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Cobalt(II)-mediated synthesis of 2,6-bis[5,7-di-*tert*-butyl-1,3-benzoxazol-2-yl]-pyridine: Structural analysis and coordination behavior

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HIGHLIGHTS

- ▶ Benzoxazole derivative obtained from a 2,6-bis(arylimino)pyridine derivative.
- ▶ 2,6-bis[5,7-di-tert-butyl-1,3-benzoxazol-2-yl]-pyridine. Structural properties.
- ► Formation of a 7-coordinate cobalt(II) intermediate is proposed.
- ► Cation:receptor properties of 2,6-bis[5,7-di-tert-butyl-1,3-benzoxazol-2-yl]-pyridine.
- ▶ Structure of zinc(II) nitrate with 2,6-bis[5,7-di-tert-butyl-1,3-benzoxazol-2-yl]-pyridine.

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ABSTRACT

The oxidative cyclization of 2,6-bis[2,4-di-*tert*-butyl-6-(methylidenylamino)phenol]-pyridine (**L1**) in acetonitrile, through the cobalt(II) coordination compound of **L1**, has resulted in a convenient route for the preparation of 2,6-bis[5,7-di-*tert*-butyl-1,3-benzoxazol-2-yl]-pyridine (**L3**). The X-ray diffraction analysis of **L3** shows a planar molecule, with the oxygen atoms from the benzoxazole rings oriented to the pyridine nitrogen atom (conformer **L3a**). *Ab initio* calculations indicate that from the three possible planar conformers of **L3**, the more stable is **L3a**. The solid state conformation of the free ligand **L3** and the relative energy of the three calculated conformers indicated stabilizing N \rightarrow 0 interactions. Calculations of the protonated derivative of **L3**, compound **7**, indicated that the most stable conformer has the benzoxazole nitrogen atoms pointing to the protonated pyridine NH (**7c**). The X-ray crystal analysis of ligand **L3** coordinated to cobalt(II) nitrate, compound **4** is presented and conformer **L3c** is found in this compound.

Two acid:base complexes $[Zn(NO_3)_2(H_2O)_2][L3c]_2$, compound **5**, and $[NEt_2H_2Cl][L3c]$, compound **6**, have also been investigated. Complex **5** crystallized and its X-ray diffraction analysis is reported, whereas compound **6** was studied in solution by NMR, mass spectrometry and *ab initio* calculations. Both complexes show that conformer **L3c** can form stable hydrogen bonding associations, with molecules having the motif YH₂ (Y = N or O), that are of interest for building up supramolecular associations.

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1. Introduction

The 2,6-bis(arylimino)pyridine family of Schiff base ligands are known for more than 60 years [1]. Since then, several studies related to the coordination properties of these versatile compounds have been fully described along with their chemical interaction with metal ions and their catalytic properties; some examples are given in Scheme 1 [2–10].

Benzoxazoles are present in several natural products and are relevant targets in drug synthesis. The synthetic routes described in the literature involve in many cases cyclization by dehydration using strong acids and high temperatures, microwave irradiation [11,12], mesoporous material catalysis [13] or by metal-based catalysis [14–20].

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Scheme 1. Co- and Fe-coordination compounds of 2,6-bis(arylimino)pyridine derivatives.

We have been developing new coordination compounds from transition metals like Ru and Au and 2,6-bis(arylimino)pyridine derivatives [21] with potential anticancer activity. Due to the electron releasing character of tert-butyl groups, these were introduced in 2,6-bis[2,4-di-tert-butyl-6-(methylidenylamino)phenol]pyridine (L1), with the aim to synthesize coordination compounds with increased cytotoxic effect. Therefore, we have been studying the reactivity of first-row transition metal complexes with L1. During the synthesis of the cobalt(II) derivative in acetonitrile, described herein, we have found an unexpected oxidative cyclization of the ligand L1, resulting in a new bis-benzoxazolylpyridine **3**, Scheme 2. This finding appears to be in accord with the known role of cobalt(II) salts in acetonitrile as oxidation agents [22,23]. It has been reported that cobalt(II) complexes catalyze the synthesis of benzoxazole derivatives by elimination of hydrogen halides by K₂CO₃ and cyclization [24].

Chemical evidence indicated that, prior to the cyclization, a seven-coordinated cobalt(II) complex **2** is formed, which was isolated and spectroscopically characterized, see Scheme 2. Complex **2**, upon standing in acetonitrile, resulted in the formation of 2,6bis[5,7-di-tert-butyl-1,3-benzoxazol-2-yl]-pyridine **L3**. The unexpected one-pot high yield cyclization of **L1** appears to be of interest in heterocyclic synthesis. The structure of **L3** was determined by spectroscopic and X-ray diffraction analyses. When a similar reaction of compound **L1** with cobalt(II) nitrate in acetonitrile was performed, colorless crystals of **L3** were obtained together with few brownish-red crystals of complex **4**, which corresponded to the cobalt(II) coordination compound with ligand **L3**. When the X-ray crystal diffraction analysis was carried out on compound **L3** an unexpected conformation was observed, where the two oxygen atoms were pointing to the pyridine nitrogen atom, whereas the cobalt(II) coordination compound **4** showed a different conformation (see later). These results motivated us to calculate the three different possible planar conformations of **L3** by HF/6-31G(d), in order to investigate which is the most stable and compared them with that found in the crystal.

Molecular recognition of organic species with labile protons is of interest on construction of supramolecular assemblies. Due to the planar conformation of compound **L3** and the location of its sp^2 lone pairs, we found relevant to investigate the formation of its acid–base adducts.

The reaction of compound **L1** with zinc(II) nitrate in acetonitrile was carried out and single crystals of complex **5** were isolated. Their X-ray diffraction analysis showed that compound **L3** was associated by hydrogen bonds to $[Zn(NO_3)_2(H_2O)_2]$, and the structure will be described below. Another complex **6**, from reaction of **L3** with diethyl ammonium chloride, which was likewise prepared and studied by NMR, mass spectrometry and *ab initio* calculations [25–27], is also described.

2. Experimental

2.1. Materials and physical measurements

All of the chemicals and analytical grade solvents were purchased from various commercial sources and were used without further purification unless otherwise stated. Co(CH₃COO)₂·4H₂O was purchased from J.T. Baker and 5-di-*tert*-butyl-1,2-benzoquinone and 2,6-pyridinedimethanol from Aldrich. Dry solvents, when required, were prepared using standard procedures. All reactions were performed with freshly distilled and dried solvents.

Melting points were obtained on a Fisher–Johns apparatus and are uncorrected. IR spectra were recorded on a Perkin Elmer Spectrum 400 spectrophotometer (ATR reflectance mode) in the 4000–400 cm⁻¹ range. UV–Vis–NIR spectra (diffuse reflectance, 40,000–5000 cm⁻¹) were obtained using a Cary 5000 (Varian) spectrophotometer. ¹H and ¹³C NMR spectra were recorded using a 300 MHz spectrometer (Bruker). The chemical shifts were referenced to



Scheme 2. Compounds L1, 2 and L3.

TMS. Electrospray mass spectra were recorded on an Agilent 6410 triple quadrupole instrument using an electrospray ionization technique (ESI-MS). Stock solutions of **3** (0.021 M) were prepared in methanol and diluted with methanol:formic acid 0.1% (85:15 v/v) to reduce the concentration to 50%.

IR for compounds **L1**, complex **2** and **L3**, NMR spectra for compounds **L1**, **L3** and complex **6**, as the mass spectra for **6** are included on the Supplementary data (SI).

2.2. Synthesis

2.2.1. 2,6-Bis[2,4-di-tert-butyl-6-(methylidenylamino)phenol]-pyridine (L1)

The synthetic procedure was previously reported [21] and was followed with minor modifications, as described below: To a solution of 2,6-pyridinedicarboxaldehyde (560 mg, 4 mmol) in absolute ethanol (20 mL) was successively added 2-amino-4,6-di-tertbutylphenol (2.23 g, 8 mmol) [28], and the resulting mixture was refluxed for 6 h over molecular sieves (4 Å). 2,6-Pyridinedicarboxaldehyde was synthesized according the reported procedures [29]. The reaction mixture was filtered while hot. Upon cooling, a yellow crystalline solid (L1) was obtained in high yield (2.13 g, 95%). Mp 236 °C. IR, v (cm⁻¹): 3380-3215, 2953-2867, 1586-1560, 1480-1455, 1412-1361, 1294, 1248-1201, 964, 953, 863, 762, 643 and 593. NMR (300 MHz, CDCl₃, 21 °C), δ (ppm), ¹H: 8.94 (s, 2H, H4), 8.30 (d, 2H, H2), 7.94 (t, 1H, H3), 7.74 (d, 2H, H7), 7.37 (s, 2H, H9), 7.34 (s, 2H, OH), 1.47 (s, 18H, CH₃-10), and 1.34 (s, 18H, CH₃-8). ¹³C: 154.6 (4C, C4, C5), 149.4 (2C, C1), 141.8 (1C, C3), 141.7 (2C, C10), 137.4 (2C, C6), 135.7 (2C, C8), 124.9 (2C, C9), 122.5 (2C, C2), 110.3 (2C, C7), tBu groups: 35.0, 34.6 (2C, C_a), 31.6, 29.4 (2C, CH₃). ESI-MS, *m*/*z*: 543.02, [(C₃₅H₄₈N₃O₂)]⁺. Elemental analysis for C₃₅H₄₇N₃O₂: Calcd. (%): C, 77.59; N, 7.76; H, 8.74. Found: C, 77.25; N, 7.75; H, 8.60.

2.2.2. $[Co(L1)(H_2O)_2](2)$

Co(CH₃COO)₂·4H₂O (25 mg, 0.1 mmol) was dissolved in acetonitrile (10 mL) and 54 mg (0.1 mmol) of compound **L1**, previously dissolved in acetonitrile (10 mL), were added to the solution. The reaction mixture was refluxed for 4 h. The solvent was immediately removed, by reduced pressure in a rotary evaporator. A dark-purple solid was collected by filtration, washed with plenty of cold acetonitrile (10 mL), cold water (10 mL) and finally dried with diethyl ether under vacuum (27 mg, 42%). Mp 290 °C dec. IR, v (cm⁻¹): 3050–2860, 1595.5, 1476–1440, 1377, 1334, 858, 606 and 452. Elemental analysis for Co(C₃₅H₄₅N₃O₂)(H₂O)₂: Calcd. (%): C, 66.23; N, 6.62; H, 7.78. Found: C, 65.98; N, 6.42; H, 7.89.

2.2.3. 2,6-Bis[5,7-di-tert-butyl-1,3-benzoxazol-2-yl]-pyridine (L3)

Co(CH₃COO)₂·4H₂O (25 mg, 0.1 mmol) was dissolved in acetonitrile (10 mL) and 54 mg (0.1 mmol) of L1, previously dissolved in acetonitrile (10 mL), were added to the solution. The reaction mixture was refluxed for 4 h. Then, the solution was let aside at rt. A visible reduction in color was observed after several hours. The dark purple acetonitrile solution turned light brownish. After 3 days colorless cubic prisms, suitable for X-ray diffraction studies, were obtained, (51 mg, 93%). Mp. 237–239 °C. IR, v (cm⁻¹): 3063– 2869, 1640, 1586, 1564, 1456, 1371, 1337, 1188, 874, 854, 757 and 719. NMR (300 MHz, CD₃CN–CDCl₃ (4:2), 21 °C), δ (ppm), ¹H: 8.46 (2H, d, J = 6 Hz, H2), 4 8.15 (1H, t, J = 9 Hz, H3), 7.70 (2H, d, J = 3 Hz, H7), 7.45 (2H, d, J = 3 Hz, H9), tBu groups: 1.63 (18H, s, C10–CH₃), 1.44 (18H, s, C8-CH₃). ¹³C: 159.2 (1C, C4), 157.6 (2C, C6), 153.8 (2C, C5), 145.1 (2C, C1), 142.3 (1C, C3), 134.1 (2C, C8), 130.3 (2C, C10), 122.3 (2C, C2), 116.2 (2C, C9), 108.8 (2C, C7), 42.1 (2C, C10-C_q), 35.3 (2C, C8-C_q), 31.8 (2C, C10-CH₃), 30.4 (2C, C8–CH₃). ESI-MS, m/z: 538. Elemental analysis for C₃₅H₄₃N₃O₂₋

·0.5H₂O: Calcd. (%): C, 76.89; N, 7.69; H, 8.11. Found: C, 76.62; N, 7.50; H, 7.98.

2.2.4. $[Co(L3c)(H_2O)_3](NO_3)_2 \cdot H_2O \cdot 2CH_3CN$ (4)

 $Co(NO_3)_2 \cdot 6H_2O$ (58.2 mg, 0.2 mmol) was dissolved in acetonitrile (30 mL) and 108.2 mg (0.2 mmol) of **L1**, previously dissolved in acetonitrile (30 mL), were added to the solution. The reaction mixture was refluxed for 4 h. The solution was let to stand under vacuum for 2 h. A microcrystalline solid was obtained and it was recrystallized on acetonitrile. After a week, red-brownish crystals suitable for X-ray diffraction studies were obtained (78.5 mg, 70%). IR, v (cm⁻¹): 3262–2871, 1762, 1631, 1562, 1530, 1483– 1365, 1303, 1200, 1161, 1077, 872, 703 and 660. Elemental analysis for [Co(**L3c**)(H₂O)₃](NO₃)₂·H₂O·2CH₃CN: Calcd. (%): C, 53.54; N, 11.21; H, 6.57. Found: C, 52.72; N, 10.74; H, 6.08.

2.2.5. $[Zn(NO_3)_2(H_2O)_2][L3c]_2$ (5)

 $Zn(NO_3)_2 \cdot 6H_2O$ (43.9 mg, 0.15 mmol) was dissolved in acetonitrile (30 mL) and 80.0 mg (0.15 mmol) of **L1**, previously dissolved in acetonitrile (30 mL), were added to the solution. The reaction mixture was refluxed for 4 h. The solution was let to stand under vacuum for 2 h. Pale yellow crystals suitable for X-ray diffraction studies were obtained (60.1 mg, 31%). IR, v (cm⁻¹): 3086–2870, 1771, 1623, 1562, 1540, 1483–1445, 1364, 1336, 1292, 1157, 873.3 and 660.5. Elemental analysis for [Zn(NO₃)₂(H₂O)₂][**L3c**]₂: Calcd. (%): C, 64.63; N, 8.61; H, 6.97. Found: C, 64.42; N, 8.70; H, 7.01.

2.2.6. Acid:base complex (**6**) of bis[benzoxazol-2-yl]-pyridine (**L3c**) and diethyl ammonium chloride. ¹H NMR titration

Equimolar ratio of diethyl ammonium chloride and compound **L3** was mixed in CD₃CN–CDCl₃ (2:1). ¹H NMR spectra were recorded and its ESI MS spectrum was performed m/z: 612, [C₃₉H₅₄₋DN₃O₂]⁺ 612.6.

2.3. X-ray crystallography

Single crystals of compounds L3, and 4 were mounted on a glass fiber. X-ray diffraction data were measured using standard procedures [30] on a Bruker Kappa CCD area detector diffractometer using Mo K α (λ = 0.71073 Å) radiation at 293(2) K and 173 K. The samples were mounted in MicroMounts (MiTeGen company) [31] with paratone-N oil. Data collection, determination of unit cell and integration of frames were carried out using the suite Collect software [32]. Intensities were measured using $\phi + \omega$ scans. A semi-empirical absorption correction method (multi-scan SADABS) [33] was applied. Data were solved by use of SHELXS and refined against F^2 on all data by full-matrix least-squares with SHELXL-97 [33]. All crystallographic programs were used under WinGX program [34]. Anisotropic displacement parameters were determined for all non-hydrogen atoms. H atoms bonded to C were positioned geometrically and refined using a riding model, with $U_{iso}(H) = 1.2U_{eq}(aromatic C)$ and $1.5U_{eq}(methyl C)$. The H atoms bonded to the water O atom were located in a difference Fourier map and their position were refined freely with $U_{iso}(H) = 1.5U_{eq}(O)$. The crystallographic details are summarized in Table 1. Selected bond lengths and angles are listed in Table 2.

Diffraction data for complex **5** were collected on an Oxford Diffraction Gemini "A" diffractometer with a CCD area detector (λ_{Mo} $_{K\alpha}$ = 0.71073 Å, monochromator: graphite) source, equipped with a sealed tube X-ray source at 298 °C. Unit cell constants were determined with a set of 15/3 narrow frame/runs (1° in ω) scans. Data sets consisted of 214 frames of intensity data collected with a frame width of 1° in ω , a counting time of 1.0–42.5 s/frame, and a crystal-to-detector distance of 55.00 mm. The double pass method of scanning was used to exclude any noise. The collected

Table	1

Crystallographic data of compounds L3 and 5.

Compound	L3	5
Chemical formula Formula weight (g mol ⁻¹)	C ₃₅ H ₄₃ N ₃ O ₂ ·0.5 (H ₂ O) 546.73	C ₇₀ H ₉₀ N ₈ O ₁₂ Zn 1300.87
Crystal size (mm)	0.25 × 0.25 × 0.08	$0.37 \times 0.20 \times 0.20$
Crystal color	Colorless	Pale yellow
Crystal system	Monoclinic	Orthorhombic
Space group	P21/c	$P 2_1 2_1 2$
Unit cell dimensions		10 0000(10)
a (A)	12.4448(3)	18.9806(12)
b (A)	14.3029(3)	16.8840(9)
<i>c</i> (A)	18.0372(3)	11.1605(6)
α (°) = γ (°)	90.0	90
β (°)	90.585(1)	90
$V(Å^3)$	3210.4(1)	3576.6(4)
Formula units Z	4	2
$D_{\text{calc.}}$ (g/cm ³)	1.131	1.208
μ (mm $^{-1}$)	0.07	0.406
F (000)	1180	1384
Temp. (K)	173 (2)	298 (2)
θ Range (°)	3.1-27.5	3.44-26.05°
Index range	$-16 \leqslant h \leqslant 16$	$-20 \leqslant h \leqslant 23$
	$-18 \leqslant k \leqslant 18$	$-16 \leqslant k \leqslant 20$
	$-23\leqslant l\leqslant 23$	–13 ≤ <i>l</i> ≤ 13
Reflections collected	42,747	17,826
Independent reflections	7301	7047
Reflections	5358 $[I > 3\sigma(I)]$	7047
R _{int}	0.051	0.0551
Parameters	388	429
R	0.053	0.0645
R _w	0.143	0.1174
S	1.02	1.050
Maximum Δ/σ	0.001	0.001
$\Delta \rho$ maximum (e/Å ³)	0.25	0.327
$\Delta \rho$ minimum (e/Å ³)	-0.29	-0.687
_r		2.007

 $\begin{aligned} \text{Rint} &= \sum |F_o^2 - \langle F_o^2 \rangle| / \sum F_o^2, R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|, wR_2 = |\sum w(F_o^2 - F_c^2)^2 / \\ &\sum w(F_o^2)^2|^{1/2}. \end{aligned}$

Table 2	
Selected bond lengths (Å), bond angles (°) and torsion angles (°) for com	pound L3

Bond	Length (Å)	Bond	Angles (°)
C2-N1	1.338(2)	C6-N1-C2	117.0(1)
C2–C8	1.468(2)	C8-N9-C15	103.8(1)
C6-N1	1.337(2)	C8-07-C14	103.7(1)
C6-C25	1.467(2)	N1-C2-C8	116.1(1)
C8-N9	1.295(2)	N1-C6-C25	116.1(1)
C8-07	1.369(2)	N9-C8-C2	127.7(1)
C14-07	1.378(2)	N26-C25-C6	127.2(1)
C15-N9	1.403(2)	07–C8–C2	116.3(1)
C25-N26	1.295(2)	024	117.3(1)
C25-024	1.370(2)	Torsion angles (°)	
C31-024	1.382(2)	N1-C2-C8-07	4.0(2)
C32-N26	1.401(2)	N1-C6-C25-O24	2.9(2)
		N1-C2-C8-N9	-176.9(1)
		N1-C6-C25-N26	-177.9(1)
		C5-C6-C25-N26	2.2(2)
		C3-C2-C8-N9	3.4(2)

frames were integrated by using an orientation matrix determined from the narrow frame scans. CrysAlisPro and CrysAlis RED software packages [35] were used for data collection and data integration. Analysis of the integrated data did not reveal any decay. Final cell constants were determined by a global refinement of 7047 reflections ($\theta < 26.05^{\circ}$). Collected data were corrected for absorbance by using Analytical numeric absorption correction [36] using a multifaceted crystal model based on expressions upon the Laue symmetry using equivalent reflections. Structure solution and refinement were carried out with the program SHELXL-97 [33]. All crystallographic programs were used under WinGX program [34]. Full-matrix least-squares refinement was carried out by minimizing $(Fo^2 - Fc^2)^2$. All non-hydrogen atoms were refined anisotropically. The H atoms of the water group (H—O) were located in a difference map and refined isotropically with $U_{iso}(H) = 1.5U_{eq}$ for (O). H atoms attached to C atoms were placed in geometrically idealized positions and refined as riding on their parent atoms, with C—H = 0.93 and 0.96 Å with $U_{iso}(H) = 1.2U_{eq}(C)$ and $U_{iso}(-H) = 1.5U_{eq}(C)$ for methyne and aromatic groups respectively. Crystal data and experimental details of the structure determination are listed in Table 1.

2.4. Ab initio calculations

Calculations were performed in order to obtain the molecular geometries of compounds L3, 6 and the protonated structure (7) of compound L3 using the Gaussian 98 package [37]. Geometries were checked to be the minimal by means of the frequency analysis.

3. Results and discussion

3.1. Compound L1 and its cobalt(II) complex 2

The ligand **L1** was prepared with high yield, in one step from the condensation of two equivalents of 2-amino-4,6-di-*tert*-butylphenol and one of 2,6-pyridinedicarboxaldehyde. Compound **L1** was characterized by ¹H and ¹³C NMR, IR (C=N [1619–1569], C=C [1480–1455] and O–H [3380–3215] cm⁻¹) and elemental analysis.

The cobalt(II) compound was prepared by treating stoichiometric amounts of Co(CH₃COO)₂·4H₂O with **L1** in acetonitrile under reflux for 4 h, Scheme 2. Immediately after, the solid was recovered under reduced pressure, washed and dried under vacuum. It was characterized by IR spectroscopy and elemental analysis. The ligand looses protons after coordination as was confirmed in the IR spectrum. Typical C=N and C=C stretching frequencies [21] are shifted to lower values in the cobalt(II) compound (1585-1516 and 1475-1410 cm⁻¹) compared to the free ligand **L1**. Co–O stretching vibration is observed at 590 cm⁻¹. By comparison it is deduced that the cobalt(II) compound **2** has a similar structure to that observed by X-ray diffraction analysis in a coordination compound derived from a related ligand, 2,6-bis(2-hydroxyphenyliminomethyl)-pyridine, [38]. Elemental analysis indicated that two water molecules were present in compound **2**.

3.2. Compound L3

When working in the slow crystallization of the compound **2** in acetonitrile solutions, a visible reduction in color was observed after several hours. The dark purple solution turned to light brownish and after 3 days small colorless square prisms of **L3**, were obtained, Scheme 2. Hydrate cobalt(II) acetate as a pink powder was also isolated after complete evaporation of mother liquor and characterized by IR spectroscopy.

Transformation of **L1** into **L3** was evident from the IR spectrum of the crystals. The broad band of the O—H stretching vibration of the phenol (3380–3215 cm⁻¹) was absent and a strong band (1643 cm⁻¹) [39] was assigned to C—O stretching vibration of an oxazole ring. The C=N (oxazole), C=C and C=N (pyridine) stretching modes were observed in the expected range. ¹H and ¹³C NMR spectra were in agreement with the dibenzoxazole pyridine structure of **L3**.

Compound L3 displays a molecular ion peak of high to medium intensity in their positive ESI mass spectrum, confirming the structure (m/z = 538). Characteristic fragmentation patterns in the spec-



Scheme 3. Reaction path for the oxidative cyclization of compound 2.

trum and fragmentation ions interacting with solvent molecules were observed. All peaks exhibit the correct isotopic distribution.

The reaction of compound **L1** with cobalt(II) nitrate in acetonitrile afforded also compound **L3**. From the reaction product few brownish-red crystals of complex **4** were obtained, which corresponded to the cobalt(II) coordination compound with ligand **L3**.

The syntheses of benzoxazole from phenol amines occur by dehydration and/or dehydrohalogenation promoted by diverse reaction conditions [12,13,19,20,24]. The relevance of the formation of compound L3 is that it occurs by an oxidative closure of ligand L1, *via* a cobalt(II) acetate or nitrate coordination compound. The ligand closure is an oxidation reaction where each imine loses a hydride. A possible pathway for the ring closure could be that the solvent coordination to Co(II) promotes the breaking of the O—Co bond. Rotation of the phenyl ring C—N bond (90°) lets approach the phenolate to the imine carbon, followed by formation of a C—O bond and elimination of a hydride. Both steps are activated by the metal coordination which favors the phenolate anion attack to the imine and the most probable acetonitrile reduction, because the reaction do not proceed in methanol or ethanol, see Scheme 3.

3.3. Crystal structure of compound L3

Single crystals ($P2_1/c$ space group) of compound **L3** suitable for X-ray diffraction studies were obtained after 3 days in the acetoni-

trile solution. The ORTEP representation of L3 is depicted in Fig. 1 and the crystallographic data are presented in Tables 1 and 2. The relevance of this X-ray crystal structure is the molecule conformation of the oxygen atoms pointing towards the pyridine nitrogen, usually this type of molecules is represented with the heterocyclic nitrogen atoms pointing towards the pyridine nitrogen [12,25–27]. This representation may come from the X-ray diffraction structures of coordination compounds where the metal atoms are bound to the three nitrogen atoms, and this conformation was careless adopted for the free representation of the ligands. Therefore the solid state conformation of compound L3 motivated us to calculate the energy of the three planar conformers, to investigate if the solid state conformation of L3 was the result of the crystal packing or the free enthalpy energy of the conformers. Examination of the data from the Cambridge Crystallographic Data Center showed that there is only another X-diffraction structure of a free benzoxazole-pyridine (2-benzoxazolepyridine) [40], in spite of several examples of coordination compounds with benzoxazole pyridine derivatives [41]. It is important to note that the conformation of this benzoxazole has the oxygen atom pointing towards the pyridine nitrogen. Even more, a sulfur analogue, 2,6-bis-(benzothiazol-2-yl)-pyridine, presents a similar conformation with the sulfur atoms close to the pyridine nitrogen [42,43].

Compound **L3** has a central pyridine with two benzoxazole groups in C2 and C6. The molecule has tBu groups at the C11,



Fig. 1. ORTEP diagram of the hydrate of compound L3 with ellipsoids presented at the 50% probability level. Hydrogen atoms were omitted for clarity.

C13, C28 and C30 positions of the phenylene groups. It was expected that this planar molecule could be present in three different conformations. One with oxygen atoms on the same side of the pyridinic nitrogen (conformer **L3a**), a second one, with a nitrogen and an oxygen close to the pyridinic nitrogen (conformer **L3b**) and a third one with two nitrogen atoms pointing to the central nitrogen (conformer **L3c**). The X-ray diffraction analysis of solid **L3** showed that the crystals contain conformer **L3a**. The tBu groups in conformer **L3a** produce a steric effect which could give a high energy structure, as is shown in the space-filling representation of the solid state structure of compound **L3a**, Fig. 2. The intermolecular interactions in the crystal packing were examined and



Fig. 2. Space-filling representation of the compound **L3** showing the crowded cavity in front of the pyridine nitrogen atom.

there are not interactions with the benzoxazole nitrogen atoms that could be responsible for the stabilization of the solid state conformation. *Ab initio* calculations were therefore performed in order to analyze the energy of the different conformations.

The electron delocalization in compound **L3** is denoted by its planarity and the bond lengths [40,41]. The double bond nature of the oxazole C8–N9 bond is confirmed by the bond length [1.295(2) Å], while C8–O7 has a slightly longer bond distance [1.369(2) Å], is typical of a single bond between sp² atoms.

A dimer of compound **L3** is formed in the crystal through interactions with lattice water molecules, Fig. 3. Hydrogen bonding [C—H···O (2.62 Å) and O—H···N (1.96 Å)] and O—H··· π interactions (N1···H 2.38, C2···H 2.89, C8···H 2.88, O7···H 2.43 Å) of the water molecules to **3** give place to the dimeric structure, which is also stabilized by π -stacking [C25···C6 (3.49 Å)], Fig. 4. The hydrogen bond between the water molecule and the oxazole-nitrogen is in agreement with reported data [O—H···N (1.85 Å)] about preferred protonation at this donor site in a related thio-aromatic system [42].

3.4. Preliminary structure of cobalt(II) coordination compound 4

Red-brownish crystals of compound **4** collected from the reaction of ligand **L1** and cobalt(II) nitrate in acetonitrile were solved by X-ray diffraction analysis (Supplementary data, SI 9–10). Even though the quality of the crystals did not allow to obtain a good refinement of the structure, it was possible to observe the ligand conformation and its coordination towards the octahedral cobalt(II) atom. Anions and solvent molecules could not be refined. The ligand is planar and is strongly bound to the cobalt(II) atoms



Fig. 3. Dimer of compound **L3** in the crystal. Water molecules stabilize two molecules of **L3** through C–H···O (2.62 Å) and O–H···N (1.96 Å) hydrogen bonds and O–H···π interactions (N1···H 2.38, C2···H 2.89, C8···H 2.88, O7···H 2.43 Å).



Fig. 4. π-Stacking in compound L3. The distance between the two aromatic planes, (C25...C6) is 3.49 Å.



Fig. 5. Schematic representation of the X-ray crystal structure cationic part of the cobalt(II) coordination compound [Co(L3c)(H₂O)₃](NO₃)₂:H₂O·2CH₃CN (4).

by the three nitrogen atoms. This structure confirms the stabilization of the conformer with the three nitrogen atoms linked to the metal atom, and the coordination completed by three water molecules, Fig. 5.

3.5. Ab initio calculations

In order to analyze the energy of the three possible planar conformers as to have insight of the solid state conformation of **L3**, we calculated the minimum energy structure of each of them. The calculated conformers and some atomic distances are presented in Figs. 6–8. The validation of the calculations was performed by comparison with the X-ray data of conformer **L3a**. The calculation reproduces accurately the structure. The most stable conformer is **L3a**, followed by **L3b** which is less stable than **L3a** by 8.2 kJ/mole. Compound **L3c** being less stable than **L3a** by 17.7 kJ/mole. The difference in energy is related to the dipolar moment [**L3a** (0.32 D), **L3b** (2.06), **L3c** (3.16 D)]. The repulsion between the N lone pair



Fig. 6. Conformer L3a with some atom distances (Å) and bond angles (°).



Fig. 7. Conformer L3b with some atom distances (Å) and bond angles (°).



Fig. 8. Conformer L3c with some atom distances (Å) and bond angles (°).

electrons for conformer **L3c** can be appreciated by comparison of the angles N9–C8–C2, with those of conformer **L3a** O7–C8–C2.

The sum of the van der Waals radii for nitrogen and oxygen is 3.15 Å, however, the distance between oxygen and the pyridinic nitrogen atom in conformer **L3a** is 2.76 Å, while in the crystal it is 2.66 Å; therefore a stabilizing interaction $N \rightarrow O$ appears possible. This weak interaction has been reported for distances N—O of 2.85 Å [43,44], 2.542(2) Å and 2.74(2)–2.87(3) Å [45]. Another point to note is that the distance between the two oxygen atoms in conformer **L3a** is 4.68 Å (Fig. 6), whereas in conformer **L3c** the distance between the nitrogen atoms is 5.10 Å (Fig. 8).

In order to investigate the conformational behavior of compound **L3** upon protonation, we have calculated the three conformers of the monoprotonated molecule **7** at pyridine (Figs. 9–11), indicating that **7c**, with two nitrogen atoms pointing to the pyridine NH is more stable than **7a** by 9.0 kJ/mole and then **7b** by 3.3 kJ/mole. The difference between the more stable conformers **L3a** and **7c** could be explained by the fact that in **L3a** N \rightarrow O inter-



Fig. 9. Conformer of protonated compound 7a with some distances between atoms (Å), bond angles (°) and hydrogen bonding.



Fig. 10. Distances between O and N atoms and hydrogen bonds for conformer 7b.



Fig. 11. Some distances between nitrogen atoms, bond angles (°) and hydrogen bonds for conformer 7c.

actions stabilize the configuration, while in **7c** the proton on the pyridine favor N…H hydrogen bonds and neutralizes the two nitrogen lone pairs repulsion. Conformer **L3c** has a distance of 5.10 Å between the two benzoxazolic nitrogen atoms (Fig. 8), whereas in the protonated molecule **7c** is of 4.71 Å, due to the fact that the two N…H hydrogen bonds (2.4 Å) approach the benzoxazolic nitrogen atoms, Fig. 11.

Another interesting point is that conformer **L3a** has a small cavity with room for only one proton (Fig. 2), while in conformer **L3c** there is enough space for a metal ion as it is shown in the spacefilling model of **7c**, Fig. 12. Therefore, it is expected that in coordination compounds, the ligand would acquire conformation **L3c**, as is indeed observed in cobalt(II) compound **4**, Fig. 5.



Fig. 12. Space-filling model for the protonated conformer 7c.

3.6. Acid:base complexes of bis[benzoxazol-2-yl]-pyridine (L3c)

From the solution of the reaction mixture of ligand **L1** with zinc(II) nitrate in acetonitrile few crystals were isolated. The X-ray diffraction analysis of compound **5** was performed, crystals were composed by the acid-base complex of the **L3** formulated as $[Zn(NO_3)_2(H_2O)_2][$ **L3c** $]_2$ Fig. 13. Crystallographic data are included in Tables 1 and 3. The hexacoordinated Zn^{II} ion is bound to two chelating nitrates and two water molecules. The ligand **L3c** is associated to the zinc(II) compound using two strong bifurcated hydrogen bonds from the coordinated water molecules to the bisbenzoxazole pyridine cavity. The pyridine nitrogen is linked by two hydrogen atoms from a water molecule and each O–H proton is interacting in a bifurcated way with two nitrogen atoms.

Each nitrate group of the Zn^{II} compound is hydrogen bonded to the external part of a ligand through the nitrate oxygen atoms and the C3—H from the pyridine and a neighboring *tert*-butyl C—H, as shown in Fig. 14. The intermolecular interactions give place to a 2D supramolecular arrangement. Each Zn^{II} compound is interacting with four ligand molecules, Fig. 15.

The formation of the zinc(II) complex **5** with the ligand **L3** motivated us to also study the acid:base interactions of **L3** with diethyl ammonium chloride in solution. The molecular recognition of cationic species by families of benzoxazole derivatives have been studied by other authors [25–27]. 2,6-Bis(2-oxazolyl)pyridine (pybox) derivatives have been used as building blocks for supramolecular assemblies in combination of secondary dialkyl ammonium cations [25]. In those systems the 2-oxazoline rings probed to be



Fig. 13. Asymmetric unit of the zinc(II) complex 5 showing the hydrogen bonds between one coordinated water molecule and ligand L3.

Table 3		
Selected bond lengths (Å)	bond angles (°) and torsion	angles (°) for compound 5

Bond	Length (Å)	Bond	Angles (°)
C5-N1	1.329(5)	C5-N1-C1	117.9(4)
C5–C6	1.478(6)	C6-N4-C12	103.8(4)
C1-N1	1.338(5)	C6-02-C7	103.3(3)
C1-C13	1.473(6)	N1-C5-C6	113.6(4)
C6-N4	1.280(5)	N1-C1-C13	113.5(4)
C6-02	1.367(5)	N4-C6-C5	126.3(4)
C7—O2	1.393(5)	N3-C13-C1	127.4(4)
C12-N4	1.404(5)	02-C6-C5	117.4(4)
C13—N3	1.274(5)	01-C13-C1	116.5(4)
C13-01	1.374(5)	Torsion angles (°)	
C14-01-C19-N3	1.393(5)	N1-C5-C6-02	-173.4(4)
	1.407(5)	N1-C1-C13-01	168.9(4)
		N1-C5-C5-N4	4.0(6)
		N1-C1-C13-N3	-6.2(7)
		C2-C1-C13-N3	176.1(5)
		C4-C5-C6-N4	-177.5(5)



Fig. 14. Hydrogen bonding between coordinated oxygen nitrate groups and the pyridinic C3H and a CH from a tert-butyl group in complex 5.



Fig. 15. 2D supramolecular aggregate in complex 5.

unstable under acidic conditions, producing N-(2-hydroxy-ethyl)amide or polymers through hydrolysis and ring opening. However, 2-benzoxazole pyridine has the advantage to resist acidic conditions [27].

Therefore, we investigated whether or not an acid:base complex can be formed when an equimolar amount of compound **L3** and diethyl ammonium chloride are put together in solution, see Scheme 4.

The ¹H NMR spectrum of the ammonium salt (CD₃CN–CDCl₃, 2:1 ratio) shows the corresponding CH₃— and $-CH_2$ — resonance peaks. ¹H NMR titration of the ammonium salt with **L3** caused slight chemical shift of the CH₃— protons belonging to the ammonium and negligible changes in the protons of **3**. Higher frequency shift of the broad NH-signal from 7.71 to 8.42 ppm, was observed due to hydrogen bonding with the benzoxazole nitrogen atoms.



Scheme 4. Cation of complex 6.

A lower frequency shift of the signal of C7–H protons ($\Delta \delta$ = 0.15 ppm) is observed, while the chemical shift of the other protons is slightly changed. This could be interpreted as that coordination with the benzoxazole nitrogen atoms is involved in the complex formation.

The presence of the acid–base complex **6** in the solution as seen from the NMR analysis was further confirmed by ESI-MS spectrum



Fig. 16. Calculated cation of the complex 6 between compound 3 and [NEt₂H₂]⁺.

shows a peak at m/z = 612.6, which was assigned to the cation [C₃₉₋H₅₄DN₄O₂]⁺ (Supplementary data, S.8 spectrum).

The 1:1 complex **6** between the NEt₂H₂ cation and compound **L3** was also calculated by *ab initio* methods. The structure shows a perfect fit between compound **L3c** and the cation. The complex has two very strong N—H—N hydrogen bonds with distances between the two nitrogen atoms of 2.4 and 2.5 Å. The angles N—H—N are 174 and 178°. Fig. 16 shows the calculated cation of the complex between compound **3** and [NEt₂H₂]^{*}. No interaction between an N—H and the pyridine nitrogen was observed.

The study of the protonated molecule **7c**, and complexes **5** and **6**, show that interactions with species with labile protons can occur with the conformer **L3c**, as this is an appropriate receptor of YH_2 species, enabling stable intermolecular and supramolecular structures.

4. Conclusion Remarks

It has been found that cobalt(II) in acetonitrile promotes an oxidative cyclization process that could be of interest in heterocyclic chemistry and in the development of new catalytic processes. Herein we report the successful conversion of 2,6-bis(2-hydroxy-3,5-*tert*-butylphenyliminomethyl) pyridine **L1** into the cyclization benzoxazole product **L3** and the X-ray diffraction analysis of the free ligand. The crystallographic data of compound **L3** are of particularly value, due to the reduced number of crystalline structures of related systems found in the literature.

A relevant fact is that crystal structure of compound L3 reveals an unusual conformation with the oxygen atoms pointing towards the nitrogen lone pair electrons, where stabilizing N \rightarrow O interactions could be invoked.

Calculations of the three possible conformers of the free ligand **L3** indicated that the conformer **L3a**, with the two oxygen atoms pointing to the pyridine nitrogen, is the most stable one. Whereas, in the calculated monoprotonated molecule **7** the most stable conformer is **7c**, with the two benzoxazole nitrogen atoms pointing to the cavity.

The preliminary structure of the cobalt(II) in compound **4** indicates that the proposed reaction pathway with this intermediate for the formation of **L3** could occur. This structure also shows that metal coordination is only possible with conformer **L3c**.

Two acid:base complexes **5** (in the solid) and **6** (in solution) are reported. Both showed that ligand **L3** forms stable hydrogen bonding associations through conformer **L3c**, with molecules having the motif YH_2 (Y = N or O), that are of interest for the supramolecular domain.

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Appendix A. Supplementary material

Crystallographic data of compounds **L3** and **5** in CIF format (CCDC 880828 and 896804) and details of (IR, NMR) characterization. This material is available free of charge via the Internet at http://www.ccdc.cam.ac.uk/conts/retrieving.html. Supplementary data associated with this article can be found, in the online version,

at http://dx.doi.org/10.1016/j.molstruc.2012.09.078. These data include MOL files and InChiKeys of the most important compounds described in this article.

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