¹H NMR spectrum of **2** in CD₂Cl₂ at 293 K, with enlarged aromatic region (top left) showing the “doublet, doublet, double-doublet” multiplicity pattern of the salicylidene ring.

Table 1
Selected bond distances (Å) and angles (°) for **2**.

Distances			
Ni(1)–O(1)	1.846(3)	Ni(1)–O(2)	1.844(3)
Ni(1)–N(1)	1.856(3)	Ni(1)–N(2)	1.851(3)
O(1)–C(11)	1.298(4)	O(2)–C(23)	1.322(4)
N(1)–C(13)	1.315(5)	N(2)–C(17)	1.302(5)
N(1)–C(15)	1.472(5)	N(2)–C(16)	1.464(5)
C(6)–C(11)	1.477(5)	C(11)–C(12)	1.369(6)
C(12)–C(13)	1.418(5)	C(15)–C(16)	1.510(5)
C(17)–C(18)	1.434(6)	C(18)–C(23)	1.402(5)
C(20)–O(3)	1.393(4)	C(24)–O(3)	1.407(5)
C(24)–C(25)	1.506(6)	C(25)–C(26)	1.283(7)
Angles			
O(1)–Ni(1)–N(1)	94.67(13)	O(1)–Ni(1)–O(2)	84.49(11)
O(2)–Ni(1)–N(2)	93.92(13)	N(1)–Ni(1)–N(2)	86.94(14)
O(1)–Ni(1)–N(2)	177.94(14)	O(2)–Ni(1)–N(1)	178.73(12)
Ni(1)–O(1)–C(11)	126.4(3)	Ni(1)–N(1)–C(13)	126.9(3)
Ni(1)–O(2)–C(23)	127.6(3)	Ni(1)–N(2)–C(17)	119.6(3)
C(20)–O(3)–C(24)	117.8(3)	C(24)–C(25)–C(26)	125.0(4)

and a multiplet at 6.03 ppm, assigned to the oxomethylene, the *cis* and *trans* vinylic methylene, and the vinylic methine protons (integral ratio 2:1:1:1), respectively. Lastly, the azomethine proton resonates as a singlet at 7.41 ppm as the most downfield shifted signal.

The decoupled $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum fully supports the interpretation outlined above, clearly demonstrating the unsymmetrical nature of the compounds. Since each carbon atom in complex **2**, except those of the unsubstituted cyclopentadienyl ring which are magnetically equivalent, gives rise to separate resonances, 20 lines were observed. For instance, the two carbons of the ethylene bridge appear at 51.43 and 60.26 ppm, and the six unequivalent carbons of the 5-substituted salicylidene ring give rise to six lines: a set of four singlets in the range 118.80–124.52 ppm for C-1, C-3, C-4, and C-6, and two deshielded singlets at 147.96 and 160.69 ppm for the carbons linked to an oxygen atom (C-2 and C-5, respectively). The allyl group shows up as three singlets at 69.93 ppm (O–CH₂), 117.37 ppm (=CH₂), and 133.79 ppm (–CH=). On the ferrocenyl enaminoketonate side, the methine carbon resonates at 97.30 ppm, whereas the low field signal at 176.06 ppm is assigned to the carbonyl carbon atom. On the other hand, the downfield shifted signals of the imine carbon atoms at 160.57 and 163.99 ppm, indicate some multiply bonded carbon–nitrogen bond character, in agreement with the C–N bond lengths found in the solid state (see Section 3.2).

The UV–Vis spectrum of **2** recorded in CH₂Cl₂ ($\epsilon = 8.90$) consists of two intense broad absorption bands in the visible region. This spectrum is essentially identical to those reported earlier for related compounds [13]. The origin of the high-energy absorption band in the range 230–390 nm, is assumed to be an intraligand $\pi\text{--}\pi^*$ charge-transfer (ILCT) transition, and the low-energy absorption band in the region 400–600 nm is assumed to involve both the ligand and the metal–ligand charge-transfer (CT) transitions of the central {Ni(ONNO)} Werner-type bridge and the ferrocenyl fragment [13,15b]. Upon increasing the solvent polarity (DMSO, $\epsilon = 47.6$), the low-energy CT bands exhibit a slight hypsochromic shift, indicating a reduction in the dipole moment upon electronic excitation [22].

3.2. X-ray crystallographic study

Recrystallization of the neutral Schiff base derivative Ni[CpFe($\eta^5\text{-C}_5\text{H}_4$)–C(O)CH=C(CH₃)NCH₂CH₂N=CH–(2-O,5-OCH₂CH=CH₂–C₆H₃)], by slow evaporation of the solvent from a concentrated dichloromethane solution of the complex in an open Erlenmeyer flask, deposited plate-shaped X-ray quality crystals of **2** · H₂O. Details of data collection and refinement as well as crystal data are given in Section 2.3. Selected bond distances and angles are reported in Table 1. Fig. 3 presents an ORTEP drawing of the molecular structures of **2** · H₂O, along with the atom numbering scheme. Complex **2** consists of a ferrocenyl fragment linked to an unsymmetrical Schiff base complex of nickel(II) forming monomeric units that are separated by normal van der Waals distances. Compound **2** · H₂O crystallizes in the monoclinic space group $P2_1/c$, with one binuclear entity and one water crystallization molecule present in the asymmetric unit. Organometallic–inorganic hybrid **2** can be described as a classical Werner-type coordination compound where the nickel(II) center is coordinated by an unsymmetrical quadridentate Schiff base ligand which is doubly deprotonated at the enamine nitrogen and phenol oxygen atoms, and formally binds nickel(II) ion through two nitrogen atoms (amido and imine) and two oxygen (carbonyl and phenolato) atoms. This multidentate binding leads to the formation of a six-, five-, six-membered chelate ring arrangement (6–5–6) around the central metal ion.

The nickel atom is surrounded by two pairs of nitrogen and oxygen atoms located in *trans* positions. The metal ion adopts a nearly perfect square-planar geometry: (i) the bond lengths associated with the nickel atom are virtually equal within the error of the measurement (see Table 1), (ii) the two diagonal angles, O(1)–Ni(1)–N(2) and O(2)–Ni(1)–N(1), of 177.94(14) and 178.73(12), respectively, barely deviate from linearity, (iii) the sum of the four

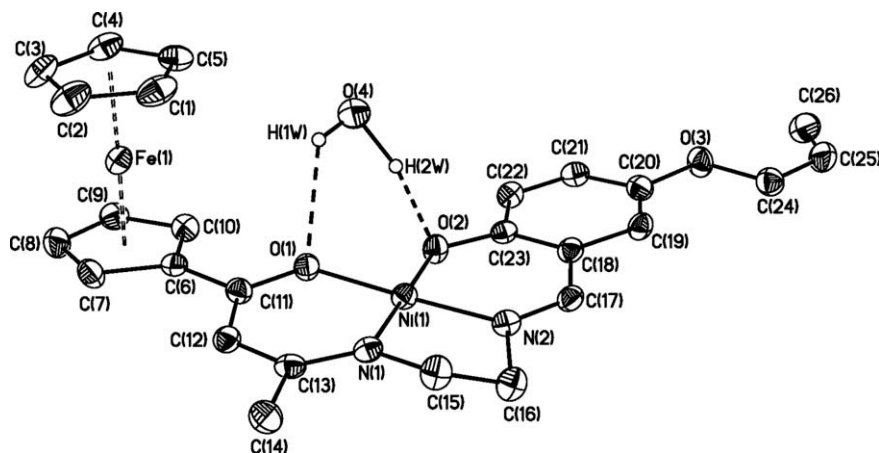


Fig. 3. Molecular structure of **2** · H₂O showing bridging hydrogen-bonding interactions involving H₂O (dashed lines), and the atom numbering scheme. Other hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at 40% probability.

Table 2
Hydrogen-bonding interaction parameters.

Donor-H...Acceptor	D-H (Å)	H...A (Å)	D...A (Å)	D-H...A (°)
O(4)–H(2w)...O(2)	1.219	1.660	2.813	155
O(4)–H(1w)...O(1)	0.862	2.315	2.989	135

angles at nickel is very close to 360°, and (iv) as a result, the metal center is located 0.003 Å from the mean ONNO plane, a deviation from square-planar not significant as the NMR spectra were free from linebroadening (see above). Such a behavior is similar to those observed in related Ni(II) unsymmetrical Schiff base complexes reported by us [13] and others [6a,23].

The two heteroconjugated six-membered metallocycles [O(1) to N(1)] and [O(2) to N(2)], are strictly planar and practically coplanar to the coordination basal plane with dihedral angles of 8.75 and 9.49°, respectively. Moreover, the plane of the metallocycle involving the organometallic enamino moiety [O(1) to N(1)] is almost coplanar with the substituted cyclopentadienyl ring of the ferrocenyl unit (dihedral angles = 7.39°, whereas the dihedral angles between the plane of the second metallocycle [O(2) to N(2)] and that of the salicylidene C₆-ring is 3.25°. One can also note that this latter plane is almost coplanar with the mean plane containing the allyl ether functionality (dihedral angle = 7.69°). In contrast, the five-membered ring defined by the nickel atom and diaminoethane moiety is definitely nonplanar, the ethylene bridges have a gauche conformation as usually observed with a torsion angle of 37.34° [13].

The bond length patterns within the two six-membered ring systems O–C–C–C–N suggest partial delocalization of bonding electron density as the O–C, C–C, C–C and C–N bond distances (see Table 1) fall between the measured values for related normal single and double bonds [24]. Some degree of electronic communication must therefore be expected between both metal centers through the delocalized Schiff base π-system. In addition, the molecular structure of **2** reveals almost eclipsed cyclopentadienyl rings for the ferrocenyl subunit. The two C₅-ligands are essentially parallel, with the ring centroid-iron-ring centroid angles of 178.31°, and ring centroid-iron distances of 1.642 and 1.648 Å for the ring with and without the side-chain, respectively. Those structural parameters are in full agreement with the typical metallocene coordination mode [24].

Interestingly, the water crystallization molecule found in the asymmetric unit interacts with the two oxygen atoms of the Schiff base ligand, forming in the solid state, a distorted six-membered ring through intermolecular hydrogen bonds (see Fig. 3). However, the two hydrogen-bonding interactions are quite distinct: a strong one characterized by a very short H(2w)...O(2) separation of 1.660 Å, and a much weaker one where the H(1w)...O(1) distance has increased by 0.655 Å [25] (Table 2). This difference of hydrogen bond strength presumably results from a higher electronic density at the phenolato oxygen than at the carbonyl oxygen of the tetradentate chelate.

4. Concluding remarks

In summary, we have described the synthesis by a Williamson coupling reaction, the full spectroscopic and structural characterization including a X-ray crystal structure determination of a new organometallic/inorganic hybrid consisting in a ferrocenyl fragment linked to a classical Werner-type complex made of an unsymmetrical quadridentate N₂O₂ Schiff base ligand with a pendant allyloxo functionality. The structure of **2** · H₂O shows that the Ni(II) center displays a square-planar geometry with the nitrogen and oxygen atoms occupying *trans* positions, and that the

water crystallization molecule interacts through two distinct intermolecular hydrogen bonds with the two oxygen atoms of the tetradentate chelating ligand. Furthermore, owing to the presence of the allyloxo function as potential anchoring group, this unsymmetrical redox active binuclear Schiff base complex might be covalently bound to oligomer and polymer backbones or on a surface through a single point of attachment, and serve either as immobilized catalyst for carbon–carbon coupling reactions or to obtain oriented non-centrosymmetric materials exhibiting NLO responses [26].

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Appendix A. Supplementary material

CCDC 706220 contains the supplementary crystallographic data for **2**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2008.12.036](https://doi.org/10.1016/j.jorganchem.2008.12.036).

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