

Synthesis, characterization and catecholase biomimetic activity of novel cobalt(II), copper(II), and iron(II) complexes bearing phenylene-bis-benzimidazole ligand



Juan Chirinos^{a,b,*}, Darmenia Ibarra^b, Ángel Morillo^b, Ligia Llovera^c, Teresa González^c, Jeannette Zárraga^{a,b}, Oswaldo Larreal^d, Mayamarú Guerra^e

^a Centro de Investigación y Desarrollo Tecnológico para el Desarrollo Sustentable, CENIT, La Serena, Chile

^b Departamento de Química, Facultad Experimental de Ciencias, Universidad del Zulia, Maracaibo, Venezuela

^c Centro de Química, Instituto Venezolano de Investigaciones Científicas (IVIC), Altos de Pipe, Venezuela

^d Departamento de Matemáticas y Estadísticas, Instituto de Ciencias Básicas, Universidad Técnica de Manabí, Portoviejo, Ecuador

^e Facultad de Ciencias Básicas, Universidad Tecnológica de Bolívar, Cartagena, Colombia

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ABSTRACT

Transition metal complexes of Co(II), Cu(II), and Fe(II) bearing a rigid symmetrical 2,2'-(1,2-phenylene)bis(1H-benzimidazole) ligand, PhBIm₂, were synthesized and fully characterized by ESI-MS, FT-IR, ¹H NMR (for paramagnetic species), UV-Vis spectroscopy and microanalytical techniques. Besides the cobalt complex was subject of X-ray structural analysis. The molecular crystal structure of the PhBIm₂Co(II)Cl₂ complex revealed the metal center in a pseudo-tetrahedral environment with not significant lengthening or compressing of the bonds in the PhBIm₂ framework upon chelation of the ligand. All complexes catalyze the aerobic oxidation of *o*-catechol to *o*-quinone under mild conditions. The results show that the oxidation rate depends on the electronic stabilizing effect to the metal center rather than the steric hindrance of the ligand. Kinetic parameters (V_{max} , k_{cat} , K_M) were estimated by mean of the Michaelis-Menten model and Lineweaver-Burk plot. Catechol oxidation rates of complexes **2–4** are in the same order of magnitudes of mononuclear and dinuclear Cu(II) complexes bearing imidazole-based ligands but lower than observed for the catecholase enzyme.

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1. Introduction

Catecholase is a metalloprotein that contains an active site of binuclear Cu(II) linked by an OH bridge and coordinated to the nitrogen groups of three histidine molecules. This metalloenzyme catalyzes the oxidation of catechol to *o*-quinones [1,2]. As *o*-quinone plays an important role in the natural production of melanin, oxidation of catechol to quinones remains a subject of broad industrial and scientific interest. From the industrial view, quinones are intermediated products to synthesize fine chemicals, perfumes, cosmetics, drugs, adhesives, among others [3–8]. Meanwhile, academy challengers on this topic are dealing with the understanding of mechanistic and kinetic aspects of catecholase oxidation and the mimicking of catecholase enzyme functions by different molecular metal complexes [9–17].

Among the metal complex models of catechol oxidase, those of copper dinuclear bearing a symmetrical or asymmetrical ligand based on pyridine, imidazole, Schiff-Base, or pyrazole to mimic imidazole donors from the histidine group has attracted much attention [18–23]. Besides the use of dicopper complexes with high accessibility to the coordination sites results in a highly active catalyst for catechol oxidation. A single but useful way of modeling catecholase functions comprises the use of mononuclear metal complexes, containing structural features of interest that permit an effective interaction catalyst-substrate [9,24]. These complexes are readily synthesized and further variation of ligand can be achieved reasonably. In this sense, transition metal complexes of imidazole and benzimidazole chelating ligands have been the focus of extensive studies directed towards the mimicking of structural, spectroscopic, and catalytic features of the active sites of metalloenzymes. Benzimidazole and its derivate are known to be strong chelating agents coordinating through the C=N atoms to a metal center. Due to the stabilizing effect of nitrogen chelate ligands on reactive metal centers, imidazole-based complexes have found

* Corresponding author.

E-mail address: jchirinos@fec.luz.edu.ve (J. Chirinos).

important use in several catalytic applications. In particular, Bis(2-benzimidazolyl) compounds and their metal complexes have shown a huge potential for catalytic [25–30] and biological applications [31–35], because the coordination chemistry of these compounds can be tuned to affords geometrically constraining systems. In contrast to metal complexes bearing two bis(2-benzimidazolyl) ligands with rigid spacer [36], the studies on the complexes formed by metal coordinated to one bis(2-benzimidazole) with a bonded rigid bridge group are scarcely described in the literature.

On the other hand, the reactivity of cobalt and iron complexes toward the oxidation of phenolic substrates indicates that a compromise between electronic and structural features determines their catalytic performances. The structure/reactivity effects make cobalt(II) and copper(II) imidazole complexes of huge interest to elucidate mechanistic aspects of catecholase activity [32,36–38], to synthesize active mononuclear catalysts and gain an insight into their structure/reactivity relationship, we envisage that metal complexes of type LM_tCl_n ($M_t = Fe, Co, Cu; n = 2$) supported on rigid symmetrical $N^{\wedge}N^{\wedge}$ ligand would allow high accessibility of substrate to the metal centers affording active catalysts for catechol oxidation under mild conditions.

As an approach to mimic the catecholase functions we targeted a series of stable Co(II), Cu(II) and Fe(II) complexes bearing the scarcely described ligand 2,2'-(1,2-phenylene)bis(1H-benzimidazole) [39].

In this paper, we report the synthesis, characterization, and catecholase activity study of a new family of metal complexes bearing a PhBIm₂ rigid ligand, in a stoichiometric ratio, namely PhBIm₂-CuCl₂, PhBIm₂CoCl₂, PhBIm₂FeCl₂. Besides, the crystal structure of PhBIm₂CoCl₂ is described.

2. Experimental

2.1. General considerations

Synthesis of complexes were carried out under anaerobic atmosphere of nitrogen using standard Schlenk and cannula techniques. The reagents were purchased from Aldrich or Fluka and used as received. Solvents were refluxed over an appropriate drying agent and distilled and degassed before use.

Nuclear magnetic resonance (NMR) spectra were recorded on Bruker spectrometer at 300 MHz (¹H) and 75 MHz (¹³C) at 298 K using a 0.5 M solution of HCl/D₂O as a solvent for ligands and CD₃-OD as a solvent for complex; chemical shifts are referenced to the residual proton impurity of the deuterated solvent. The UV–Vis spectra were recorded at room temperature on a Perkin-Elmer Lambda 3 spectrometer using DMSO as a solvent in the wave range of 200–800 nm. IR spectra were obtained as KBr disk on a Perkin-Elmer 1760X FT-IR spectrometer in the range 4000–400 cm⁻¹. The ESI (electrospray ionization) mass spectra were obtained using GC-MS Varian Saturn, operating in negative ion mode. The magnetic susceptibility of the paramagnetic complex was determined by the Evans NMR method at room temperature [40]. The effective magnetic moment was calculated using the equation $\mu_{\text{eff}} = 2.84 (\chi_{\text{m}}T)^{1/2}$. Conductivity measurements of metal complexes were carried out in DMSO solution of 10⁻³ mmol by mean of an Orion 3S-tar conductivity meter.

X-ray data collection and structure determination. A pink block crystal (0.49x0.45x0.40 mm) of compound cobalt was used for data collection. The complex **2** was mounted on a glass fiber and the data set was collected at 298(2) K on a Rigaku diffractometer [41], AFC-7S, Mercury-CCD detector, Mo-K α ($\lambda = 0.71073$ Å) radiation. Data collection was performed using φ and ϕ scan. Non-hydrogen atoms were located from the difference maps using

directs methods [42], and the structural data were refined by full-matrix least-squares methods on F² using the SHELXL-2013 crystallographic software package [43]. Anisotropic thermal parameters were used to refine all non-hydrogen atoms. All H atoms were placed at the calculated positions and treated using the riding model, with C–H distances of 0.93–0.97 Å. The Uiso (H) parameters were fixed at 1.2Ueq (C). All geometrical calculations were made using the Platon program [44]. Table 1 summarizes the crystal data, intensity data collection, and refinement details for complex **2**. Selected bond lengths and angles are given in Table 2. CIF file containing complete information on the studied structure was deposited with CCDC, deposition number 1037736, and is freely available upon request from the following web site: www.ccdc.cam.ac.uk/data_request/cif.

2.2. Synthesis and characterization of pro-ligand and complexes

2,2'-(1,2-phenylene)bis-1H-benzimidazole, PhBIm₂, (**1**) was synthesized as followed: *o*-Phenylenediamine (6.09 g, 56.38 mmol) and dimethyl phthalate (4.6 ml, 28.19 mmol) were stirred in ethylene glycol (20 ml) at 190 °C for 4 h. During reaction, the evolved methanol was distilled out. Then, the mixture was allowed to cool-down to ambient temperature and stirred overnight. The product was treated with water (120 ml), filtered, washed with water (4 × 20 ml) and finally dried at 60 °C under vacuum for two days to give a beige powder. Yield 7.80 g (25.16 mmol, 90%). ¹H NMR (300 MHz, J = Hz, D₂O/HCl, r.t.) δ (ppm) = 7.46 (dd, AA ϵ XX ϵ system, 4H, $J_{H-H} = 3$, HBz), 7.58 (dd, AA ϵ XX ϵ system 4H, $J_{H-H} = 3$; HBz), 7.91 (dd, AA ϵ XX ϵ system, 2H, $J_{H-H} = 3$; HPh), 8.01 (dd, AA ϵ XX ϵ system, 2H, $J_{H-H} = 3$ Hz; HPh). ¹³C {¹H} NMR (75 MHz, D₂O/HCl, r.t.) δ (ppm) = 113.62 (CBz), 126.67 (CBz), 132.28 (CPh), 133.64 (CPh), 145.79 (Cq, Bz), 130.98 (Cq, Ph PhCq), 122.24 (Cipso). IR (KBr, ν /cm⁻¹), 3000 (NH, s), 3050 (Ar-H, s), 1625–1525 (ArC = C, C=N, m), 1430, 1410 (NH, s), 1275 (CN, s), 750 (Ar-H, m). Anal. Calc. for C₂₀H₁₄N₄ (F.W. 310.35) C 77.40, H 4.55, N 18.05%. Found C 77.62, H 4.45, N 17.66%.

2,2'-(1,2-phenylene)bis-1H-benzimidazolyl cobalt(II) chloride (2). A suspension of PhBIm₂ (0.50 g, 1.61 mmol) in MeOH (10 ml) was added dropwise to a solution of CoCl₂·6H₂O (0.38 g, 1.61 mmol) in THF/MeOH (10 ml). Once completed the addition of PhBIm₂, the solution was refluxed for 4 h. After cooled at room temperature, the product was filtered and dried under vacuum to obtain **2** as naive semi-crystalline powder. Yield 0.60 g (1.35 mmol, 84%). The solid was redissolved in methanol/THF and recrystallized by slow diffusion of a pentane layer over the complex solution to give crystals suitable for X-ray analysis. IR (KBr, ν /cm⁻¹), 3200 (NH, s), 3000 (Ar-H, s), 1618–1556 (ArC = C, C=N, m), 1437, 1424 (NH, s), 1275 (CN, s), 750 (Ar-H, m). UV–VIS (CH₃CH₂OH): λ_{max} /nm (ϵ_{max} /dm³mol⁻¹cm⁻¹) = 581 (102), 616 (127), 650 (125). ESI-

Table 1
Selected bond lengths and bond angles.

Bond length (Å)			
Co–N(1)	2.003(6)	C(14)–N(3)	1.338(8)
Co–N(3)	2.020(5)	C(20)–N(3)	1.394(9)
C(7)–N(1)	1.327(8)	C(14)–N(4)	1.338(9)
C(1)–N(1)	1.410(9)	C(15)–N(4)	1.375(10)
C(7)–N(2)	1.368(9)	Co–Cl(1)	2.209(2)
C(6)–N(2)	1.373(9)	Co–Cl(2)	2.265(2)
Selected bond angles (°)			
N(1)–Co(1)–N(3)	96.8(2)	C(7)–N(1)–Co(1)	125.3(5)
N(1)–Co(1)–Cl(1)	111.63(18)	C(14)–N(3)–Co(1)	124.4(5)
N(3)–Co(1)–Cl(1)	115.21(17)	C(20)–N(3)–Co(1)	129.9(5)
N(1)–Co(1)–Cl(2)	112.41(17)	Co(1)–N(1)–C(1)	128.8(5)
N(3)–Co(1)–Cl(2)	110.66(17)	N(1)–C(7)–C(8)	126.8(6)
Cl(1)–Co(1)–Cl(2)	109.67(9)	N(3)–C(14)–C(13)	127.6(6)
C(7)–N(1)–C(1)	105.4(6)		

Table 2
Crystal data and structure refinements of complex **2**.

Complex	2
Chemical formula	C ₂₆ H ₃₀ Cl ₂ CoN ₆ O ₈
Molecular weight (g/mol)	684.39
Wavelength (nm)	0.71073
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ /c (no. 14)
a (Å)	12.403(3)
b (Å)	15.021 (4)
c (Å)	15.684 (4)
α (°)	90
β (°)	100.591 (6)
γ (°)	90
V (Å ³), Z	2872.4(1), 4
Diffractometer	Rigaku, AFC7S Mercury
Absorption correction	Multi Scan, Jacobson, R. (1998) Private communication
T _{min} , T _{max}	0.679, 0.727
Dcalc (g/cm ³)	1.583
μ (mm ⁻¹)	0.844
F (000)	1412
θ range (°)	2.64–56.09
Reflections collected	34,767
Reflection unique	5944
Reflections with I > 2σ (I) (Rint = 0.076)	3544
No. of restraints/parameters	85/336
R[F ² > 2σ(F ²)], wR(F ²)	0.098, 0.323
Goodness of fit on F ²	1.05
Max/min Δρ (e Å ⁻³)	0.99, -0.49

MS (*m/z*), 309.09 (31%, M - CoCl₂), 401.95 (27), 437.92 (M, 100), 439.92 (63), 440.95 (15), 441.94 (10). Calculated (*m/z*) 437.985 (100%), 438.988 (22), 439.982 (65), 440.985 (14), 441.979 (10). μ_{eff} = 3.93 BM. Anal. Calc. for C₂₀H₁₄N₄Cl₂Co (F.W. 440.2) C 54.57, H 3.21, N 12.73%. Found C 54.69, H 3.31, N 12.57%.

2,2'-(1,2-phenylene)bis-1H-benzimidazolyl copper(II) chloride (3). The procedure used was as described for **2**, using **PhBIm**₂ (0.29 g, 0.94 mmol) and CuCl₂·2H₂O (0.16 g, 0.94 mmol). Yield 0.33 g (0.74 mmol, 79%). IR (KBr, ν/cm⁻¹) 3150 (NH, s), 1621–1559 (ArC = C, C=N, m), 1442, 1477 (NH, s), 1280 (CN, s), 747 (C–H, m). UV–VIS (CH₃CH₂OH): λ_{max}/nm (ε_{max}/dm³mol⁻¹cm⁻¹) = 717 (90). ESI-MS (*m/z*): 407.94 (M - Cl), 371.55 (M - 2Cl), 442.98 (M - 2H), 443.92 (M - H), 444.98 (M). Calculated (*m/z*), 442.989 (100%), 443.993 (22), 444.986 (65), 444.987 (45). μ_{eff} = 1.9 BM. Anal. Calc. for C₂₀H₁₄N₄Cl₂Cu (F.W. 444.80) C 54.00, H 3.17, N 12.60%. Found C 53.65, H 3.21, N 12.88%.

2,2'-(1,2-phenylene)bis-1H-benzimidazolyl iron(II) chloride (4). The procedure used was as described for **2**, using **PhBIm**₂ (0.30 g, 0.97 mmol) and FeCl₂·4H₂O (0.19 g, 0.97 mmol). Yield 0.29

g (0.66 mmol, 68%). IR (KBr, ν/cm⁻¹) 3250 (NH, s), 1623–1559 (ArC = C, C=N, m), 1445, 1473 (NH, s), 1280 (CN, s), 748 (C–H, m). UV–VIS (CH₃CH₂OH): λ_{max}/nm (ε_{max}/dm³mol⁻¹cm⁻¹) = 400–800 (20, broad). ESI-MS (*m/z*): 309.06 (27%, M - CuCl₂), 434.96 (100, M), 436.62 (62), 438.19 (36), 442.89 (17). Calculated (*m/z*) 434.987 (100%), 435.990 (22), 436.984 (65), 437.987 (14), 438.981 (10). μ_{eff} = 4.9 BM. Anal. Calc. for C₂₀H₁₃N₄Cl₂Fe (F.W. 437.10) C 54.96, H 3.23, N 12.82%. Found C 55.25, H 3.08, N 12.55%.

2.3. General procedure for catechol oxidation reactions

The catecholase activities of either Cu, Co, or Fe complexes were studied by following the catechol oxidation reaction to *o*-quinone using spectrometric measurements. In a typical experiment, 1.0 ml of methanol complex solution (1 × 10⁻³ mol/L) were mixed with 2 ml of methanol catechol solution (0.04–0.4 equivalents; 0.02–0.2 mol/L; 0.04–0.4 N) in a UV–Vis cell, at room temperature

in contact with O₂ from the air. For kinetic studies, the method of initial rates was employed. The evolution of the product was followed by monitoring the absorbance at 410 nm. Reactions were monitored for 30 min. Kinetic parameters (*V*_{max}, *k*_{cat}, *K*_M) were estimated by mean of the Michaelis–Menten model and Lineweaver–Burk plot.

During the catechol oxidation, the formation of hydrogen peroxide was spectrometrically monitored by following a literature-reported method [45].

3. Results and discussion

3.1. Synthesis and characterization of ligand and complexes (1–4).

Bis(benzimidazole) compound bridged by a bulky, rigid, and non-coordinating group was targeted to assess the coordination chemistry of the expected bidentate ligand around the Co(II), Cu(II), and Fe(II) centers. 2,2'-(1,2-phenylene)bis-1H-benzimidazole, **1**, was synthesized by condensation of *o*-phenylenediamine and dimethyl phthalate (Scheme 1, equation 1). **1** was readily isolated as a beige solid in high yields (90%). The synthesis of **1** has been proposed elsewhere and crystal structure reported [39]. However, in solution NMR full characterization has not been reported yet due to its insolubility in common organic solvents.

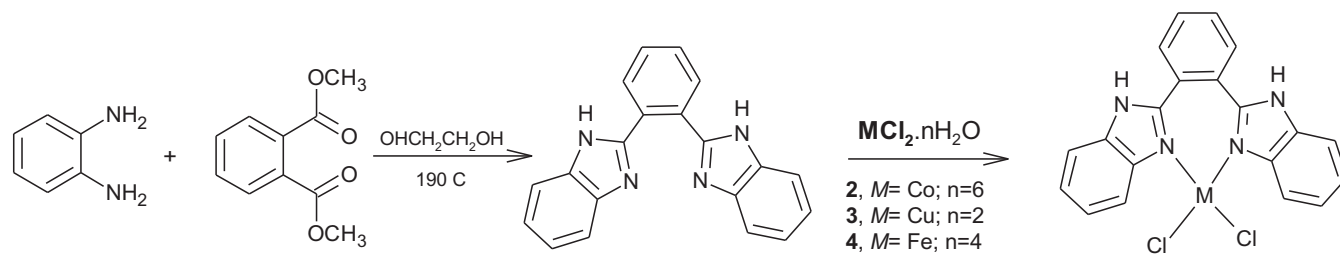
We managed to solubilize **1** to afford in solution unambiguous ¹H and ¹³C NMR characterization. Besides, compound **1** was characterized by IR and UV–Vis, spectroscopies. The IR spectra of **1** possessed the characteristic bands of the benzimidazole and benzene framework, with the ν(N–H) stretch centered at about 3100, ν(Ar–H) 3050, ν(C–N) at 1275 and ν(C=C + C=N) between 1625 and 1525 cm⁻¹, respectively. Also, peaks corresponding to out-of-plane deformations of the ring at 1430 and (C–H) 750 cm⁻¹ were observed. The UV–Vis absorption spectrum showed bands assigned to π → π* type transitions of the aromatic ring (below 300 nm) and the C=N chromophore (337 nm).

The ¹H and ¹³C NMR spectra of **1** are consistent with the expected structure. The ¹H NMR spectrum includes four sets of aromatic resonances, two between δ 8.03–8.00 and 7.93–7.90 (*J*_{H–H} = 3 Hz) assignable to protons on the benzene ring, and two between 7.60 and 7.56 and 7.48–7.45 (*J*_{H–H} = 3 Hz) corresponding to protons on the benzimidazole rings. The ¹³C{¹H} NMR spectrum corroborates the ¹H NMR characterization with the aromatic resonances of the benzene and quaternary resonances of benzimidazole appearing downfield. All the assignments were supported by ¹³C–¹H HMQC (Heteronuclear Multiple-Quantum Correlation) experiment.

Neutral cobalt, copper, and iron complexes, **2**, **3**, and **4** respectively, were synthesized by reacting the corresponding metal halide salt (CoCl₂·6H₂O, CuCl₂·2H₂O, and FeCl₂·4H₂O) with **1** in methanol/THF at room temperature (Scheme 1). Complexes **2**–**4** were isolated as air- and moisture-stable colored semi-crystalline materials in reasonable good yields (ca. 68–84%), which were soluble in tetrahydrofuran and methanol. The complexes have been characterized by ESI-MS spectrometry, UV–VIS and IR spectroscopy, and magnetic susceptibility measurements. Besides, complex **2** was the subject of single-crystal X-ray structural analyses.

The mass spectra (ESI-MS) of Co(II), Cu(II), and Fe(II) complexes show a molecular ion peak [M]⁺ at *m/z* 440(63%), 444(15%), and 437(64%), respectively. The latter suggests a monomeric complex with a 1:1 metal to ligand ratio for all the complexes. Also peaks assignable to [M–H], [M–Cl], and [M–M_rCl_n]⁺ were observed.

All complexes show similar IR spectral features with the ν(N–H) at about 3200 cm⁻¹, ν(C=C + C=N) at 1559 cm⁻¹ and the out-of-plane bending of the benzimidazole ring (N–H) at 1500–



Scheme 1. Synthesis of pro-ligand, **1**, and complexes **2–4**.

1455 cm^{-1} . These bands appear shifted to higher wavenumbers relative to the free ligand, indicating coordination of the ligand to the metal center. These features have already been observed in complexes bearing related imidazole or benzimidazole ligands [28,39,46].

The electronic spectra of the cobalt complex show the typical $d-d$ spin-allowed electronic transition expected for the tetrahedral d^7 cobalt(II) center. The main transition, corresponding to $\nu_1 [^4A_2(F) \rightarrow ^4T_1(P)]$, is observed between 550 and 700 nm [47]. The observed two-shoulder band results from distortion in symmetry around the metal center. The complex presents an intense blue color consistent with most high-spin tetrahedral Co(II). In general, the electronic transitions and the splitting energies found for **2** is similar to those reported for complexes of cobalt bearing bidentate bis(benzimidazole) [48] and Schiff-base [49].

The UV–Vis spectrum of complex **3** displays a broadband in the region 590–850 nm that were assigned to $[^2T_2 \rightarrow ^2E]$ $d-d$ transition suggesting a tetrahedral geometry of the copper ion.

The spectrum of the iron complex exhibited strong absorption bands in the 200–260 nm region, which can be assigned to the $\pi-\pi^*$ intraligand transitions. The spectrum of the colorless iron(II) complex is essentially featureless in the range 400–800 nm, and $d-d$ transitions are hardly observable.

For the paramagnetic complexes **2–4**, the solution magnetic moment was determined using Evans' NMR method. The Co(II) complex affords a $\mu_{\text{eff}} = 3.93$ BM consistent with three unpaired electrons for mononuclear tetrahedral d^7 compound ($\mu_s = 3.87$ BM). The effective magnetic moment value of the Cu(II) complex (1.9 BM) is consistent with a d^9 system of an unpaired electron ($\mu_s = 1.73$ BM). Finally, the magnetic moment found for the Fe(II) complex (4.9 BM) is just in the range of the expected for a d^6 system with 2 unpaired electrons, where μ_{eff} value would be in the range 5.0–5.6B [50].

The low molar conductivity values of **2**, **3** y **4** in DMSO (1.0×10^{-3} M solutions) corroborate the no-electrolytic nature of these complexes [51]. These molar conductivity values remain unchanged up to 24 h.

X-ray quality blue crystals of complex **2** were obtained by slow diffusion of pentane vapor into its MeOH/THF solution. The solid-state structure of **2** is shown in Fig. 1 and relevant bond lengths and angles are summarised in Table 1. Crystallographic details are shown in Table 2.

The asymmetric unit of this structure contains a neutral and discrete complex and a tetrahydrofuran solvent molecule, which is oriented in two positions with an occupancy factor (0.55: 0.45). The cobalt atom has a distorted tetrahedral coordination geometry from two chlorine atoms and two nitrogen atoms of the bidentate PhBIm₂ ligand. The length of the Co–Cl(1) bond is slightly shorter than the Co–Cl(2) linkages, by about 0.06 Å, probably due to the non-symmetrical geometry of the backbone group. On the other hand, no differences were observed in the length of the Co–N linkage. All Co–N and Co–Cl bonds are of typical lengths for tetrahedral Co(II) complexes bearing *N*-chelate ligands.

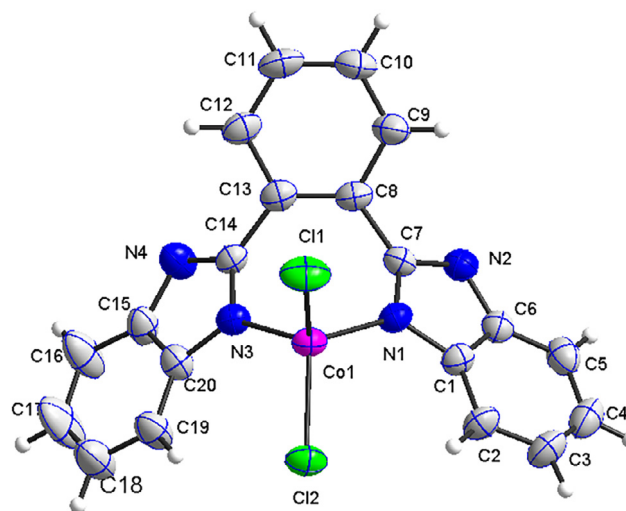


Fig. 1. Molecular structure of **2** showing the atomic numbering scheme. Displacement ellipsoids are drawn at a 50% probability level. H atoms are shown as spheres of arbitrary radii and they were not labeled for a better visualization.

The C–N bond lengths in the imidazole ring are between 1.327 (8) and 1.410(9) Å, which is shorter than the single bond length of 1.470 Å and longer than the typical C=N distance of 1.280 Å indicating partial double-bond character. This can be interpreted in terms of conjugation in the heterocycle ring. These modifications of bond distances are also in good agreement with the shifts of both $\nu(\text{C}=\text{N})$ and $\nu(\text{N}-\text{H})$ observed in the IR studies. However, not significant lengthening or compressing of the bonds in the PhBIm₂ framework was observed upon chelation of the ligand.

The small ligand bite angle results in a large distortion of the expected bond angles that involve the metal center (109.5°). The bond angles for Cl(1)–Co(1)–Cl(2), N(1)–Co(1)–N(3), N(1)–Co(1)–Cl(2) and N(3)–Co(1)–Cl(1) of 109.67(9), 96.8(2), 112.41(17) and 115.21(17)°, respectively, results in a complex with distorted tetrahedral configuration.

3.2. Oxidation reaction of catechol to *o*-quinone

Complexes **2–4** catalyze the oxidation of *o*-catechol to the corresponding *o*-quinone in methanol solution. The kinetics of the reaction was followed by mean of UV–Vis spectroscopy and was studied by the Michelis–Menten [52,53] model for the enzymatic reaction. Fig. 2 displays the Lineweaver–Burk curves [54] for complexes **2**, **3**, and **4** respectively, while the kinetic parameters are presented in Table 3.

As shown in Table 3, the Co(II) complex displayed the highest rate ($6.10 \times 10^{-3} \text{ Ms}^{-1}$), and the iron(II) complex the lowest one ($1.10 \times 10^{-3} \text{ Ms}^{-1}$).

The values of k_{cat} for cobalt complexes are between two and three folds higher than the reported for mono and tri-nuclear

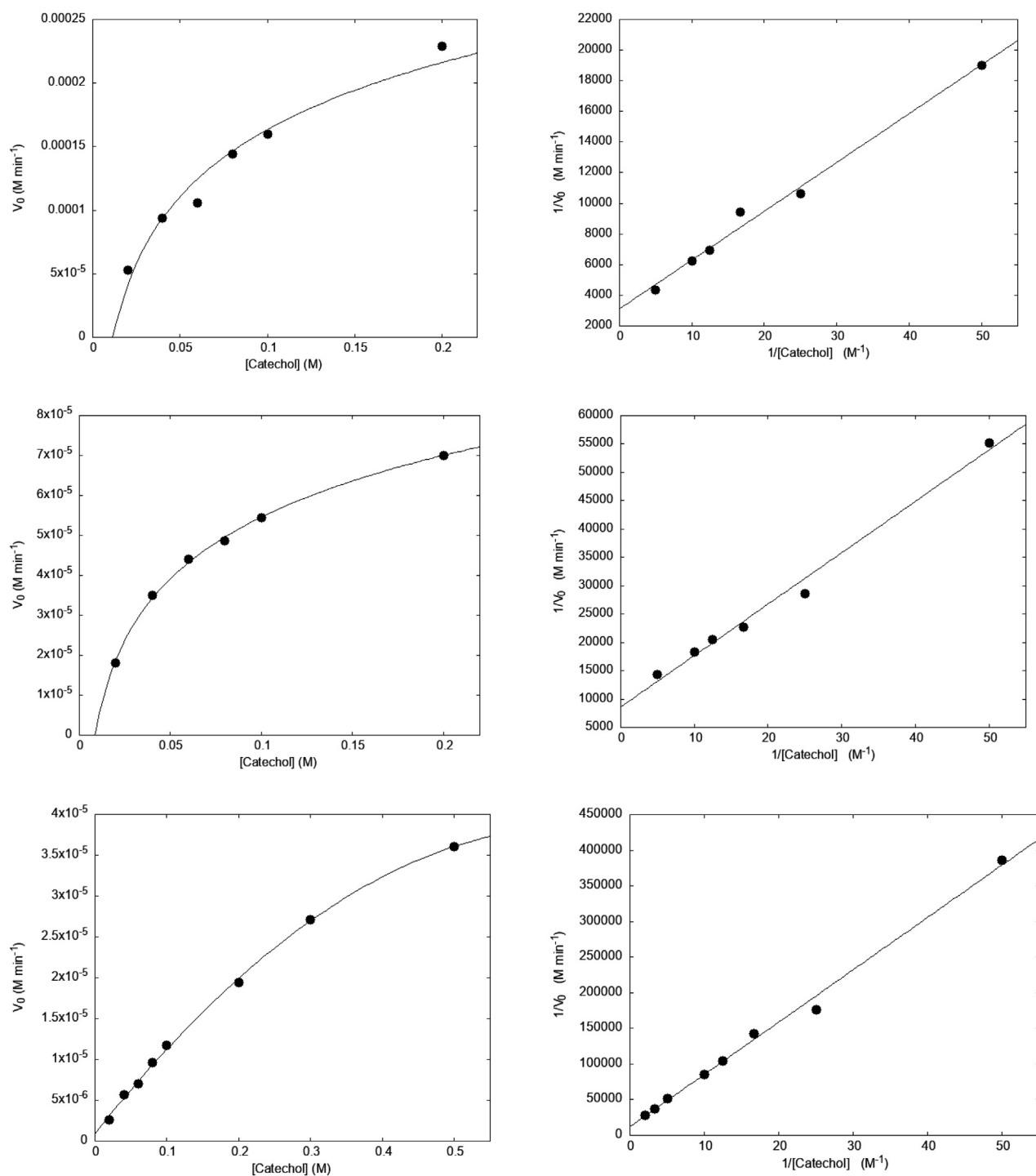


Fig. 2. Plots of the initial reaction rates vs. catechol concentration and reciprocal Lineweaver-Burk for the complexes 2, 3, and 4.

cobalt complexes (entry 4 and 5). On the other hand, it is noteworthy that catecholase activities of copper model complexes have shown a wide range of k_{cat} values. It spans from 0.0031 s⁻¹ to 6.0 s⁻¹ for mononuclear complexes, and about 0.87 s⁻¹ for dinuclear complexes. It means that complex **3** affords an intermediate catalytic activity for catechol oxidation. Finally, the observed k_{cat} for the iron complexes, although lower than the Co and Cu homologues, is four orders of magnitude higher than the found for dinuclear iron complexes reported before. [58] Because the metal complexes bear the same heterocyclic bis(2-benzimidazole) ligand with a bonded rigid bridge group, it is apparent that a balance of

steric and electronic stabilizing effect of the ligand to the metal center plays a determining role in the observed catecholase activity.

The K_M values give an inverse approach to the affinity of the metal complex to the substrate. From Table 3, complex **4** showed the lowest complex-substrate affinity and **2** the highest.

The oxidation of catechol by complexes **2–4** undergoes with reduction of molecular oxygen to hydrogen peroxide rather than water. The formation of H₂O₂ in this work was followed by iodine titration using UV-VIS spectroscopy (352 nm; $\epsilon = 26,400 \text{ M}^{-1} \text{ cm}^{-1}$). Marion et al. [9] has previously reported a family of mononuclear

Table 3
Kinetic parameters for aerobic oxidation of *o*-catechol to *o*-quinone with complexes 2–4.

	$k_{cat} \times 10^3$ (s ⁻¹)	St Error	K_M (mM)	St Error	$V_{max} \times 10^3$ (mM s ⁻¹)	St Error	k_{cat}/K_M (M ⁻¹ s ⁻¹)	Ref.
2	6.10	0.73	118	21.3	6.10	21.3	0.0517	This work
3	1.57	0.13	110	9.9	1.57	9.9	0.014	This work
4	1.41	0.61	623	38.4	1.41	32.4	0.0023	This work
^a [CoL ₂]Cl	32.78	–	1.8	7.50x10 ⁻⁴	3.28	5.62x10 ⁻⁷	18.21	[55]
^b [Co ₃ (OMe) ₄ L ₂]ClO ₄	922	–	7.81	5.27x10 ⁻³	1.5	4.47x10 ⁻⁵	118.05	[56]
^c [Cu ₂ (L) ₂ (H ₂ O) ₂]	866.67	–	4.3	–	104.6	–	201.55	[22]
^d CuLCl ₂	3.1	–	1.62	–	–	–	1.9	[9]
^e CuLCl ₂	60.1	–	0.28	–	1.30	–	214.64	[57]
^f CuLCl ₂	108.9	–	0.45	–	2.36	–	242	[57]
^h (L)Fe ^{III} (μ-O _{phenoxo})Fe ^{III}]	1.21	–	7.20	–	–	–	0.17	[58]

^aHL = (E)-2-((3-(2-hydroxyethylthio)propylimino)methyl)phenol;

^bH₂L = *N,N'*-dimethyl-*N,N'*-bis(2-hydroxy-3,5-dimethylbenzyl)ethylenediamine;

^cH₂L = 2-[(2-hydroxy-5-*R*-benzyl)amino]cyclohexane-1-carboxylic acid;

^dL = 6-(((1*H*-Pyrazol-1-yl)methyl)(thiophen-2-ylmethyl)amino)hexan-1-ol;

^eL = [(2-(pyridyl-2-yl)ethyl)((1-methylimidazol-2-yl)methyl)imine];

^fL = [(2-(pyridyl-2-yl)ethyl)((1-methylimidazol-2-yl)methyl)amine];

^hL = [(bbpmp)(H₂O)(Cl)Fe^{III}(μ-O_{phenoxo})Fe^{III}(H₂O)(Cl)]Cl

copper complexes that reduce dioxygen to produce one mole of dihydrogen peroxide per mole of 3,5-di-tertbutylquinone.

4. Conclusion

A new family of transition metal complexes bearing the symmetrical rigid-bridge ligand PhBlm₂ was synthesized, in high yields, to assessing their structure/catalytic properties in *o*-phenol oxidation. These complexes are air-stable materials and were fully characterized by conventional analytical and spectroscopic techniques. Solid-state structural analysis of complex **2**, showed the bidentate ligand coordinated at a cobalt(II) center in a stoichiometric ratio 1:1, resulting in a distorted tetrahedral geometry about the metal. The principal geometric distortions are due to the small bite angle of the ligand with not significant lengthening or compressing of the bonds in the PhBlm₂ framework upon chelation of the ligand, due to moderate electrophilicity of the Co(II) center.

These compounds were targeted to mimic the catecholase activity. Complexes **2–4** oxidize catechol to *o*-quinone with low activity. The kinetics of this reaction was studied by the MM method. Although the PhBlm₂ ligand offers low steric hindrance to substrate coordination it is seemingly that electronic stabilizing effect to the metal center is the governing factor for the moderate to low activity found.

CRedit authorship contribution statement

Juan Chirinos: Conceptualization, Investigation, Writing - review & editing. **Darmenia Ibarra:** Investigation, Methodology. **Ángel Morillo:** Validation, Data curation. **Ligia Llovera:** Investigation. **Teresa González:** Investigation. **Jeannette Zárraga:** Data curation, Validation, Writing - review & editing. **Oswaldo Larreal:** Software, Formal analysis. **Mayamarú Guerra:** Validation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.poly.2021.115232>.

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