Colorimetric metal ion (II) Sensors Based on imine boronic esters functionalized with pyridine

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ABSTRACT

The one-step synthesis of three imine boronic esters functionalized with pyridyl groups is described (**1a-1c**). The presence or absence of a methyl group affects the whole conformation, being bent “L” or linear as determined by X-ray crystal diffraction. C-H...O, C-H...N, C-H...F and C-H ... π hydrogen bond interactions support 2D supramolecular arrangements. Ligands were tested as metal ion (M^{2+}) sensors in solution. The addition of metal cations (Fe^{2+} , Co^{2+} and Cu^{2+}) to **1a** using methanol as solvent, showed significant color changes (purple, orange and green, respectively), while for metal cations Ni^{2+} , Zn^{2+} , Cd^{2+} cations no color changes were observed. The sensitivity of compound **1a** towards Fe^{2+} , Co^{2+} and Cu^{2+} was monitored by UV-Vis spectroscopy, where the presence of Fe^{2+} produces new bands at 360 and 566 nm. For Co^{2+} and Cu^{2+} a remarkable intensity increase was observed at 290 nm band and new bands appear at 340 and 462 nm, respectively. The stoichiometry of the complexes **1a-Fe**²⁺, **1a-Co**²⁺ and **1a-Cu**²⁺ was determined by Job's plots being 1:3 (metal:ligand, complex [$Fe(1a)_3$]²⁺), in contrast with the stoichiometry 1:1 observed for **1b-Fe**²⁺. In fact, the computed ΔG formation associated value showed a strong stabilization for the complex [$Fe(1a)_3$]²⁺ (−65.5 kcal/mol) in comparison with the possible complex [$Fe(1b)_3$]²⁺ (−29.7 kcal/mol). Detection limits are in the mM range (determined by UV-Vis) and μM range (determined by Fluorescence). An analogous bis-bidentate derivative (**2a**) also shows similar behavior but stoichiometric interaction changes to 2:3 (metal:ligand) and detection limits are in the mM range obtained by UV-Vis and Fluorescence techniques.

1. Introduction

Boronic acids have been widely used as building blocks for self-assembly processes [1] but also have attracted interest in sensing methods [2,3]. Boronic acids are easily condensed with 1,2 and 1,3 diols to give rise to the formation of 5- or 6-membered cyclic boronic esters, respectively [1,4,5]. One interesting characteristics for these compounds is the Lewis acid character of the tricoordinated boron atom, which can form adducts by interaction with Lewis bases [6,7]. The above reactivity has been used for the construction of species of different nature, such as macrocycles [1,4,8,9] and polymers [7–9], even, more recently the formation of metal-organic species has been possible from

the combination with coordinating groups such as Schiff bases and pyridyl groups [10–12].

In addition, Schiff bases have been used as sensors for metal cations, mainly because of the easy formation of the N→M coordination bonds together with the chelate effect, thus, high selectivity and sensitivity for heavy and transition metal ions is obtained [13–16]. Over the last years, they have received considerable research attention because of their important applications in biological, industrial and environmental processes as chemical sensors [17–21]. Schiff bases are an important type of colorimetric chemosensors because their interaction with analytes can be detected by naked eye, without the use of expensive equipment [22–24] It is well known that for colorimetric chemosensors, the shifts at

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the absorption spectra are affected by the respective increase or decrease in electron density on the chromophore moiety [25]. Furthermore, the color changes are more successfully observed when the interacting species includes electrostatic charges (i. e., cation-anion) than for neutral molecules [26].

The search of metal sensors is an important topic today [27–35], especially iron and copper metals have significant relevance because they are involved in several biological and environmental processes [36, 37]. Iron is one of the most abundant essential transition metal ion in human body, acting as cofactor for many proteins in a wide range of biochemical reactions such as electron transport and the enzyme oxidoreductase [38]. On the other hand, copper is an essential metal found as traces in all living organisms, it helps to provide the energy needed for the biochemical processes of heme oxygenase in blood [39].

The synthesis of ligands that selectively coordinates with metals of biological importance is still under research attention. To the best of our knowledge, until now no boronic ester coupled to the imine-pyridine fragment has been used as metal sensors. Previously, we reported the one-step synthesis of imine-boronic esters functionalized with pyridine moieties, which were found to form 2D structural arrangements by mean of intermolecular interactions [40,41]. In the present work, the synthesis of imine-pyridine-boronic ester derivatives was carried out, the compounds include pyridyl moieties in *ortho* position within the Schiff base, the structural 1,4 N–N' disposition allows the metal centers to form five member chelates. Complexation was monitored by naked-eye, UV–Vis and Fluorescence techniques.

2. Experimental

2.1. Materials and measurements

All reagents and solvents were acquired from commercial suppliers and used without further purification. The ^1H , ^{13}C and ^{11}B spectra were recorded at room temperature using a Varian VXR 400 MHz spectrometers and CDCl_3 as solvent. TMS (internal, ^1H , $\delta = 0.00$ ppm, ^{13}C , $\delta = 0.0$ ppm) and $\text{BF}_3\cdot\text{Et}_2\text{O}$ (external, ^{11}B , $\delta = 0.0$ ppm) were used as standard references. Mass spectra were obtained with Jeol JMS 700 equipment. Melting points were determined with a Büchi B-540 digital apparatus. The absorption and fluorescence spectra were recorded in a Thermo Scientific Genesys 10S UV–Vis and a Varian CaryEclipse in 2.00 mL quartz cells with 1 cm path length using methanol as solvent. All data treatment were analyzed with Origin software [42].

2.2. General synthesis of compounds 1a - 1c

The synthesis of the compounds was carried out using one-step reactions. Starting materials were added in equimolar ratio (following the order carboxypyridine, boronic acid and aminodiol), to a flask containing the solvent mixture of methanol (25 mL)/toluene (5 mL). The mixture was heated under reflux conditions for 24 h using a Dean Stark trap to remove the condensation water. After work up, the solvent was reduced to <10 mL to induce the precipitation of compounds, the obtained solids were washed with 10 mL of diethyl ether.

2.2.1. Synthesis of compound 1a

Obtained from 4-(trifluoromethyl)phenylboronic acid (399.7 mg, 2.102 mmol), 2-amino-1,3-propanediol (193.2 g, 2.102 mmol) and 2-pyridinecarboxaldehyde (200 μL , 2.102 mmol). 34% yield of a pale-yellow solid. M.P. = 145–148 °C. IR (ATR) ν : 1640 (C=N, w), 1309 (m), 1251 (m) 1103 (s), 648 (s). ^1H NMR (400 MHz, CDCl_3) δ = 8.64 (dd, $J_{\text{ortho}} = 4.9$ Hz, $J_{\text{meta}} = 1.6$ Hz, 1 H, H-8), 8.53 (s, 1H, H-3), 7.97 (dd, $J_{\text{ortho}} = 7.8$ Hz, $J_{\text{meta}} = 1.6$ Hz, 1 H, H-5), 7.90 (d, $J = 7.8$ Hz, 2 H, H-10), 7.72 (ddd, $J_{\text{ortho}} = 7.8$ Hz, $J_{\text{ortho}} = 7.8$ Hz, $J_{\text{meta}} = 1.6$ Hz, 1 H, H-6), 7.58 (d, $J = 7.8$ Hz, 2 H, H-11), 7.33 (ddd, $J_{\text{ortho}} = 7.8$ Hz, $J_{\text{ortho}} = 4.9$ Hz, $J_{\text{meta}} = 1.6$ Hz, 1 H, H-7), 4.24 (d, $J = 6$ Hz, 4 H, H-1), 3.93 (q, $J = 6.2$ Hz, 1 H, H-2), ^{13}C NMR (126 MHz, CDCl_3) δ = 164.5 (C-3), 154.0 (C-4), 149.8 (C-

Table 1

Selected crystallographic data of compounds 1a-1c.

Identification code	1a	1b	1c
Empirical formula	$\text{C}_{16}\text{H}_{14}\text{BF}_3\text{N}_2\text{O}_2$	$\text{C}_{17}\text{H}_{16}\text{BF}_3\text{N}_2\text{O}_2$	$\text{C}_{16}\text{H}_{16}\text{BBR}\text{N}_2\text{O}_2$
Formula weight	334.10	348.13	359.03
Crystal size (mm³)	0.22 × 0.12 × 0.08	0.28 × 0.16 × 0.12	0.26 × 0.14 × 0.12
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	P-1	$P2_1/c$	$P2_1/c$
Temp. (K)	100	100	293
Unit cell dimensions			
a [Å]	8.9366 (8)	6.6530 (3)	6.63819 (13)
b [Å]	9.4794 (8)	9.8202 (5)	9.7342 (2)
c [Å]	9.7470 (7)	24.317 (2)	24.1639 (5)
α [°]	73.290 (7)	90	90
β [°]	87.498 (6)	93.859 (5)	92.8341 (17)
γ [°]	73.545 (8)	90	90
Volume [Å³]	757.81 (11)	1585.16 (17)	1559.51 (5)
Z	2	4	4
ρ_{calcd} [g/cm³]	1.464	1.459	1.525
μ [mm⁻¹]	1.039	0.119	3.654
Collected refl.	4728	7408	5184
Independent refl (R_{int})	2912	3603	3028
Observed refl. [I > 2σ (I)]	2578	3024	2743
Parameters	344	720	724
R [I > 2σ (I)] R₁/wR₂	0.0424/0.1174	0.0641/0.1697	0.0386/0.1035
R (all data) R₁/wR₂	0.0472/0.1228	0.0745/0.1688	0.0416/0.1069
GOOF	1.034	1.028	1.041

8), 136.9 (C-6), 134.4 (C-10), 132.6 (q, $J_{\text{C-F}} = 37.8$ Hz, C-12), 125.5 (C-7), 124.4 (q, $J_{\text{C-F}} = 273$ Hz, $-\text{CF}_3$), 124.4 (q, $J_{\text{C-F}} = 12$ Hz, C-11), 122.0 (C-5), 66.3 (C-1), 65.1 (C-2), (B–C was not observed). ^{11}B NMR (128 MHz, CDCl_3) δ = 26, $h_{1/2} = 563$ Hz. EI^+ -MS-HR for $\text{C}_{16}\text{H}_{14}\text{O}_2\text{N}_2\text{F}_3\text{B}$, m/z : found 334.1113 $\pm$ 3.7, Calc. 334.1013.

2.2.2. Synthesis of compound 1b

Obtained from 4-(trifluoromethyl)phenylboronic acid (182.7 mg, 1.05 mmol), 2-amino-2-methyl-1,3-propanediol (110.3 g, 1.05 mmol) and 2-pyridinecarboxaldehyde (100 μL , 1.05 mmol). 44% yield of a white solid. M.P. = 153–155 °C. IR (ATR) ν : 1637 (C=N, w), 1293 (s), 1251 (m), 1102 (s), 842 (m), 649 (s). ^1H NMR (400 MHz, CDCl_3) δ = 8.60 (dd, $J_{\text{ortho}} = 5$ Hz, $J_{\text{meta}} = 1.6$ Hz, 1H, H-8), 8.52 (s, 1 H, H-3), 7.98 (dd, $J_{\text{ortho}} = 7.6$ Hz, $J_{\text{meta}} = 1.6$ Hz, 1H, H-5), 7.88 (d, $J = 7.6$ Hz, 2 H, H-10), 7.68 (ddd, $J_{\text{ortho}} = 7.6$ Hz, $J_{\text{ortho}} = 7.6$ Hz, $J_{\text{meta}} = 1.6$ Hz, 1H, H-6), 7.55 (d, $J = 7.6$ Hz, 2H, H-11), 7.28 (ddd, $J_{\text{ortho}} = 7.6$ Hz, $J_{\text{ortho}} = 5$ Hz, $J_{\text{meta}} = 1.6$ Hz, 1 H, H-7), 4.32 (AB, $J_{\text{AB}} = 11$ Hz, 4 H, H-1), 1.31 (s, 3 H, H-13). ^{13}C NMR (100 MHz, CDCl_3) δ = 160.9 (C-3), 153.7 (C-4), 149.9 (C-8), 137.3 (m, C-6 y C-12), 134.7 (C-10, C-12), 125.4 (C-7), 124.4 (q, $J_{\text{C-F}} = 4$ Hz, C-11), 124.4 (q, $J_{\text{C-F}} = 268$ Hz, $-\text{CF}_3$), 121.7 (C-5), 70.3 (C-1), 65.3 (C-2), (B–C was not observed). ^{11}B NMR (128 MHz, CDCl_3) δ = 26, $h_{1/2} = 460$ Hz. EI^+ -MS-HR for $\text{C}_{17}\text{H}_{16}\text{O}_2\text{N}_2\text{F}_3\text{B}$, m/z : found 348.1235 $\pm$ 6.2, Calc. 348.1280.

2.2.3. Synthesis of compound 1c

Obtained from 4-bromo-phenylboronic acid (210.9 mg, 1.05 mmol), 2-amino-2-methyl-1,3-propanediol (110.2 g, 1.05 mmol) and 2-pyridinecarboxaldehyde (100 μL , 1.05 mmol). 83% yield of a white solid. M.P. = 201–204 °C. ^1H NMR (400 MHz, CDCl_3) δ = 8.60 (dd, $J_{\text{ortho}} = 4.7$ Hz, $J_{\text{meta}} = 1.2$ Hz, 1 H, H-8), 8.51 (s, 1 H, H-3), 7.96 (dd, $J_{\text{ortho}} = 7.8$ Hz, $J_{\text{meta}} = 1.2$ Hz, 1 H, H-5), 7.87 (d, $J_{\text{ortho}} = 7.8$ Hz, 2 H, H-10), 7.69 (ddd, $J_{\text{ortho}} = 7.8$ Hz, $J_{\text{ortho}} = 7.8$ Hz, $J_{\text{meta}} = 1.2$ Hz, 1 H, H-6), 7.44 (d, $J_{\text{ortho}} = 7.8$ Hz, 2 H, H-11), 7.29 (ddd, $J_{\text{ortho}} = 7.8$ Hz, $J_{\text{ortho}} = 4.7$ Hz, $J_{\text{meta}} = 1.2$ Hz, 1 H, H-7), 4.12 (AB, $J_{\text{AB}} = 10.8$ Hz, 4 H, H-1), 1.30 (s, 3 H, H-13). ^{13}C NMR (100 MHz, CDCl_3) δ = 160.7 (C-3), 154.8 (C-4), 149.6 (C-8), 136.9 (C-6), 135.9 (C-10), 131.0 (C-11), 125.9 (C-12), 125.3 (C-7), 121.5 (C-5), 70.3 (C-1), 59.4 (C-2), 20.2 (C-13), (B–C was not observed). ^{11}B NMR

Scheme 1. Synthetic strategy to obtain **1a-1c** compounds. Numbering is for NMR assignments.

(128 MHz, CDCl₃) δ = 26, $h_{1/2}$ = 520 Hz. EI⁺-MS-HR for C₁₆H₁₆O₂N₂BrB, m/z : found 358.0493 $\pm$ 1.3, Calc. 358.0488.

2.3. X-ray measurements

Crystal intensity data were collected at T = 100 K for **1a** and **1b**, (293 K for **1c**), using Cu-K α radiation λ = 1.54184 Å, for **1a** and **1c** (Mo-K α radiation λ = 0.71073 Å for **1b**), graphite monochromator on an Agilent Technologies SuperNova diffractometer equipped with the EOsS2 CCD area detector and an Oxford Instruments Cryogen cooler. Crystal data, data collection parameters and convergence results are listed in Table 1. The measured intensities were reduced to F^2 and corrected for absorption using spherical harmonics (CryAlisPro) [43]. Intensities were corrected for Lorentz and polarization effects. Structure solution, refinement, and data output were performed with the OLEX2 program package [44] using SHELXL-2014 [45] for the refinement. Non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in geometrically calculated positions using the riding model. Intermolecular distances were analyzed with MERCURY [46]. The Hirshfeld surfaces were calculated by CrystalExplorer software [47].

2.4. Computational studies

The geometries of ligands **1a** (transoid) and **1b** (bent “L”), as well as the complexes [Fe(**1a**)₃]²⁺, [Fe(**1b**)(MeOH)₄]²⁺ and [Fe(**1b**)₃]²⁺ were fully optimized using the Gaussian-09 program package [48] within the framework of the Density Functional Theory (DFT). The computed geometries of the five species are provided as supplementary materials. In any case, the computations were performed in the presence of methanol as the solvent, which was modeled by the Polarizable Continuum Model (SCRF=PCM method) [49]. The combination of the widely used B3LYP hybrid functional [50,51], with the double- ζ basis set 6-31G* [52], was employed. The UV-Vis spectra were computed by Time-Dependent Density Functional Theory (TD-DFT), using the geometries of the optimized cations. In order to select the suitable method for these computations, several functional were tested (B3LYP, B3PW91, CAM-B3LYP, and PBE0). Finally, the B3PW91 [50] was chosen for its better accuracy to reproduce the experimental transition energies (<0.5 eV). The spectra were drawn by Gabedit software [53].

Fig. 1. X-ray crystal structures of compounds **1a-1c**.

Table 2Selected bond distances (Å), angles (°) and torsion angles (°) of compounds **1a-1c**.

	1a	1b	1c
B1–O1	1.358 (2)	1.362 (3)	1.362 (3)
B1–O2	1.358 (2)	1.361 (3)	1.357 (3)
B1–C10	1.571 (2)	1.578 (3)	1.568 (3)
N1–C2	1.4639 (18)	1.487 (3)	1.486 (2)
N1–C4	1.267 (2)	1.264 (3)	1.246 (3)
O1–B1–C10	118.16 (13)	118.04 (19)	118.37 (17)
O1–B1–O2	123.72 (14)	124.20 (2)	123.7 (2)
O2–B1–C10	118.02 (13)	117.68 (19)	117.92 (17)
C2–N1–C4	116.34 (12)	117.99 (18)	119.15 (17)
C11–C10–B1–O1	5.9 (2)	2.6 (3)	1.9 (3)
C10–B1–O1–C1	–173.1 (1)	179.0 (2)	179.3 (2)
B1–O1–C1–C2	–29.6 (2)	24.8 (2)	26.1 (2)
O1–C1–C2–N1	172.2 (1)	69.2 (2)	69.5 (2)
C1–C2–N1–C4	100.6 (2)	–169.1 (2)	170.0 (2)
C2–N1–C4–C5	178.3 (1)	179.6 (2)	–179.3 (2)
N1–C4–C5–C6	–5.1 (2)	8.7 (3)	7.4 (3)

3. Results and discussion

3.1. Syntheses and characterization

The present work describes one-step reactions using 4-substituted arylboronic acids (4-(trifluoromethyl)phenylboronic acid for **1a** and **1b**, 4-bromophenylboronic acid for **1c**), 2-amino-2-methyl-1,3-propanediol for **1b** and **1c** (2-amino-1,3-propanediol for **1a**), and 2-pyridine carboxaldehyde to obtain the three pyridine-imine boronic esters **1a-1c** (Scheme 1). Presence of the CF₃ and Br as 4-substituent at arylboronic acids, were introduced in order to modify the acid character of the boron atom on the ester formed, and to get the formation of more structured complexes by self-assembly using N→B coordination bonds. Compounds **1b** and **1c** were isolated as white solids (pale yellow for **1a**) which were soluble in organic solvents. Spectroscopy characterization was done using IR spectroscopy, mass spectrometry, ¹H, ¹³C and ¹¹B NMR spectroscopy and X-ray diffraction analysis.

First evidence for the formation of compounds **1a-1c** was obtained from IR spectra, the C=N imine band was observed around 1650 cm^{–1}, being characteristic for these type of compounds [1,41]. Using high resolution mass spectrometry (HR-EI⁺ technique), the *m/z* peak corresponding to the molecular ion [M]⁺ was observed for all three compounds showing good agreement between the isotopic distribution calculated and experimental data [54]. The ¹H NMR spectra showed the signal for the imine hydrogen shifted at δ = 8.53, 8.52 and 8.51 ppm for **1a**, **1b** and **1c**, respectively, being in the reported range for imines [55, 56]. Hydrogen signals corresponding to aryl moieties were observed at

low field δ = 7.60–8.60 ppm. Signals for hydrogens of methylene groups (CH₂) were observed as AB system at δ = 4.32 and 4.12 ppm, for compounds **1b** and **1c** respectively. For **1a**, the CH₂ group was observed as doublet at δ = 4.24 ppm. The ¹³C NMR spectra showed signals corresponding to imine groups at δ = 164.6, 160.9 and 160.7 ppm for **1a-1c**, respectively. The ¹¹B NMR spectra showed signals around δ = 26 ppm, in agreement with the formation of tri-substituted boronic esters [57].

3.2. X-ray crystal structures

Suitable crystals for X-ray diffraction analysis were obtained from slow evaporation of the mother liquor for all three compounds. Fig. 1 shows the molecular structures for the three compounds (**1a-1c**). Table 1 summarizes the selected crystallographic data and Table 2 shows selected bond distances, angles and torsion angles. The X-ray diffraction confirms the formation of boronic esters and imine bonds, all compounds have a tricoordinated boron atom having angles close to 120°, corresponding to a distorted trigonal planar geometry. Results indicated that, despite the presence of Lewis acid moieties (boronic ester) and Lewis bases (pyridine and imine moieties), the N→B dative bond was not observed, being attributed to electronic and steric effects as already reported [40]. The B–O lengths are in the range of 1.358 and 1.362 Å, which are less than the sum of covalent radius because of the π retro-donating effect. It is interesting to remark that the whole conformation of compounds depends on the substituent at the C2 of the 6-membered heterocycle, thus when a hydrogen atom is present (**1a**) the compound acquires a linear conformation, whereas when it is replaced by a CH₃ group, a bent “L” conformation is observed. This effect has been observed in analogous compounds and mainly attributed to steric effects [41].

An aspect that immediately strikes upon comparison of the solid-state X-ray structure of **1a** and **1b** is the observation of so different molecular structure for entities, which differ by a methyl group only. This rather surprising difference rises the issue of its origin, either intramolecular or intermolecular, by virtue of packing effect. At first, it seems that the magnitude of intermolecular interactions is similar in **1a** and **1b** with densities calculated of 1.464 and 1.459, respectively. Additionally, the number of intermolecular short contacts is equal to 19 for **1a**, and 16 for **1b**, which suggests no significant difference in the strength of the interactions network for both species. At the molecular level, the Gibbs free energies (G) were calculated by DFT for the two species in the linear and in the bent “L” conformations [48]. In the case of **1a**, the linear form appears to be the more stable with the bent conformation located at 3.55 kcal/mol above the ground state conformation. It is worth pointing out that the stable conformation corresponds to the *transoid* structure depicted in Scheme 2, which is indeed

Scheme 2. *Transoid* and *cisoid* conformations for **1a**, and the bent “L” conformation for **1b**.

Table 3Main non-covalent interactions present in **1a-1c**.

Compound	Interaction	Distance (Å) D-X ... A	Distance (Å) X ... A	Angle (°) D-X ... A	Symmetry operation
1a	C (3)-H (3B) ... F (2)	3.287	2.550	132.7	$X, -1+y, z$
	C (8)-H (8) ... F (2)	3.388	2.521	155.1	$X, 2+y, 1+z$
	C (12)-H (12) ... N (2)	3.539	2.662	157.5	$-x, 3-y, -z$
	C (4)-H (4) ... N (2)	3.587	2.667	170.4	$-x, 4-y, -z$
	C (1)-H (1A) ... O (1)	3.440	2.580	147.8	$-x, 3-y, -z$
	C (7)-H (7) ... π	3.502	2.643	153.9	$1-x, 3-y, -z$
	C (3)-H (3A) ... F (1)	3.068	2.609	109.2	$-x, -1/2+y, 1/2-z$
1b	C (12)-H (12) ... F (3)	3.338	2.628	133.6	$-1-x, -1/2+y, 1/2-z$
	C (3)-H (3A) ... N (2)	3.586	2.743	145.7	$1-x, 1-y, 1-z$
	C (16)-F (3) ... B (1)	4.197	3.288	126.0	$-1+x, y, z$
	C (15)-H (15) ... π	4.293	3.474	148.3	$3-x, 1/2+y, 1.5-z$
1c	C (7)-H (7) ... O (1)	3.467	2.611	153.2	$3-x, -y, 2-z$
	C (7)-H (7) ... O (1)	3.467	2.611	153.2	$3-x, -y, 2-z$

that observed in the solid state. By contrast, the bent “L” conformation appears more stable in the case of **1b**, with the linear *transoid* structure located at 1.51 kcal/mol above the ground state geometry. Altogether, these computations fully agree with the observed geometries and leads to the conclusion that the solid-state conformation in both systems are mainly governed by intramolecular effects.

3.3. Non-covalent interactions

As mentioned above, N→B dative bond formation was constrain by electronic and steric effects, in addition, the boronic ester is part of a six-membered heterocycle, wherein the boron atom acidity is diminished in comparison with the analogous five-membered heterocycles where the N→B interaction is favored [6]. Nevertheless, the imine-boronic esters **1a-1c** contain several functional groups which can form non-covalent intermolecular interactions such as hydrogen bonding, π interactions and halogen interactions. The non-covalent interactions observed for all three compounds are summarized in Table 3. Mainly, hydrogen bonding

C-H...O (2.580, 2.611 Å), C-H...N (2.662, 2.667 and 2.743 Å) and C-H...F (2.521, 2.550 and 2.609 Å) are the most common non-covalent interactions observed (Fig. S1). Additionally, C-H ... π (2.643 and 3.474 Å) interactions for **1a** and **1c**, C-F...B (3.288 Å) donor-acceptor interaction for **1b** and, C-H...F (3.068–3.338 Å) interactions for **1a** and **1b** were observed, distances are in the range already reported [58–60]. The C-H...F interactions allow the formation of 2D arrangements as depicted at Fig. 2.

Hirshfeld surface analysis [61–63] was carried out to obtain additional information on the nature of intermolecular interactions. The red areas on the surface mapped with d_{norm} function were located on electronegative atoms which are responsible of strong hydrogen bonds. Fig. 3 shows the Hirshfeld surface for compound **1a** (for compounds **1b** and **1c** see supplementary information, Figs. S2 and S3 respectively), showing the red areas located at oxygen atoms (boronic ester) and nitrogen atoms (pyridine groups) which participate in C-H...O and CH ... N hydrogen bonds. When 2D fingerprint plots are partitioned [50], the H/H interaction are seen to be the most dominant interactions in all three cases, followed by F-H contacts (for compounds **1a** and **1b**) which are responsible of the molecular packing, in contrast, for compound **1c** the second dominant interaction is the C-H ... π . Table 4 summarizes the relative contribution of interactions (%) for compounds **1a-1c**.

3.4. Cation sensing studies

The imine-pyridine [22,64] or imine-phenol [65] moieties have been reported to act as chromophores for a variety of compounds since their photophysical properties can be modify by mean of metal-ligand interaction. Compounds **1a-1c** showed an absorption band at 290 nm (Fig. S4). Sensitivity tests were carried out for compound **1a** towards some metal cations from the first-row transition metals ($M^{2+} = \text{Fe}^{2+}$, Co^{2+} , Ni^{2+} , Cd^{2+} , Cu^{2+} and Zn^{2+}). Visible color changes were observed when methanol solutions of M^{2+} (1×10^{-3} M) were added to **1a** methanol solution in a 1:1 ratio (metal:ligand). Although most of the sensory analysis are carried out in aqueous solution because of the environmental, industrial and medical applications, many related reports use methanol as medium to determinate these properties [15,16, 66]. Herein, boronic esters decompose gradually in water solution and thus, methanol was the selected solvent for the analysis. Fig. 4 shows the colorimetric behavior observed for **1a** after the addition of M^{2+} solutions. The most representative change was noticed using Fe^{2+} , the solution turns purple from an initial colorless solution from free **1a**. By addition of Co^{2+} and Cu^{2+} methanol solutions, the **1a** solution turns orange and green, respectively. Color changes variations were also monitored by UV-Vis titration experiments, it was observed that the

Fig. 2. 2D supramolecular polymer formed by C-H...F interactions of **1a**.

Fig. 3. Hirshfeld surface of compound **1a** (up) and most representative finger prints (down).

Table 4

Relative contribution of interactions (%) for compounds **1a-1c**.

	Compound		
	1a	1b	1c
C-H/H-C (%)	19.4	16.5	11.8
H-H (%)	31.0	37.7	44.6
H-X/X-H (%)	22.4	18.7	9.9
H-N/N-H (%)	8.6	6.4	6.7
H-O/O-H (%)	6.2	7.3	8.1

X = F for **1a** and **1b**, Br for **1c**.

Fig. 4. Colorimetric behavior of compound **1a** towards the addition of metal ions in methanol solutions.

spectrum of **1a** shows increasing intensity of the band at 290 nm and the appearance of new bands at higher wavelengths when Fe^{2+} , Co^{2+} and Cu^{2+} methanol solutions were gradually added (Fig. 5). For instance, UV-Vis spectrum for the solution mixture of **1a-Fe**²⁺ showed two new bands at 360 and 566 nm which are attributed to ligand-metal charge transfer in addition to *d-d* transitions respectively. Additionally, the absorption bands are maintained when the anion changes (i.e. SO_4^{2-}), which suggests that the contranion does not affect the formation of the complex (Fig. S5). Similar behavior was observed for the absorption spectra of Co^{2+} and Cu^{2+} solutions, nonetheless lower intensity bands at 360 and 462 nm (respectively) were obtained.

The association constant (K_a) of **1a** with Fe^{2+} , Co^{2+} and Cu^{2+} were determined during titration experiments by the following equation [67]:

Fig. 5. UV-Vis spectral changes of **1a** (1×10^{-3} M) in methanol upon the addition of equimolar concentration of different metal ion solutions (1:1 (v/v), ml).

$$K_a = \frac{A - A_0}{(A_{\max} - A_0)[M^{2+}]}$$

where A and A_0 represent the absorbance of **1a** (at 566, 360 and 290 nm for Fe^{2+} , Co^{2+} and Cu^{2+} respectively) in the presence and absence of M^{2+} , $A_{\max}$ is the saturated absorbance of **1a** in the presence of excess amount of M^{2+} , while $[M^{2+}]$ is the concentration of the corresponding metal ion added. The association constant K_a resulted to be $5.51 \times 10^3 \text{ M}^{-1}$, $3.46 \times 10^3 \text{ M}^{-1}$ and $3.75 \times 10^3 \text{ M}^{-1}$ for Fe^{2+} , Co^{2+} Cu^{2+} respectively by 1:1 binding mode. The values show a trend of $\text{Fe}^{2+} > \text{Cu}^{2+} > \text{Co}^{2+}$ which is congruent with the observed spectral changes depicted at Fig. 6.

Titration experiment with Fe^{2+} , Co^{2+} and Cu^{2+} methanol solutions allowed also to determine the stoichiometric ratio (Fig. S6), the Job's graphs are depicted at Fig. 7a-c. Results showed that **1a-Fe**²⁺ complex

Fig. 6. Absorption spectra obtained during the titration of **1a** with Fe^{2+} (top), Co^{2+} (middle), Cu^{2+} (bottom) and profile of absorbance change at 566, 360 and 290 nm respectively. Methanol solutions (1×10^{-3} M).

shows the maximum absorption when the fraction/molar ratio is about 0.75, indicating a 1:3 metal:ligand stoichiometry, thus, each metal coordinates three units of **1a** suggesting the hexacoordination for metals forming a $[\text{Fe}(\text{1a})]^{2+}$ complex as depicted at Fig. 7d. In the case of **1a**- Co^{2+} and **1a**- Cu^{2+} titrations, the Job's plots show a maximum in 0.71 indicating also a stoichiometry near to 1:3 (spectral changes for each experiment are shown at Figs. S7–S9). Similar experiments were carried out for compounds **1b** and **1c**, these ligands show less absorbance compared with **1a**. The titrations Job's experiments showed a 1:1 stoichiometry for **1b** while a 2:1 stoichiometry for **1c** was observed (Fig. S10). The observed stoichiometric changes are attributed to the presence of $-\text{CH}_3$ group which induce different ligand conformation and, consequently, major steric effect.

To determinate the use of **1a** as selective sensor, a study of the possible interferences from competing ions was done. Experiments were carried out by adding simultaneously into methanol solutions of **1a**, first

a methanol solution of Fe^{2+} followed by methanol solutions of either Co^{2+} , Ni^{2+} , Cu^{2+} or Zn^{2+} (at 1 equivalent) Fig. 8a and b shows the absorbance values at 290 and 620 nm respectively for these combinations. Only small variations were observed at 290 nm, showing that in this region the interference is minor upon the further addition of a second metal ion species. On the other hand, in the region of the iron-ligand complex absorption (620 nm), addition of cation Cu^{2+} is revealed in the form of significant diminishing absorption to almost 50% (Fig. 8b). The last observation could be the result of the possible competitive interaction between Fe^{2+} - Cu^{2+} to the ligand.

Additionally, the previously reported compound **2a** [41] with analogous structure, was also tested as sensor for the metal ions described above. Compound **2a** is a boronic ester bis-N-bidentate ligand and consequently, the coordination of two metal centers at the same ligand is possible forming more structured complexes (Fig. 9). The UV-Vis analysis reveals that compound **2a** also showed colorimetric and

Fig. 7. Job's plots from UV-Vis spectra for compound **1a** with Fe^{2+} (a), Co^{2+} (b) and Cu^{2+} (c); d) proposed interaction between ligand **1a** and metal center.

Fig. 8. Absorbance changes at 290 (a) and 620 (b) nm of **1a-Fe** $^{2+}$ complex by the metal cation addition in methanol (1×10^{-3} M) to each compound. (To 620 nm, the ligand **1a** no absorb).

spectral sensitivity in methanol (5×10^{-4} M concentration) towards Fe^{2+} , Co^{2+} and Cu^{2+} cations in 2:3 (metal:ligand) binding stoichiometry. Thus, each metal center interacts with three molecules of **2a** and, each **2a** molecule interacts with two metal centers, this stoichiometry has been observed in the formation of polyhedral species of greater complexity as for instance the tetranuclear systems depicted at Fig. 9 [68–71].

Due to the biological and environmental importance of iron and copper, the synthesis of new sensors detecting metals at low concentrations with the smallest detection and quantification limits (LOD and LOQ) is currently of high importance [73,74]. For compounds **1a** and **2a**, LOD and LOQ values determination was done by using UV-Vis and Fluorescence spectroscopy employing standard deviation and graphic slopes [75–81]. Table 5 shows the LOD and LOQ values obtained for the two compounds using both techniques (Figs. S11–S15). Data from

UV-Vis spectroscopy shows that for compound **1a** the sensitivity towards metal cations follows the order $\text{Fe}^{2+} > \text{Cu}^{2+} > \text{Co}^{2+}$, while for **2a** it follows the order $\text{Cu}^{2+} > \text{Co}^{2+} > \text{Fe}^{2+}$. Differences on sensitivity can be attributed to the fact that the bis-imine boronic ester has two chelating sites per ligand and thus, the possibility to form additional metal/ligand species increases, but at the same time, the complexes stability decreases. On the other hand, using the Fluorescence technique, LOD and LOQ values showed that the sensitivity tendency remains as follow $\text{Fe}^{2+} > \text{Cu}^{2+} > \text{Co}^{2+}$ for both compounds, although for compound **1a** the lower values observed indicate a better sensitivity. It is important to remark that the LOD values observed in this work for the cation copper (II), are lower than those reported in the literature using the fluorescence technique (1.25 mM–0.01 mM) [82–86], and even lower than the maximum allowed value in blood (15.7–23.6 μM) [87] and in drinking water (<30 μM) [88,89] (Figs. S13 and S14).

Fig. 9. Proposed interaction between ligand **2a** and metal center. a) Graphical representation of tetrahedral structure in which the ligands are in the edges and the metal centers in the vertices. b) Optimized molecular structure of tetrahedral structure by Spartan [72].

Table 5

LOD and LOQ values determined for compounds **1a** and **2a** toward metal cations.

UV-Vis Spectroscopy		Fe ²⁺	Co ²⁺	Cu ²⁺
1a	LOD (mM)	0.48	0.94	0.85
	LOQ (mM)	1.45	2.86	2.58
	LOD (mM)	0.72	0.67	0.49
	LOQ (mM)	2.18	2.04	1.50
Fluorescence				
1a	LOD (μM)	2.66	4.37	2.89
	LOQ (μM)	8.07	13.24	8.78
2a	LOD (μM)	12.92	15.49	15.92
	LOQ (μM)	39.15	46.92	48.25

As described above, the mixture **1a**-Fe²⁺ has an intense purple color when it is freshly prepared, nevertheless the color changes over time, indicating instability under normal environmental conditions. Color changes of the **1a**-Fe²⁺ solution were monitored over 96 h and are shown in Fig. 10a, during the first 2 h the color changes from purple to green, later the intensity of color diminishes being almost colorless at the final of the observed period. The UV-Vis spectral changes are shown in Fig. 10b, whereby the band at 566 nm shown a bathochromic effect (up to 630 nm), obtaining a maximum point after 2 h, later this band disappears gradually. At the end, a colorless solution was observed having a wide band around 300 nm. UV-Vis spectral changes indicate that the boron ester and imine groups have been hydrolyzed over the observed period resulting in starting materials. In fact, after 96 h, the final spectrum obtained for the mixture **1a**-Fe²⁺, corresponds to the spectrum observed for the serinol/FeCl₂ mixture confirming the decomposition of the initial complex (Fig. S16).

Compounds **1a** and **2a** also were tested as sensors for Fe³⁺ cation. Therefore, a methanol solution of FeCl₃ was added to the methanolic solutions of **1a** and **2a**. Results showed pale-yellow solutions in both cases being the same as for the only Fe³⁺ methanol solution (Fig. 11a). Furthermore, UV-Vis spectroscopy analysis for the Fe³⁺/**1a** (**2a**) mixture solutions showed only a broad band at 350 nm which corresponds to the same observed for free FeCl₃ in methanol solution. As mentioned above, a purple color is observed when the ion Fe²⁺ is used,

indicating clearly the selectivity of compounds **1a** and **2a** towards Fe²⁺, so that these compounds can differentiate Fe²⁺ from Fe³⁺ ions in solution (Fig. 11b).

3.5. Computational calculations

A computational investigation has been carried out to suggest the role devoted to the methyl group in the stoichiometry observed for metal complexes built up from ligands having the same coordinating capabilities (**1a**, **1b**). Due to the large number of possible isomers in the ML₃ complexes, the two following assumptions were introduced for the sake of simplifications: (i) the linear (form **1a**) or bent (form **1b**) conformation of the free ligands is maintained in the complexes. This is reasonable, if the linear $\Rightarrow$ bent transformation imply C – C chemical bonds to be broken and rebuilt. (ii) the more stable geometry for the ML₃ complexes, is not C₃ in which the three ligands are oriented in the same direction, but rather the geometry in which one ligand is oriented head to tail with the respect to the other ones (C₁). This was confirmed in the case of the iron complexes, in which the C₃ geometry is located at an average of 1 kcal/mol above the C₁ geometry. (iii) the computations were performed on Fe^{II} in close shell d⁶ configuration but are applicable to any pseudo-octahedral metal complexes. Under these assumptions and considering methanol as the solvent, to following reactions were considered:

The associated changes in the Gibbs free energies (ΔG) are found to be equal to -15.8 kcal/mol and -17.9 kcal/mol for (1) and (2) equations, respectively. It is worth pointing out that the conformation of **1a** is the linear *transoid* form depicted in Scheme 2, in any cases. Interestingly, the same computations carried out for iron-**1b** complexes lead to ΔG values of -17.0 kcal/mol and -12.7 kcal/mol for the related (1) and (2) equations, respectively. At this stage, and although the replacement of the 6 methanol molecules seems not to be as favorable for [Fe(**1b**)₃]²⁺ than for [Fe(**1a**)₃]²⁺, the overall behavior can be regarded as roughly similar for both **1a** and **1b** based complexes. However, [Fe(**1a**)₃]²⁺ can be subjected to an additional evolution as follows:

Fig. 10. a) Color changes observed for mixture $1a-Fe^{2+}$ solution monitored by 96 h. b) UV-Vis spectra obtained at different times in methanol at 2×10^{-3} M. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

The associated ΔG value for equation (3) is equal to -31.8 kcal/mol which leads to a strong stabilization of $[Fe(1a)_3]^{2+}$, this effect cannot take place in $[Fe(1b)_3]^{2+}$, leading to total ΔG values of -65.5 kcal/mol and -29.7 kcal/mol for the formation of $[Fe(1a)_3]^{2+}$ and $[Fe(1b)_3]^{2+}$, respectively. Altogether, the values presented above are all negatives, which suggest that the coordination of three ligand should be possible in any case, one must take them qualitatively as a clear trend towards much better coordinating capabilities in the case of ligand **1a**, as observed experimentally. The reason for such difference can be further evaluated based on the computed molecular geometries of the complexes. The averaged Fe-N bond length values are gathered in Table 6. The observation of longer Fe-N bond lengths in the proximity of the methyl group (Fe-N=C) reflects a steric hindrance in $[Fe(1b)_3]^{2+}$. It leads to a distortion of the ideal octahedral symmetry of the Fe-N₆ coordination sphere, and hence to a lowering of the stabilization energy for this species.

In addition, a TD-DFT approach has been used at the B3PW91/6-31G* level to find a rational for the differences observed in the UV-Vis of spectra of $1a-Fe^{2+}$ and $1b-Fe^{2+}$ complexes, which can be summarized as

follows: For **1a**: (i) the addition of iron (II) to **1a** leads to the gradual appearance of new bands at 360 nm (weak) and 566 nm (strong) (Fig. S6a); (ii) the intensity of these bands increases gradually with the concentration of iron added to the solution; (iii) the shape of the spectra remains grossly unaffected. Altogether, these observations suggest that a dominant complex is present in the mixture, the formula of which can tentatively be ascribed to $[Fe(1a)_3]^{2+}$. For **1b**: (i) the addition of iron (II) to **1b** leads to the appearance of an intense transition at 380 nm and a far less intense transition at 535 nm (Fig. S10); (ii) on going from Fe-**1b** stoichiometry of 1:1 to 1:3 a rather small modification of the intensity (absorbance/concentration of metal) is observed; (iii) the shape of the spectra is grossly unaffected by the concentration of ligand. These observations suggest a dominant complex, tentatively ascribed to $[Fe(1b)(MeOH)_4]^{2+}$.

The computed spectra for $[Fe(1a)_3]^{2+}$, $[Fe(1b)(MeOH)_4]^{2+}$, and $[Fe(1b)_3]^{2+}$ are gathered in Table 7 and compared with the UV-visible data. The shape of the three computed spectra is provided in Fig. S17. In the case of **1a**, the shape of the computed spectrum corresponds to the experimental UV-visible spectrum. The discrepancy in energy between theory and experiment is significant at the low energy band (0.45 eV) but still acceptable for an inorganic complex subjected to potential long-range charge transfer effects. The discrepancy becomes more

Fig. 11. a) Changes in color solution for compounds **1a** and **2a** towards Fe²⁺ and Fe³⁺ to naked eye. b) Spectral changes observed for compounds **1a** and **2a** upon the addition of iron (II) and iron (III) cations, in methanol (1×10^{-3} M). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Table 6

Averaged DFT computed Fe–N bond length for [Fe (**1a**)₃]²⁺ and [Fe (**1b**)₃]²⁺.

	Fe–N _(py)	Fe–N _(N=C)
[Fe (1a) ₃] ²⁺	2.004 Å	2.017 Å
[Fe (1b) ₃] ²⁺	2.002 Å	2.178 Å

Table 7

Computed data for [Fe (**1a**)₃]²⁺, [Fe (**1b**) (MeOH)₄]²⁺ and [Fe (**1b**)₃]²⁺.

Compound	UV–visible		Compound	TD-DFT/6-31G*	
	λ _{max}	intensity*		λ _{max}	f
1a -Fe ²⁺	566	<i>m</i>	[Fe (1a) ₃] ²⁺	467	0.167
	360	<i>w</i>		302	0.010
1b -Fe ²⁺	535	<i>w</i>	[Fe (1b) (MeOH) ₃] ²⁺	444	0.039
	380	<i>s</i>		263	0.385
				441	0.109
			[Fe (1b) ₃] ²⁺	307	0.032

*s, strong; m, medium; w, weak.

pronounced at higher energy transition, which prohibits a detailed analysis of the origin of the electronic effects related to these new transitions. The proposed formula ([Fe (**1a**)₃]²⁺) appears satisfactory for this specie. In the case of **1b**, where two formula may be envisioned, either [Fe (**1b**)₃]²⁺ or [Fe (**1b**) (MeOH)₄]²⁺, it is interesting to observe that the associated computed spectra are significantly different, thus leading to a possible mean to discriminate between the two formulas. Indeed the more intense transition stands at low energy in [Fe (**1b**)₃]²⁺ (like in [Fe (**1a**)₃]²⁺), while the intense transition is expected at high energy for [Fe (**1b**) (MeOH)₄]²⁺. With this respect, the experimental spectrum (Fig. S10) is in better agreement with [Fe (**1b**) (MeOH)₄]²⁺, as anticipated and in agreement with the UV–Vis experimental determinations.

4. Conclusions

Three imine-boronic esters functionalized with pyridine were

synthesized in good yield by condensation reactions. Besides the presence of donor (N) and acceptor (B) atoms, N→B dative bond formation was not observed because of electronic and steric effects influence. Nonetheless, hydrogen bonds (C–H...O, C–H...N, C–H...F and C–H ... π) are observed in the solid state and support the formation of 2D molecular structure arrangements. The presence of two N-donor coordinating groups (in the compounds) was used for sensing experiments towards metal cations M²⁺. The colorimetric studies showed that compounds **1a** and **2a** are suitable for detection of Fe²⁺, Co²⁺ and Cu²⁺ ions. The association stoichiometry for ligand **1a** with the metal ions (M²⁺) was determined to be 1:3 (metal:ligand), in contrast with the stoichiometry 1:1 observed when using the ligand **1b**. The above behavior was attributed to the linear conformation of the ligand **1a** in contrast with the bent “L” geometry observed for ligand **1b** in which the steric effects have an important effect. In addition, the ΔG calculated values showed that complex [Fe (**1a**)₃]²⁺ is 35.8 kcal/mol more stable than the compared value for complex [Fe (**1b**)₃]²⁺. Moderate values of LOD and LOQ were observable being for Cu²⁺ less than the allowed in drinking water. Ligands **1a** and **2a** are suitable to real-time simple-to-use and naked-eye detection of Fe²⁺ over Fe³⁺.

CCRediT authorship contribution statement

Paola Sánchez-Portillo: The author certify that all . **Aime Hernández-Sirio:** and approved the final version of manuscript “Colorimetric Metal Ion (II) Sensor Based on Imine Boronic Esters Functionalized with Pyridine”. They warrant that the article is the author’s original work, hasn’t received prior publication and isn’t under consideration for publication elsewhere, The author certify that all , and approved the final version of manuscript “Colorimetric Metal Ion (II) Sensor Based on Imine Boronic Esters Functionalized with Pyridine”. They warrant that the article is the author’s original work, hasn’t received prior publication and isn’t under consideration for publication elsewhere, and approved the final version of manuscript “Colorimetric Metal Ion (II) Sensor Based on Imine Boronic Esters Functionalized with Pyridine”. They warrant that the article is the author’s original work, hasn’t received prior publication and isn’t under consideration for publication elsewhere, and approved the final version of manuscript

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