Journal Pre-Proof

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 PII:
 S0277-5387(19)30507-8

 DOI:
 https://doi.org/10.1016/j.poly.2019.07.029

 Reference:
 POLY 14079

To appear in: Polyhedron

Received Date:11 May 2019Revised Date:15 July 2019Accepted Date:21 July 2019



Please cite this article as: A. Datta, C. Massera, E. Garribba, A. Frontera, 5,5'-Dibenzoimidazole as Building Block for a New 3D Co(II) Coordination Polymer: A Combined EPR and DFT Study Using UB3LYP Model, *Polyhedron* (2019), doi: https://doi.org/10.1016/j.poly.2019.07.029

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5,5'-Dibenzoimidazole as Building Block for a New 3D Co(II) Coordination Polymer: A Combined EPR and DFT Study Using UB3LYP Model

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Keywords: Co(II) 3D coordination polymer; Crystal structure; Topology; EPR; DFT

A B S T R A C T

A new Co(II) three-dimensional coordination polymer, $[Co(L)(L')]_n$ (1) [where L = 5,5'-dibenzoimidazole, and L' = doubly deprotonated terephthalic acid] has been synthesized hydro(solvo)thermally and its molecular and crystal structure have been elucidated through single crystal X-ray diffraction analysis. Each Co(II) ion displays a slightly distorted trigonal bipyramidal geometry, the apical positions being occupied by the nitrogen atoms of two symmetry-related dibenzoimidazole ligands, while the oxygen atoms from three distinct terephthalic acids are in the equatorial plane.. Considering the $Co_2C_2O_6$ dimeric moieties as nodes, and the ancillary ligands as connectors, the structure can be simplified as a 8-c uninodal net of the type **bcu**, body centered cubic, with point symbol $\{4^{24}.6^4\}$ and symbol vertex *]. The EPR spectra for 1 have been reported, showing $g_{\parallel} = 2.176$ and $g_{\perp} = 2.052$ at RT (room temperature), and $g_{\parallel} = 2.172$ and $g_{\perp} = 2.060$ at LNT (liquid nitrogen temperature). Finally, the electronic nature of the molecular geometry of 1 has been explored by DFT computation applying the UB3LYP/def2-TZVP level of theory, showing the energy difference between the high spin and low spin configurations.

1. Introduction

The main strategy for the preparation of novel multifunctional materials is still based on self-assembly methods which employ polydentate organic ligands containing N- or O-donor as building blocks. In this context, those ligands containing imidazole or carboxylate groups are of special interest due to their good coordination ability and diverse coordination modes [1-4]. Up to now, however, there are still few studies reporting the use of ligands containing both imidazole and carboxylate moieties as building blocks for the construction of functional MOFs [5-9]. Moreover, in the case of metal-organic complexes, not only the organic ligands, but also the choice of the metal ion employed is very important to determine the functionality of the resulting compounds [10]. It is well known that Co(II) is a good candidate for the construction of magnetic or luminescent metal-organic materials [11-18] because it can adopt diverse coordination modes in combination with N- or O-donor ligands. Recently, a few CPs and MOFs with intriguing topologies have been reported, containing different aromatic carboxylates and bis(imidazole) as precursors [19-21]. Moreover, inspired by the use of some flexible bis(imidazole) ligands [22-24], Lee et. al. have used 9,10-di(1H-imidazol-1-yl)anthracene (dia) possessing a flat anthracenyl ring to exploit its ability in exploiting two different coordination sites [25]. Thus, inspired by recent research paths which exploit flexible ligands to get enthralling metal organic

frameworks endowed with interesting topologies [19-21], in the present contribution we have decided to use the symmetrical terephthalic acid (H₂L') as bifunctional bridging organic tecton in combination with 5,5'-dibenzoimidazole (L) as N-donor connector (see **Scheme 1**). The hydro(solvo)thermal reaction of cobalt chloride hexahydrate as metal salt with L' and L has produced the new three dimensional CP $[Co(L)(L')]_n$ (1) in moderate yield. Its solid-state structure, topological analysis and solid state EPR spectra are here described. DFT computation has been also employed to evaluate the energy differences between its high spin and low spin configurations and to interpret the EPR spectra both in solution and in the solid state.



Scheme 1. Molecular sketch of the ligands employed to generate the coordination polymer (1): 5,5'-dibenzoimidazole (L, left) and terephthalic acid (H_2L' , right)..

2. Results and discussion

2.1. Structural description

The crystal structure of compound **1** was elucidated through X-ray diffraction analysis on single crystals. It consists of a coordination polymer of general formula [Co(L)(L')]_n, where L is 5,5'-dibenzoimidazole, and L' = $C_8H_4O_4$ is the doubly deprotonated terephthalic acid. The complex crystallizes in the monoclinic space group *P*21/*c* and its asymmetric unit comprises one Co(II) cation, one 5,5'dibenzoimidazole ligand, and two half molecules of doubly deprotonated terephtalic acid. **Figure 1** highlights the coordination environment around the metal center. Co(II) displays a slightly distorted trigonal bipyramidal geometry, with the two nitrogen atoms N1 and N4^{iv} from two symmetry-related dibenzoimidazole ligands in the apical positions, and the oxygen atoms O1, O3 and O4ⁱⁱ from three distinct molecules of terephthalic acids in the equatorial plane. Bond distances and angles are in the normal range for this type of compounds (see **Table 1** for selected geometrical parameters). As can be seen from **Figure S1**, there are two types of terephthalic acids



Figure 1. Coordination environment around the metal in 1. Symmetry codes: i = 2-x,

1-y, 1-z; ii = 1-x, 1-y, -z; iii = 1+x, y, z.; iv = 2-x, -1/2+y, 1/2-z; v = -x, 1-y, -z.

in the structure, coloured in green and magenta, respectively. In the first one, only one oxygen atom (O1) of each carboxylic group is involved in the coordination, thus connecting two metal centers at the time. On the contrary, the second ligand employs all four oxygen atoms (O3, O4 and the symmetry-related ones) to bridge four different cobalt ions.

Co1-N1	2.116(2)	N1-Co1-N3 ^{iv}	177.13(8)
Co1-N3 ^{iv}	2.137(2)	O3-Co1-O1	115.24(9)
Co1-O1	2.007(2)	O3-Co1-O4 ⁱⁱ	130.29(9)
Co1-O3	2.010(2)	O1-Co1-O4 ⁱⁱ	114.45(7)
Co1-O4 ⁱⁱ	2.004(2)		

Table 1. Selected bond lengths [Å] and angles [°] for 1.

This combination forms a sheet parallel to the *ac* plane of the unit cell. These sheets are connected by the dibenzoimidazole ligands along the *b*-axis direction of the unit cell, yielding the three-dimensional structure shown in **Figure 2**. Each ligand, which is roughly planar [the angle between the two mean planes passing through the benzimidazole motieties is of $12.93(8)^{\circ}$] bridges two metal centers through the nitrogen atoms N1 and N3.



Figure 2. View along the *a*-axis direction of the sheets formed by the terephtalic acids coordinated to the cobalt ions, connected through dibenzoimidazole ligands acting as pillars. H atoms have been omitted for clarity. The two types of terephtalic acids are represented in magenta and green, respectively.

In the crystal structure, two sets of strong H-bonds are present, involving the N-H groups of the imidazole rings which act as donors towards the oxygen atoms of the carboxylic moieties (Figure 3 and Table 2).

Table 2. Relevant geometrical parameters (Å, °) for the hydrogen binding network in

-	1	
	L	

D- H····A	D-H	Н…А	D····A	D-H ···A
N2-H2N…O1(- x+1,+y+1/2,z+1/2)	0.85(5)	2.01(5)	2.882(3)	172.6(9)
N4-H4N…O2(x+1,+y,+z)	0.88(4)	1.84(5)	2.691(3)	162.6(9)



Figure 3. View of the N-H···O hydrogen bonds (cyan dotted lines) present in the structure of 1.



Figure 4. Left: simplification used to create the net. Right: view of the of the 8-c uninodal net of the type **bcu**.

The 5,5'-bibenzo[*d*]imidazole ligand used in this work can be generally found in four different isomeric configurations (I–IV) taking into consideration the tautomeric forms of the imidazole ring (I and III) and the rotation around the *bis*-arene C–C bond (II and IV), as indicated in Scheme 2. The form I is observed in compound 1 (with an *anti*-conformation of the Co metal centers and, concomitantly, of the NH groups (Scheme 2 and Figures 1 and 2). As described above, the imidazole ligand in this form acts as pillar connecting the 2-D Co/terephtalic acids sheets along the *b*-axis direction, thus adding the third dimension to the polymer.



Scheme 2. Structural diagram of the four configurations of 5,5'bibenzo[*d*]imidazole.

A search in the Cambridge Structural Database (CSD, Version 5.38, update August 2018) [28] for complexes containing the 5,5'-dibenzoimidazole backbone yielded only two hits, none of them coordination polymers, and never featuring the ligand in forms **II** and **IV**. In particular, Yin and coworkers used different derivatives of 5,5'-bibenxo[*d*]imidazole (fully deprotonated) to obtain multinuclear ruthenium complexes with bypiridine (see for instance LIMBIT) [29]. In this structure the imidazole ligands coordinates four distinct Ru centers all showing an octahedral geometry. Moreover, a pyridine derivative of the ligand in its form **I** [bis(2-pyridyl)-5,5'-bi-benzimidazole] was used to synthesize a copper-based pseudorotaxane (RAKLEW) [30] featuring two penta-cooridinated copper(II) ions showing a square-pyramidal geometry. In both

cases, the bibenzoimidazole scaffold has proved to be a very robust and stable ligand, providing rigidity to the resulting compound. Finally, a theoretical DFT study has been recently carried out [31], to investigate the effect of different configurations of bibenzoimidazole, namely 2,2'-bibenzo[d]imidazole, 2,5'-bibenzo[d]imidazole, and 5,5'-bibenzo[d]imidazole in forming H-bonding networks with phosphporic acid. This proves the versatility of this molecule towards the rational design of 3-dimensional architectures, both as ligand in metal complexes and as synthon in supramolecular self-assembly.

A search in the CSD for cobalt, terephtalic acid and benzimidazole-containing ligands gave 17 hits, but only in 11 of them the benzimidazole was coordinated to the metal center through its N atom and in 3 of them cobalt was also coordinating other ligands such as water or methanol molecules, or chloride ions. Of the 8 structures remaining, compounds SITVEZ [32] and XAVKEL [33] are those in which the cobalt ions are penta-coordinated like in the title compound. In particular, in the case of SITVEZ, two different cobalt centers are present, with Co1 being the one surrounded by three different terephthalic acid ligands, one chelating and two bridging, and by a benzoimidazole ligand, giving rise to a very distorted squared pyramidal coordination of the tipe CoO_4N (one of the oxygen atoms of the chelating ligand is at the much longer distance of 2.445(3) with respect to the other oxygen atoms). In the compound

indicated with refcode XAVKEL the Co ion shows a distorted trigonal-bipyramidal coordination geometry of the type CoO_3N_2 : each tertephtalic acid behaves as chelating (with one carboxylate unit) and monodentate (with the other one) ligand, thus forming 1-D polymeric chains, while two benzimidazole ligands simply occupy the two left coordinating positions around the metal center.

2.2. EPR spectra

Cobalt(II) has a $3d^7$ configuration and can form both high-spin (S = 3/2 with three unpaired electrons) and low-spin (S = 1/2 with only one unpaired electron) complexes. For high-spin states, the fast spin-lattice relaxation time precludes the possibility to obtain resolved EPR spectra at room temperature (RT) and liquid nitrogen temperature (LNT) and very low temperatures are needed to detect any signal [34-37]. In contrast, species with a low-spin state give a resolved spectrum both at 298 and 77 K. The EPR spectra recorded on the polycrystalline powder of **1** are well resolved at RT and LNT (**Figure 5**). This suggests a low-spin state at both the temperatures. The two spectra are characterized by $g_{\parallel} = 2.176$ and $g_{\perp} = 2.052$ at RT, and $g_{\parallel} = 2.172$ and $g_{\perp} = 2.060$ at LNT. These data indicate a ground state based on the cobalt d_{xy} or $d_{x^2-y^2}$ orbitals [38,39].



Figure 5. X-band EPR spectra of the polycrystalline powder of 1: (a) at RT and (b) at LNT. With the asterisk the "forbidden" $\Delta M_S = \pm 2$ resonance at half-field is indicated.

In fact, for five-coordinate Co(II) complexes with trigonal bipyramidal geometry and a symmetry close to D_{3h} , such as **1**, the electron configuration is $(d_{xz})^2 (d_{yz})^2 (d_{x^2-y^2})^2$ $(d_{xy})^1$ or $(d_{xz})^2 (d_{yz})^2 (d_{xy})^2 (d_{x^2-y^2})^1$ [40]. For this situation, the EPR theory predicts a value of g_{\parallel} larger than g_{\perp} , which – in its turn – is larger than g_e (2.0023), in agreement with what was experimentally observed (see **Table 3**). Overall, the spectral pattern closely resembles that of other trigonal bipyramidal Co(II) species [41]. The weak resonances at half-field at $g \sim 4.3$ can be attributed to the "forbidden" $\Delta M_S = \pm 2$ resonance, often observed in the case of dinuclear metal complexes (for example, with copper(II)) in a doublet spin state [42]. The small distance between the two Co(II) ions would support an interaction between the two paramagnetic centers.

	Temperature	\mathcal{B}_{\parallel}	g_{\perp}	g at half-field
Solid state	RT	2.176	2.052	4.294
Solid state	LNT	2.172	2.060	4.278
Solid dissolved in DMSO	LNT	2.184	2.046	4.289
Solid dissolved in DMF	LNT	2.180	2.040	4.284
Solid dissolved in MeOH	LNT	2.179	2.046	4.287

T 11 7	X7 1 C	1	C 1	·	1 1.	1 4 4	1	•	•	1
I able 3	Values of	σ measured	tor I	in f	he soli	d state	and	$1n_0$	rganic	solutions
I UDIC C.	values of	S mousarea	101 1	111 0.	10 5011	a state	unu	III U	Banno	solutions.

When compound 1 is dissolved in an organic solvent, no significant changes in the EPR spectra – compared to those recorded in the solid state – are observed (**Figure 6**): two resonances in the magnetic field range 3000-3500 Gauss are revealed plus the transition at half-field at ca. 1570 Gauss. This suggest that, unlike other dinuclear complexes [43-53], the structure of 1 is retained in the organic solution. The values of *g* measured in DMF, DMSO and MeOH are reported in **Table 3**.



Figure 6. X-band EPR spectra recorded at LNT on the polycrystalline powder of 1 dissolved in: (a) DMSO, (b) DMF and (c) MeOH. With the asterisk the "forbidden" $\Delta M_{\rm S} = \pm 2$ resonance at half-field is indicated.

2.3. DFT computation

We have used DFT calculations to shed light on the spin state and electronic configuration of compound **1**. Due to the polymeric nature of the X-ray structure, we have used a theoretical model, which is shown in **Figure 7**. It is composed of two metal centers, two bridging terephthalic acid ligands, two additional terephthalic acid monodentate ligands and four 5,5'-dibenzoimidazole ligands occupying the apical positions. We have first computed the energy difference between the high spin (S = 3/2) and low-spin (S = 1/2) configuration at the UB3LYP/def2-TZVP level of theory for the model shown in **Figure 7**.



Figure 7. Theoretical model of 1. H-atoms have been omitted for clarity.

The low spin complex is 22.0 kcal/mol more stable than the high spin per cobalt unit, in agreement with the experimental findings. The calculated values of the g-tensor components at the B3LYP/def2-TZVP level of theory for the theoretical model of **1** are $g_{\parallel} = 2.164$ and $g_{\perp} = 2.076$, which correlate reasonably well with the experimental values. Moreover, in order to investigate the electronic configuration of the Co(II) metal center, we have represented one of both single-occupied molecular orbitals (SOMO) and the spin density plot of the model of compound **1** in **Figure 8**. The spin density plot shows that the unpaired electrons are located on the Co metal centers with some spin delocalized into the ligands. Both spin density and SOMO plots confirm the presence of the unpaired electron in the $d_{x^2-y^2}$ orbital.



Figure 8. Spin density plot (a) and SOMO (b) of the theoretical model of 1 at the B3LYP/def2-TZVP level of theory.

3. Conclusion

In summary, we have described the rational design of a thermally stable Co(II) threedimensional coordination polymer, generated by employing a carboxylate precursor, terephthalic acid, and 5,5'-dibenzoimidazole as N-donor ancillary co-ligand. Single erystal X-ray diffraction analysis has elucidated the molecular and crystal structure of the coordination polymer, highlighting the role of 5,5'-dibenzoimidazole in producing a 3D, 8-c uninodal network of the type **bcu**. EPR measurements have been carried out both in the solid state (at RT and LNT) and in organic solution to outline the electronic configuration of Co(II) on the spin-lattice location in the molecular unit. Furthermore, DFT has been employed to interpret the molecular alignment of the 3-D polymeric chain. Further work is underway, focusing on the capacitance measurements and sensor activities of MOFs and CPs incorporating dibenzoimidazole-type ligands in combination with different metal centers.

4. Experimental section

4.1. Materials

Terephthalic acid was purchased from Acros Organics. $Co(NO_3)_2 \cdot 6H_2O$, 2,4dinitroaniline and hydrazine monohydrate were purchased from Aldrich Chemicals. All the reagents were used as received for synthesis without further purification.

4.2. Physical measurements

Microanalytical data (C, H, and N) were collected on a Perkin–Elmer 2400 CHNS/O elemental analyzer. EPR spectra were recorded from 0 to 8000 Gauss at liquid nitrogen temperature (LNT, 77 K) or room temperature (RT, 298 K) with an X-band Bruker EMX spectrometer equipped with a HP 53150A microwave frequency counter. The microwave frequency was in the range 9.40-9.41 GHz, microwave power was 20 mW (which is, with the ER4119 HS resonator, below the saturation limit), time constant was 81.92 ms, modulation frequency 100 kHz, modulation amplitude 0.4 mT,

resolution 8192 points.

4.3. Synthesis of 5,5'-dibenzoimidazole

Heating of 2,4-dinitroaniline (0.183 g, 1 mmol) with N_2H_4 · H_2O (0.100 g, 2 mmol) at 110°C in presence of Pd/C first yielded 4-nitro-o-phenylenediamine (V) from which 5-nitrobenzimidazole was prepared in 70% yield. Then, refluxing of 5-nitrobenzimidazole (1 mmol) with N_2H_4 · H_2O (0.100 g, 2 mmol) at 110°C in presence of Pd/C in 30 mL of amyl alcohol afforded 5-aminobenzimidazole in 77% yield. Later reduction of diazotized 5-aminobenzimidazole generated the desired derivative (5,5'-dibenzoimidazole) in 69% yield.

4.4. Synthesis of compound (1)

A mixture of terephthalic acid (0.0996 g, 0.60 mmol), 5,5'-dibenzoimidazole (0.0936 g, 0.40 mmol) and Co(NO₃)₂·6H₂O (0.5822 g, 2.0 mmol) in water (8 mL) was placed in a 25 mL stainless steel reactor with Teflon liner and heated to 140 °C for 72 h; then it was cooled down to room temperature at the rate -6° C/h. Orange rectangular-shaped crystals were separated by filtration, washed with deionized water and dried in air. Yield: 0.071 g. Anal. Calc. for C₂₂H₁₄O₄N₄Co: C, 57.73; H, 3.09; N, 12.25. Found: C, 58.03; H, 3.29; N, 12.03%.

4.5. X-ray crystallography

The crystal structure of compound 1 was determined by X-ray diffraction methods. Intensity data and cell parameters were recorded at 190(2) K on a Bruker ApexII diffractometer (MoK α radiation $\lambda = 0.71073$ Å) equipped with a CCD area detector and a graphite monochromator. The raw frame data were processed using the programs SAINT and SADABS to yield the reflection data files [54]. The structure was solved by Direct Methods using the SIR97 program [55] and refined on F_0^2 by full-matrix least-squares procedures, using the SHELXL-2014/7 program [56] in the WinGX suite v.2014.1 [57]. The structure of the title compound was refined as a twocomponent twin. All non-hydrogen atoms were refined with anisotropic atomic displacements, while the hydrogen atoms were found in the difference Fourier map and refined freely. The weighting scheme used in the last cycle of refinement was w = $1/[\sigma^2 F_o^2 + (0.0513P)^2 + 5.1777P]$, where $P = (F_o^2 + 2F_c^2)/3$. Crystal data and experimental details for data collection and structure refinement are reported in Table 4. Crystallographic data for the structure reported have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1898073 and can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Empirical formula	$C_{22}H_{14}O_4N_4Co$
Formula weight	457.30
Temperature	190(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P21/c
<i>a</i> , Å	10.544(2)
b, Å	13.995(3)
<i>c</i> , Å	13.434(2)
β , deg	111.569(4)
Volume, Å ³	1843.5(6)
Z	4
D _{calc} (mg m ⁻³)	1.648
μ (Mo Kα) (mm ⁻¹)	0.972
F(000)	932
Total reflections	5623
Observed reflections	4428
$[F_o > 4\sigma(F_o)]$	
GOF on F ^{2a}	1.002
$R_{\text{indices}} [F_o > 4\sigma(F_o)]^b R_l,$	0.0506, 0.1228
wR_2	

Table 4. Crystallographic data of compound 1.

Largest diff. peak and	0.517, -0.622
hole, $e.Å^{-3}$	

^aGoodness-of-fit S = $[\Sigma w(F_o^2 - F_c^2)^2/(n-p)]1/2$, where n is the number of reflections and p the number of parameters. ${}^{b}R_1 = \Sigma ||F_o| - |F_c||/\Sigma |F_o|$, $wR_2 = [\Sigma [w(F_o^2 - F_c^2)^2]/\Sigma [w(F_o^2)^2]]^{1/2}$.

4.6. Theoretical methods

The calculation of the EPR g-tensor has been performed using the Gaussian-09 program [58] and the B3LYP/def2-TZVP level of theory. For the calculation in the solid state, the crystallographic coordinates have been used, where the positions of the H atoms have been optimized.

Acknowledgements

AD expresses his appreciation to the Ministry of Science & Technology (MOST), Taiwan, for financial assistance. We also thank Prof. Chen-Hsiung Hung for his valuable suggestions in crystallography.

Conflict of interest

We wish to assure that our manuscript does not contain any potential interest or "no conflict of interest".

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Synopsis and Pictogram for Graphical Abstract

5,5'-Dibenzoimidazole as Building Block for a New 3D Co(II)

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A new Co(II) three dimensional polymer has been afforded by using the Co(II) salt, 5,5'-dibenzoimidazole and terephthalic acid as precursors Topological overview and EPR interpretation was discussed. Additionally, the DFT computation study was explored applying the UB3LYP/def2-TZVP level of theory.