

First-row transition metal complexes with pyridine-benzothiazole and hexafluoroacetylacetonate ligands: supramolecular insights and biological effects

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ABSTRACT

We report the synthesis, structural elucidation, and bioactivity assessment of a novel series of isostructural coordination complexes, **M-PBT**, with the general formula $[M(PBT)_2(hfac)_2]$ ($M = Mn, Fe, Co, Ni, Cu, Zn$), incorporating 2-(pyridin-4-yl)-1,3-benzothiazole (PBT) and hexafluoroacetylacetonate ($hfac^-$) ligands. Single-crystal X-ray diffraction reveals that all complexes crystallize in the triclinic $P-1$ space group, featuring a trans-octahedral MN_2O_4 coordination geometry, where **PBT** ligands occupy axial positions and $hfac^-$ ligands coordinate in the equatorial plane. Comparative structural analysis highlights systematic trends in bond lengths and octahedral distortion parameters across the 3d metal series. Hirshfeld surface analysis and 2D fingerprint plots underscore the key role of directional supramolecular interactions, namely C–H...F non-classical hydrogen bonds, F...F contacts, and π – π stacking, in stabilizing the three-dimensional crystal packing. Theoretical studies corroborate structural findings. Biological assays using *Arabidopsis thaliana* and *Pseudomonas syringae* reveal metal-dependent inhibitory effects on plant growth and bacterial proliferation. These results demonstrate that rational selection of metal centers and ligand frameworks can modulate the physicochemical and bioactive properties of coordination complexes, with broader implications for supramolecular design and bioinorganic chemistry.

1. Introduction

The rational design of coordination compounds remains a cornerstone in the development of functional materials with tailored structural, electronic, and bioactive properties [1]. In this field, an effective strategy involves the integration of heterocyclic ligands with transition metal centers, enabling the construction of architecturally diverse and functionally rich complexes through controlled ligand design and metal variation [2]. Within this framework, thiazole- and benzothiazole-based ligands have emerged as versatile building blocks due to their rigid aromatic scaffolds, ambidentate (*N,S*) donor character, and strong tendency to engage in non-covalent interactions such as π – π stacking,

hydrogen bonding, and dipolar contacts. Those features make thiazole- and benzothiazole-based ligands great interest building blocks in the formation and stabilization of extended supramolecular architectures [3–5].

The incorporation of benzothiazole moieties into coordination complexes can significantly enhance their potential properties in bioinorganic field [6]. For instance, Ni(II) complexes incorporating 6-nitro-1,3-benzothiazole have demonstrated antimicrobial and anti-inflammatory activities [7]. Similarly, Pt(II) and Pd(II) complexes with 2,2'-dithiobis(benzothiazole) ligands have shown promising antitumor and antibacterial activities, with specific coordination modes influencing their efficacy and cellular uptake [8]. Furthermore, coordination

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complexes bearing 2-hydrazinobenzothiazole moieties and metal ions like Co(II), Ni(II) and Cu(II) showed enhanced antibacterial activity than the free ligand [9]. Moreover, the complexes with Ru(II) and saccharin (1,2-benzothiazole-3(2H)-one-1,1-dioxide) also have been investigated for DNA and protein binding, and photoinduced DNA damage activity [10]. These findings underscore the importance of benzothiazole scaffolds in coordination complexes for biological applications and show that the design of related bioactive coordination complexes is still a fertile field in inorganic chemistry [11].

On the other hand, fluorinated β -diketonate ligands, such as hexafluoroacetylacetonate (hfac^-) are also a valuable building blocks in metal-organic materials. Their strong electron-withdrawing $-\text{CF}_3$ groups can modulate the electronic environment around the metal center. Additionally, $-\text{CF}_3$ promote highly directional interactions at supramolecular level, such as $\text{C-H}\cdots\text{F}$ hydrogen bonds and $\text{F}\cdots\text{F}$ contacts, can enhance thermal and oxidative stability and govern intermolecular recognition in coordination compounds [12,13]. Additionally, the presence of peripheral fluorinated groups often enhances volatility and lipophilicity, thereby expanding their significance in the fields of surface chemistry and bioinorganic applications [14]. Despite the well-established use of hfac^- in coordination chemistry, its combined application with benzothiazole-type ligands remains relatively unexplored. In this context, the use of hfac^- ligand in combination with a pyridine-benzothiazole ligand such as 2-(pyridin-4-yl)-1,3-benzothiazole (**PBT**) offers a unique opportunity for rational design of coordination compounds. Previous studies have shown that **PBT** coordinates preferentially via the pyridyl nitrogen atom, leaving the thiazole moiety available for supramolecular engagement. This selective binding behavior renders **PBT** an ideal axial ligand for constructing *trans*-octahedral complexes, where the equatorial positions are occupied by bidentate O-donors like hfac^- [15,16].

Herein, we report a comprehensive study of a series of isostructural **M-PBT** molecular complexes with general formula $[\text{M}(\text{PBT})_2(\text{hfac})_2]$ ($\text{M} = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}$), highlighting their structural, supramolecular, and biological features. By combining systematic synthesis with single-crystal X-ray diffraction, Hirshfeld surface analysis, DFT calculations, and bioassays, **M-PBT** complexes demonstrate that the careful choice of ligands and the specific type of metal can work together to determine the characteristics of these molecular materials. Along with experimental characterization, density functional theory (DFT) calculations are crucial for comprehending the electronic structure of **M-PBT** compounds. Moreover, DFT calculations enabled **M-PBT** structural-property relationships and offered qualitative insights for the estimation of chemical reactivity and possible charge transfer processes within the series of complexes. Taken together, our findings enhance the overall comprehension of crystal engineering within molecular coordination compounds materials in supramolecular chemistry and bioinorganic applications.

2. Experimental and computational methods

The solvents and reagents used for the synthesis were purchased from Sigma-Aldrich® and Merck® and used without any further purification. The synthesis of the complexes was performed by direct mixing of the starting materials or using diffusion techniques.

2.1. Synthesis of 2-(pyridin-4-yl)-1,3-benzothiazole (**PBT**) ligand

2-aminobenzene-1-thiol, pyridine-4-carbaldehyde, metal salts and organic solvents were purchased by Sigma-Aldrich and were used without further purification. Ligand 2-(pyridin-4-yl)-1,3-benzothiazole (**PBT**) was synthesized by the aerobic catalyst-free oxidative cyclization of 2-aminothiophenol (2-athiobz) and pyridine-4-carbaldehyde (4-carpy) in a molar ratio of 1:1. The reaction was carried out in ethanol as solvent, 0.4 nm zeolite molecular sieves as drying agent (the sieves were dried in vacuum at 120 °C overnight and kept in a desiccator prior the

synthesis procedure), in aerobic conditions and without the addition of any catalyst as follows: 1.10 mL of 2-athiobz (10 mmol) and 50 mL of ethanol was added to a 250 mL round-bottom flask with molecular sieves. Then, 0.97 mL of pyridine-4-carbaldehyde (10 mmol) was added to the flask. Immediately the solution turned yellow as a sign of the condensation of the amino of 2-athiobz and aldehyde of 4-carpy. Then, the mixture was refluxed for 3 h. Afterwards, the solvent was removed from the mother liquor using a rotary evaporator giving a brown solid. Finally, the crude solid was dissolved in hot ethyl acetate and left undisturbed until crystalline platelet solid of the ligand **PBT** was formed. MW: 212.3 g/mol. Yield of 89%. Percentage calculated from the empirical formula $\text{C}_{12}\text{H}_8\text{N}_2\text{S}$ (in %): C, 67.9; H, 3.8; N, 13.2; S, 15.1. Elemental Analysis (in %): C, 68.9; H, 3.1; N, 13.9; S, 15.9. FTIR (cm^{-1} , ATR with no support): 1594.6 (w), 1551.45 (w), 1502.52 (w), 1475.04 (m), 1454.79 (w), 1431.89 (w), 1408.5 (m), 1327.75 (m), 1312.08 (m), 1285.32 (w), 1255.67 (w), 1236.63 (w), 1213.25 (m), 1159.49 (w), 1119.23 (w), 1073.43 (w), 1064.51 (w), 1011.96 (w), 976.286 (s), 940.128 (w), 854.311 (w), 821.768 (s), 754.995 (s), 735.469 (m), 724.621 (s), 704.131 (m), 667.732 (m), 664.839 (m), 621.931 (s), 554.916 (m), 476.331 (s), 454.154 (w), 430.048 (m), 420.888 (w), 416.549 (w). ^1H NMR; 400 MHz; CD_3OD ; δ (ppm): 8.72 (d, $J = 2$ Hz, 2H_{pyridine}, H16/H18), 8.10 (d, $J = 1$ Hz, 1H_{benzothiazole}, H23), 8.06–8.00 (m, $J = 3$ Hz, 2H_{pyridine}, H17/H19, 1H_{benzothiazole}, H20), 7.59 (t, $J = 1$ Hz, 1H_{benzothiazole}, H21), 7.52 (t, $J = 1$ Hz, 1H_{benzothiazole}, H22).

2.2. Synthesis of compounds $[\text{M}(\text{PBT})_2(\text{hfac})_2]$; $\text{M} = \text{Mn(II)}$ (**Mn-PBT**), **Fe(II)** (**Fe-PBT**), **Co(II)** (**Co-PBT**), **Ni(II)** (**Ni-PBT**), **Cu(II)** (**Cu-PBT**), **Zn(II)** (**Zn-PBT**).

(a) *Synthesis of compound Mn-PBT.* 0.5 mmol of $\text{Mn}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ was dissolved in 5 mL of methanol (MeOH). Under continuous stirring, 1 mmol of solid sodium hexafluoroacetylacetonate ($\text{Na}(\text{hfac})$) was added giving a pale-yellow solution. Separately, 1 mmol of **PBT** was dissolved in 5 mL of MeOH. Under continuous stirring, **PBT** solution was added to the $\text{Mn}(\text{NO}_3)_2/\text{Na}(\text{hfac})$ mixture, giving a clear yellowish solution. After three weeks, the slow evaporation of the solution gave rhombohedral single crystals of **Mn-PBT** suitable for X-ray diffraction. MW: 893.58 g/mol. Yield of 51%. Percentage calculated from the empirical formula $\text{C}_{34}\text{H}_{18}\text{N}_4\text{O}_4\text{S}_2\text{F}_{12}\text{Mn}$ for **Mn-PBT** (in %): C, 45.7; H, 2.0; N, 6.3; S, 7.2. Elemental Analysis (in %): C, 46.4; H, 1.9; N, 6.0; S, 7.0.

(b) *Synthesis of compounds Fe-PBT, Co-PBT, Ni-PBT, Cu-PBT and Zn-PBT.* Compound **Fe-PBT**, **Co-PBT**, **Ni-PBT**, **Cu-PBT** and **Zn-PBT** were obtained using the same procedure as **Mn-PBT** but using Fe (ClO_4) $_2 \cdot x\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ and $\text{Zn}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ instead of $\text{Mn}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ respectively. **Fe-PBT**; MW: 896.51 g/mol. Yield of 58%. Percentage calculated from the empirical formula $\text{C}_{34}\text{H}_{18}\text{N}_4\text{O}_4\text{S}_2\text{F}_{12}\text{Fe}$ (in %): C, 45.7; H, 2.0; N, 6.7; S, 7.2. Elemental Analysis (in %): C, 43.7; H, 2.0; N, 6.1; S, 7.0. **Co-PBT**; MW: 897.57 g/mol. Yield of 65%. Percentage calculated from the empirical formula $\text{C}_{34}\text{H}_{18}\text{N}_4\text{O}_4\text{S}_2\text{F}_{12}\text{Co}$ (in %): C, 45.4; H, 2.0; N, 6.2; S, 7.1. Elemental Analysis (in %): C, 43.7; H, 2.0; N, 6.0; S, 7.0. **Ni-PBT**; MW: 897.33 g/mol. Yield of 68%. Percentage calculated from the empirical formula $\text{C}_{34}\text{H}_{18}\text{N}_4\text{O}_4\text{S}_2\text{F}_{12}\text{Ni}$ (in %): C, 45.4; H, 1.9; N, 6.2; S, 7.1. Elemental Analysis (in %): C, 45.5; H, 2.0; N, 6.0; S, 7.0. **Cu-PBT**; MW: 904.08 g/mol. Yield of 78%. Percentage calculated from the empirical formula $\text{C}_{34}\text{H}_{18}\text{N}_4\text{O}_4\text{S}_2\text{F}_{12}\text{Cu}$ (in %): C, 45.4; H, 1.9; N, 6.2; S, 7.1. Elemental Analysis (in %): C, 45.5; H, 2.0; N, 6.0; S, 7.0. **Zn-PBT**; MW: 904.01 g/mol. Yield of 45%. Percentage calculated from the empirical formula $\text{C}_{34}\text{H}_{18}\text{N}_4\text{O}_4\text{S}_2\text{F}_{12}\text{Zn}$ (in %): C, 45.4; H, 1.9; N, 6.2; S, 7.1. Elemental Analysis (in %): C, 45.5; H, 2.0; N, 6.0; S, 7.0.

2.3. ^1H NMR

Proton nuclear magnetic resonance ^1H NMR of **PBT** was measured on a Bruker AVANCE NEO 400 MHz NMR spectrometer, using glass capillary **PBT** solution in CD_3OD as solvent (Fig. S1).

2.4. Elemental analysis

The elemental analysis of **PBT**, **Mn-PBT**, **Fe-PBT**, **Co-PBT**, **Ni-PBT**, **Cu-PBT** and **Zn-PBT** was made using a dynamic flash combustion method followed by gas chromatography (GC) separation and detection via a Thermal Conductivity Detector (TCD) on a Thermo Scientific Flash 2000 Series CHNS elemental analyzer.

2.5. Infrared spectroscopy

Fourier transform infrared spectra of **PBT**, **Mn-PBT**, **Fe-PBT**, **Co-**

PBT, **Ni-PBT**, **Cu-PBT** and **Zn-PBT** were recorded on an ATR-FTIR-4000 Jasco in the 4000–400 cm^{-1} range without using any support.

2.6. X-ray data collection and structure determination

Single crystals of **Mn-PBT**, **Fe-PBT**, **Co-PBT**, **Cu-PBT** and **Zn-PBT** were directly picked up from the reaction media, glued on the tip of a capillary glass using epoxy resin and mounted in an APEXII Bruker diffractometer using Mo- K_{α} radiation ($\lambda = 0.71073 \text{ \AA}$). Frame integration and data reduction were carried out with SAINT, [17] and the SADABS program was employed for multiscan-type absorption

Table 1

Crystal data and structure refinement for **M-PBT** compounds.

Compound name	Mn-PBT	Fe-PBT	Co-PBT
CCDC code	2428873	2428872	2428870
Empirical formula	$\text{C}_{34}\text{H}_{18}\text{F}_{12}\text{N}_4\text{O}_4\text{S}_2\text{Mn}$	$\text{C}_{34}\text{H}_{20}\text{F}_{12}\text{N}_4\text{O}_4\text{S}_2\text{Fe}$	$\text{C}_{34}\text{H}_{18}\text{F}_{12}\text{N}_4\text{O}_4\text{S}_2\text{Co}$
Formula weight	893.58	896.51	897.57
Temperature/K	296	296	100
Crystal system	Triclinic	Triclinic	Triclinic
Space group	P-1	P-1	P-1
a/ $\text{\AA}$	9.5424(4)	9.342(3)	9.4401(9)
b/ $\text{\AA}$	9.6118(4)	9.695(3)	9.4810(9)
c/ $\text{\AA}$	10.3670(4)	10.459(3)	10.0376(9)
$\alpha/^\circ$	107.3000(10)	93.734(10)	83.295(4)
$\beta/^\circ$	95.2330(10)	106.929(9)	73.685(3)
$\gamma/^\circ$	90.2390(10)	90.810(10)	89.814(4)
Volume/ $\text{\AA}^3$	903.57(6)	903.8(5)	855.90(14)
Z	1	1	1
$\rho_{\text{calc}}/\text{g cm}^{-3}$	1.642	1.643	1.741
μ/mm^{-1}	0.588	0.640	0.736
F(000)	447.0	448.0	449.0
Crystal size/ mm^3	$0.221 \times 0.125 \times 0.074$	$0.048 \times 0.028 \times 0.025$	$0.107 \times 0.053 \times 0.025$
Radiation	MoK α ($\lambda = 0.71073$)	MoK α ($\lambda = 0.71073$)	MoK α ($\lambda = 0.71073$)
2 θ range for data collection/ $^\circ$	4.134 to 76.296	4.212 to 62.328	4.328 to 54.442
Index ranges	$-16 \leq h \leq 16, -13 \leq k \leq 14, -17 \leq l \leq 14$	$-13 \leq h \leq 13, -13 \leq k \leq 14, -15 \leq l \leq 14$	$-12 \leq h \leq 12, -12 \leq k \leq 12, -12 \leq l \leq 12$
Reflections collected	34760	33155	11738
Independent reflections	7070 [$R_{\text{int}} = 0.0289, R_{\text{sigma}} = 0.0281$]	5519 [$R_{\text{int}} = 0.1375, R_{\text{sigma}} = 0.1165$]	3760 [$R_{\text{int}} = 0.1034, R_{\text{sigma}} = 0.1197$]
Data/restraints/parameters	7070/0/259	5519/0/260	3760/0/259
Goodness-of-fit on F^2	1.025	0.991	1.045
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0679, wR_2 = 0.1842$	$R_1 = 0.0786, wR_2 = 0.1961$	$R_1 = 0.0564, wR_2 = 0.1240$
Final R indexes [all data]	$R_1 = 0.1146, wR_2 = 0.2262$	$R_1 = 0.2140, wR_2 = 0.2709$	$R_1 = 0.1158, wR_2 = 0.1461$
Largest diff. Peak/hole/ $e \text{ \AA}^{-3}$	0.77/−0.66	0.60/−0.42	1.42/−0.60

Compound name	Cu-PBT	Zn-PBT
CCDC code	2428874	2428871
Empirical formula	$\text{C}_{34}\text{H}_{18}\text{F}_{12}\text{N}_4\text{O}_4\text{S}_2\text{Cu}$	$\text{C}_{34}\text{H}_{18}\text{F}_{12}\text{N}_4\text{O}_4\text{S}_2\text{Zn}$
Formula weight	904.08	904.01
Temperature/K	296	296
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
a/ $\text{\AA}$	9.4574(8)	9.395(2)
b/ $\text{\AA}$	9.6225(8)	9.642(2)
c/ $\text{\AA}$	10.3198(9)	10.385(3)
$\alpha/^\circ$	95.466(3)	94.636(8)
$\beta/^\circ$	107.783(3)	107.232(8)
$\gamma/^\circ$	90.829(3)	90.575(8)
Volume/ $\text{\AA}^3$	889.26(13)	894.9(4)
Z	1	1
$\rho_{\text{calc}}/\text{g cm}^{-3}$	1.685	1.677
μ/mm^{-1}	0.840	0.911
F(000)	451.0	452.0
Crystal size/ mm^3	$0.064 \times 0.044 \times 0.029$	$0.15 \times 0.13 \times 0.019$
Radiation	MoK α ($\lambda = 0.71073$)	MoK α ($\lambda = 0.71073$)
2 θ range for data collection/ $^\circ$	4.168 to 76.156	4.122 to 61.85
Index ranges	$-13 \leq h \leq 13, -14 \leq k \leq 16, -17 \leq l \leq 15$	$-13 \leq h \leq 13, -13 \leq k \leq 13, -14 \leq l \leq 14$
Reflections collected	34298	32,373
Independent reflections	6954 [$R_{\text{int}} = 0.1327, R_{\text{sigma}} = 0.2028$]	5355 [$R_{\text{int}} = 0.0744, R_{\text{sigma}} = 0.0641$]
Data/restraints/parameters	6954/0/259	5355/0/259
Goodness-of-fit on F^2	0.932	1.015
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0731, wR_2 = 0.1680$	$R_1 = 0.0750, wR_2 = 0.1939$
Final R indexes [all data]	$R_1 = 0.2843, wR_2 = 0.2474$	$R_1 = 0.1480, wR_2 = 0.2473$
Largest diff. Peak/hole/ $e \text{ \AA}^{-3}$	0.56/−0.54	1.02/−0.58

corrections [18].

Using the Olex2 [19] package, the crystal structures were solved with the ShelXT [20] structure solution program using Dual Methods and refined with the ShelXL [21] package using least-squares minimization based on F^2 . Crystallographic data details on data collection and refinement parameters of the crystal structure are summarized in Table 1 and Tables S1. Structure drawings have been made with Mercury software [22]. Additional data concerning the crystals and the refinement parameters are detailed in the Supporting Information.

Due to the inherent high thermal motion and/or static disorder observed in complexes at the room temperature (RT) data collection, a rapid decay of diffraction intensity was noted at high scattering angles. To ensure the quality and robustness of the final structural model, and to maximize the signal-to-noise ratio ($I/\sigma(I)$), the data sets were truncated at a resolution corresponding to $2\theta \sim 25\text{--}26^\circ$ (maximum resolution ~ 0.85 Å). Reflections beyond this limit, having $I \leq 2\sigma(I)$, were excluded from the final refinement cycles, following standard SHELXL data handling instructions. The resulting Goodness-of-Fit values (GoF around 1.0) confirm the statistical sufficiency and high quality of the refined model based on the usable data set.

The fluorine atoms of the $-\text{CF}_3$ groups in the hfac^- ligands of **Fe-PBT**, **Co-PBT**, **Cu-PBT**, and **Zn-PBT** exhibited pronounced thermal agitation at room temperature. To preserve a chemically realistic and unbiased structural model, the $-\text{CF}_3$ disorder was not explicitly modeled; instead, the fluorine atoms were allowed to refine with appropriate occupancies and anisotropic displacement parameters. This refinement strategy yielded stable models and satisfactory agreement factors for all four structures (see Tables S1–S5 for further details).

Among the four complexes, the room-temperature (297 K) data set for **Co-PBT** was of noticeably lower quality. Despite extensive refinement efforts (including multiple disorder models for the fluorine atoms) the 297 K refinement (Table S6) still generated severe alerts (RINTA01_ALERT_3_A, PLAT020_ALERT_3_A, PLAT026_ALERT_3_A). Consequently, a new data set was collected at low temperature (100K), yielding significantly improved data quality and refinement statistics.

The X-ray powder diffraction data of **Ni-PBT** were collected at room temperature on a Bruker D8 Advance diffractometer with $\text{Co K}\alpha_{1,2}$ radiation equipped with a LynxEye in the range of $5^\circ < 2\theta < 70^\circ$. Indexing of the powder patterns of **Ni-PBT** has been made with the program DICVOL06 [23]. The whole powder pattern fittings (with the Le Bail algorithm) were done employing the FULLPROF [24] program available in the software package WinPLOTR (Fig. S4) [25]. The unit-cell parameters obtained from indexing the P-XRD pattern and refined by Le Bail fitting confirm that **Ni-PBT** crystallizes in the same $P-1$ space group as the **M-PBT** analogues. The refined cell parameters for **Ni-PBT** show identical unit cell angles but slightly and equally elongated lattice lengths compared to the **M-PBT** series. This elongation could be attributed to an increased number of formula units per unit cell (Z) in **Ni-PBT** asymmetrical unit, resulting in a larger unit cell volume [26]. Consequently, the **Ni-PBT** complex remains structurally analogous to the **M-PBT** series, as supported by identical composition, FTIR spectra, and thermal behavior. This slight difference is therefore solely due to variations in crystal packing rather than any change in chemical identity. Additionally, the whole-pattern fitting of the P-XRD data confirms the high purity of the synthesized polycrystalline **Ni-PBT** samples. SHAPE [27] and Octadist [28] software were used to evaluate the octahedral distortion of the MO_4N_2 coordination geometry within the **M-PBT** series. SHAPE computes the global deviation of coordination polyhedra using the Continuous Shape Measurement (CSHM), a descriptor that evaluates how closely a given polyhedral coordination environment resembles an ideal reference geometry. Meanwhile, OctaDist evaluate de distortion of the specific octahedral geometry using the Δ , Σ and Θ deviation descriptors [29]:

Δ : the relative bond-length distortion is a normalized metric describing the relative deviation of the six M-L coordination bond distances with respect to the mean bond length:

$$\Delta = \frac{1}{6} \sum_{i=1}^6 \left(\frac{d_i - d_{\text{mean}}}{d_{\text{mean}}} \right)^2$$

Σ : the angular distortion parameter measures the deviation of L-M-L *cis* bond angles from the ideal 90° :

$$\Sigma = \sum_{i=1}^{12} |\phi_i - 90^\circ|$$

where ϕ are the twelve L-M-L *cis* angles around the metal center.

Θ : the torsional distortion parameter is a descriptor of the torsional (twisting) distortion of the octahedral geometry. It is computed from deviations angle (from the ideal 60°) of two projected triangular faces of an octahedron:

$$\Theta = \sum_{i=1}^{24} |-\phi_i - 60^\circ|$$

where θ corresponds to the angles between the vectors defined by the two pairs of triangular faces.

2.7. Hirshfeld surfaces

Hirshfeld surfaces were calculated using the CIF file of **Co-PBT** as input file in Crystalexplorer package [30]. The intermolecular interactions were identified and quantified by 2D fingerprint plots [31]. The calculated isosurfaces are represented by the normalized contact distance d_{norm} defined by

$$d_{\text{norm}} = \frac{(d_i - r_i^{\text{vdW}})}{r_i^{\text{vdW}}} + \frac{(d_e - r_e^{\text{vdW}})}{r_e^{\text{vdW}}}$$

where d_i , r_i^{vdW} , d_e and r_e^{vdW} are the distance and Van der Waals radii inside (i) and outside (e) the isosurface nucleus respectively. d_{norm} is represented by the closer contact than the sum of r^{vdW} in red, the longest contact than the sum of r^{vdW} in blue and in white the contacts in the range of the sum of r^{vdW} .

2.8. Thermogravimetric analysis

Thermogravimetric analyses were performed on a Mettler Toledo TGA/DSC-II system. The samples were introduced in an alumina holder and heated under an air atmosphere from room temperature to 900°C with a heating rate of $5^\circ\text{C}/\text{min}$.

2.9. Calculations details

The molecular structures were optimized by DFT calculations using the PBE [32] functional and the def2-SV(P) [33] basis set, as implemented in the ORCA program [34]. Complete convergence of the geometries was verified, confirming that all molecules correspond to energy minimum on the potential energy surface. From these optimized geometries, several global reactivity indices were calculated. In the context of conceptual Density Functional Theory (DFT), global reactivity descriptors are essential tools for understanding the chemical behavior of molecular systems. Chemical softness (S^{r}) is a reactivity index that indicates how easily a molecule can deform its electron density in response to external perturbations, such as the presence of nucleophiles or electrophiles. A higher softness value reflects greater polarizability and reactivity. The electrophilicity index (ω^{r}) measures the tendency of a chemical species to accept electrons and thus behave as an electrophile; it is derived from the square of the chemical potential divided by twice the global hardness. Global hardness (η^{r}), on the other hand, quantifies the resistance of a molecule to changes in its electron density upon interaction with other species and is calculated as the difference between the ionization potential (I^{r}) and the electron affinity (A^{r}),

divided by two. The ionization potential represents the energy required to remove an electron from a neutral molecule and is closely related to electronic stability; it can be approximated by the negative of the highest occupied molecular orbital (HOMO) energy. Similarly, the electron affinity reflects the tendency of a molecule to gain an electron and is estimated as the negative of the lowest unoccupied molecular orbital (LUMO) energy. Together, these descriptors provide a comprehensive picture of a molecule's electronic behavior and chemical reactivity.

While these descriptors provide useful heuristic data for comparing this isostructural compound series, it is important to note that their physical interpretation in open-shell transition-metal complexes can be subtle and is often dependent on the chosen functional and basis set. Therefore, the calculated values should be considered as preliminary indicators of reactivity trends within this series rather than as definitive absolute values.

The specific formulas used to calculate these indices are summarized in Table 2. In this work, all reactivity descriptors were calculated separately for alpha (α) and beta (β) spin electrons, allowing for a more detailed description of spin-dependent reactivity.

The **M-PBT** complexes were treated in their high-spin (HS) electronic configurations, consistent with the expected ligand-field and with the electronic occupation of 3d transition metals. PBE is known to favor high-spin states for 3d metal ions, and the observed convergence behavior is fully consistent with expectations for this functional and basis set. GGA functionals such as PBE typically yield slight spin contamination, especially for open shell 3d metals. Values within 5–10% of the ideal (S^2) are considered normal and acceptable in literature. The Ideal (S^2) vs. computed PBE/def2-SV(P) values obtained at this level of theory are included in Table S9.

2.10. Biological material

(a) *Plants.* *Arabidopsis thaliana* plants, ecotype Columbia-0, were used. Seeds were surface-sterilized with 50% sodium hypochlorite to prevent microbial contamination, then stratified for 48 h at 4 °C in the dark. After stratification, seeds were sown under sterile conditions in Petri dishes containing half-strength Murashige and Skoog medium (MS 0.5×), solidified with Phytigel. The culture medium was supplemented with **M-PBT** compounds dissolved in dimethyl sulfoxide (DMSO) with

Table 2
Global Reactivity Indices (GRIs) from spin-polarized (unrestricted) calculations [34]. These indices are computed with CDFD descriptors obtained from the HOMO (ϵ_H^α), and LUMO (ϵ_L^α) energy levels.

	Koopmans' theorem	Reference
Ionization potential (I^α)	$I^\alpha = -\epsilon_H^\alpha$	[35,36]
Electron affinity (A^α)	$A^\alpha = -\epsilon_L^\alpha$	[35,36]
Global hardness (η^α)	$\eta^\alpha = \frac{1}{2}(\epsilon_L^\alpha - \epsilon_H^\alpha)$	[35,37–41]
Electronegativity (χ^α)	$\chi^\alpha = -\frac{1}{2}(\epsilon_L^\alpha + \epsilon_H^\alpha)$	[42–44]
Electron donor ($\omega^{-\alpha}$)	$\omega^{-\alpha} = \frac{(\chi^\alpha - \eta^\alpha)^2}{16\eta^\alpha}$	[45]
Chemical potential (μ^α)	$\mu^\alpha = \frac{I^\alpha + A^\alpha}{2}$	[42–44]
Chemical softness (S^α)	$S^\alpha = \frac{1}{\eta^\alpha}$	[42–44]
Electrophilicity index (ω^α)	$\omega^\alpha = \frac{(\mu^\alpha)^2}{2\eta^\alpha}$	[45]
Electron acceptor ($\omega^{+\alpha}$)	$\omega^{+\alpha} = \frac{(3\chi^\alpha + \eta^\alpha)^2}{16\eta^\alpha}$	[46]
Net Electrophilicity ($\Delta\omega^{\pm\alpha}$)	$\Delta\omega^{\pm\alpha} = \omega^{+\alpha} + \omega^{-\alpha}$	[42]

*The α indices describe electronic reactivity from α spin. For β spin the calculations are performed in a similar way.

final concentrations of 1.0 and 10 $\mu\text{g mL}^{-1}$. Control plates were supplemented with either **PBT**, Na(hfac), or DMSO alone. Seedlings were grown under standard conditions (22 ± 2 °C, 100 μE white light, 12 h light/12 h dark photoperiod) for 14 days. At the end of the growth period, plates were photographed for leaf area quantification, and the fresh weight of the seedlings was measured.

(b) *Bacterial growth.* *Pseudomonas syringae* pv. tomato was grown overnight at 28 °C with agitation (100 rpm) in King's B (KB) medium (20 g L⁻¹ proteose peptone, 10 mL L⁻¹ glycerol, 1.5 g L⁻¹ K₂HPO₄, 1.5 g L⁻¹ MgSO₄·7H₂O; pH 7.0). The optical density at 600 nm (OD₆₀₀) was adjusted to 0.01, corresponding to $\sim 10^6$ colony-forming units (CFU) per mL, using fresh sterile KB medium. Aliquots of 1.5 mL were transferred to 24-well plates and supplemented with **M-PBT** compounds dissolved in DMSO at final concentrations of 1.0 and 10 $\mu\text{g mL}^{-1}$. Controls included **PBT**, Na(hfac), or DMSO. Plates were incubated for 24 h at 30 °C, and OD₆₀₀ was measured every 15 min using a temperature-controlled microplate reader (TECAN Infinite M Nano). Kinetic parameters were calculated from the resulting growth curves using the Dashing Growth Curves tool [47].

3. Results and discussion

3.1. Synthetical approach

Remarkably, the use of ethanol as solvent and molecular sieves as drying agent afforded the catalyst-free oxidative cyclization of 2-aminothiophenol (2-athioibz) and pyridine-4-carbaldehyde (4-carpy) in aerobic conditions with high yield (Scheme 1).

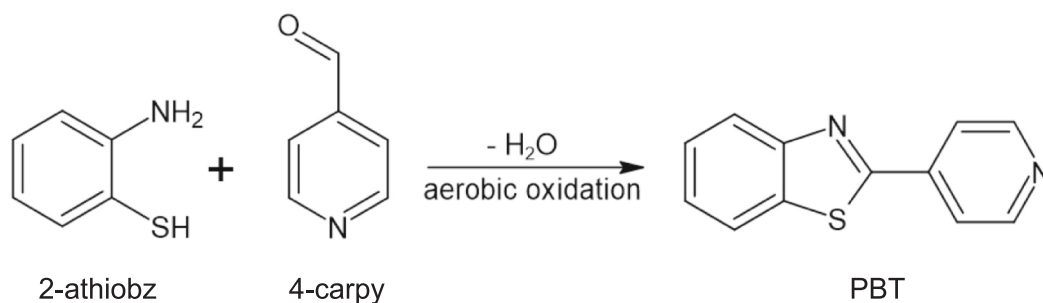
Thiazole-based ligands are excellent building blocks for coordination chemistry due to their *N,S*-heterocyclic structure, which enables coordination to both hard and soft metal ions. Additionally, the electron-rich nature of thiazole linkers enhances non-covalent interactions like H-bonding and $\pi \cdots \pi$ stacking, leading to greater thermal and chemical stability in the resulting compounds [48–50].

Following this, a novel family of molecular complexes, [M(PBT)₂(hfac)₂] (designated as **M-PBT**), was successfully synthesized by reacting **PBT** and hexafluoroacetylacetonate (hfac⁻) with various transition metal(II) salts (M = Mn, Fe, Co, Ni, Cu, Zn) (Fig. 1).

To elucidate the coordination of organic ligands within these new **M-PBT** complexes, comparative analysis of the FTIR spectra of the free **PBT** and hfac⁻ ligands (Fig. S2a) was performed using **Co-PBT** as a reference (Fig. S2b). A key observation was the distinct red-shift of the $\nu(\text{C}=\text{O})$ stretching vibrations of the hfac⁻ ligand from 1654 cm⁻¹ and 1666 cm⁻¹ in the free ligand to 1610 cm⁻¹ and 1636 cm⁻¹ in the **Co-PBT** complex. This change clearly indicates that the hfac⁻ ligand coordinates to the metal ions via the O-ketone. In contrast, the strong and sharp bands between 1300 cm⁻¹ and 1100 cm⁻¹, assigned to the C–F stretching vibrations of the hfac⁻-CF₃ substituent, remained virtually unaltered in the **Co-PBT** complex, serving as an important signature for the hfac⁻ ligand identification in the metal complexes. For the **PBT** ligand, changes in the $\nu(\text{C}=\text{C})$ and $\nu(\text{C}=\text{N})$ vibrations at 1594 cm⁻¹ and 1586 cm⁻¹ in the free **PBT** ligand coalesced into a single shoulder at 1590 cm⁻¹ in the **Co-PBT** complex, thereby confirming the coordination of the *N*-pyridine to the metal cations [51]. Same tendency is observed for the rest of **M-PBT** complexes FTIR spectrum (Fig. S3).

3.2. Structural description: Single-crystal X-Ray diffraction

Single crystal X-ray diffraction reveals that all the **M-PBT** compounds are isostructural and crystallize in a triclinic *P*-1 system, with half M(II) cation, one **PBT** and one hfac⁻ anion in the asymmetric unit (Table 1 and Table S1–S6). The crystal structure of **Co-PBT** is used as reference for the structural description. The molecular structure of **Co-PBT** consists of a mononuclear neutral complex with central Co(II) cation coordinated by four oxygen and two nitrogen atoms giving a CoO₄N₂ octahedral geometry. The equatorial plane is defined by four O-donor atoms



Scheme 1. Reaction pathway of ligand PBT.

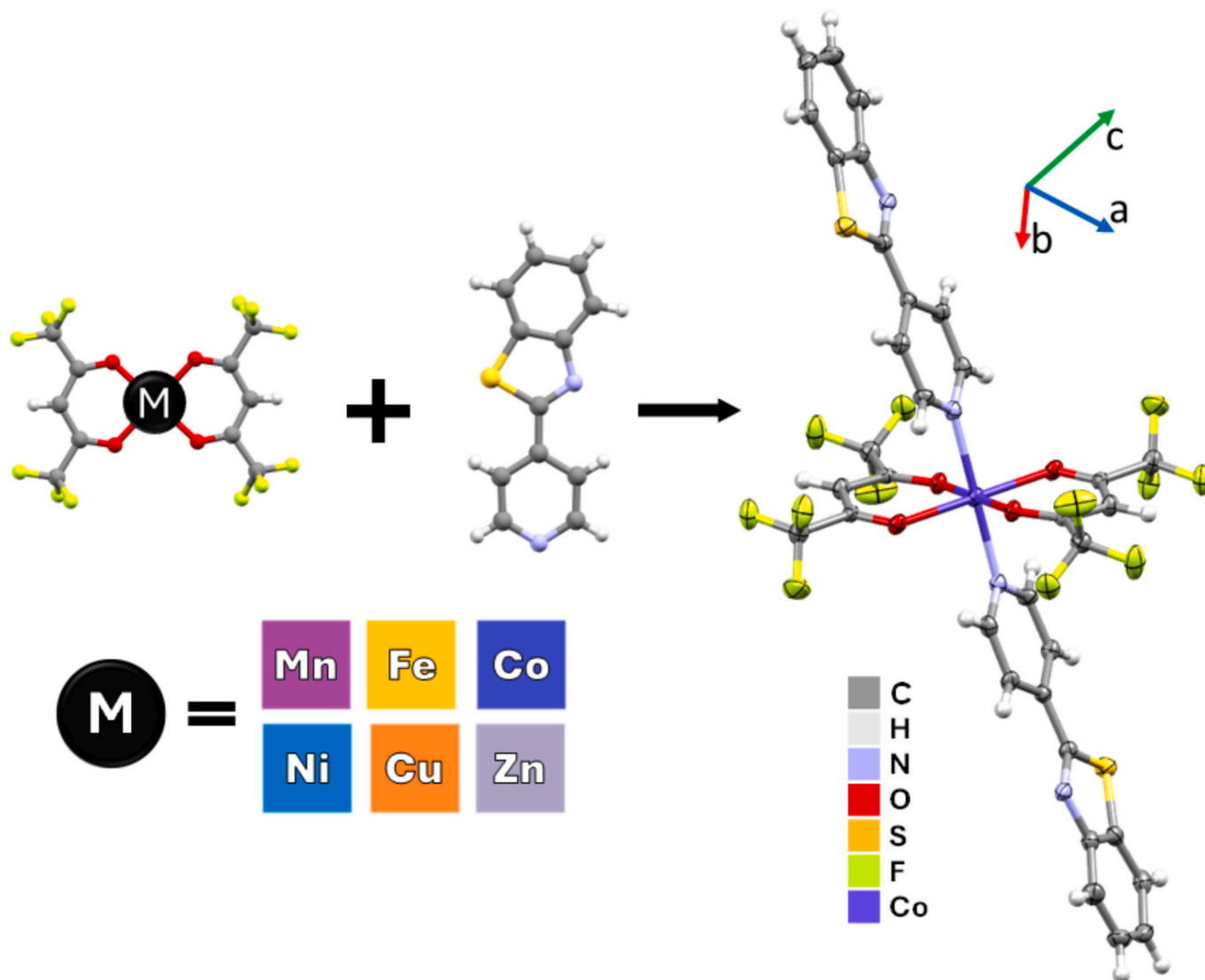


Fig. 1. Left: Scheme of M(hfac)_2 and **PBT** to form the **M-PBT** complexes ($\text{M} = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}$); Right: Molecular structure of $[\text{Co(PBT)}_2(\text{hfac})_2]$ (thermal ellipsoids were drawn at the 50% probability level, hydrogen atoms are depicted as fixed-sized spheres of 0.2 Å radius).

belonging to two hfac^- anion coordinating in a bidentate $\kappa\text{O}',\text{O}''$ fashion forming two five-membered chelate rings with $\text{Co1-O1} = 2.061(3)$ Å and $\text{Co1-O2} = 2.058(2)$ Å bond length. Meanwhile, the two axial positions are occupied by two *N*-atoms from the pyridine ring of **PBT** ligand with $\text{Co1-N1} = 2.135(3)$ Å bond length. The *trans*- $[\text{M(PBT)}_2(\text{hfac})_2]$ isomer with a CoO_4 *hfac*-equatorial plane and *trans*-**PBT** ligands is expected to be the most stable structure to minimize steric hindrance. This is consistent with the *trans*- $[\text{Zn(PBT)}_2(\text{acac})_2]$ analog compound reported

previously [51]. Likewise, **PBT** have been used for the synthesis of coordination compounds using Cd(II) , Ag(I) , Co(II) , $\text{UO}_2(\text{II})$, Sm(III) , Eu(III) and Zn(II) [51–54]. In all the cases, **PBT** coordinates by the *N*-pyridine, leading the *N,S*-atoms of the benzothiazole available for supramolecular interactions and leaving the other coordination positions available for coordination of different oxo-anions or carboxylate-based ligands.

Bond lengths for the entire **M-PBT** series are summarized in Table 3

Table 3

Coordination bond lengths in Å and octahedral distortion parameters for compounds **M-PBT** compounds.

	Mn-PBT	Fe-PBT	Co-PBT [†]	Cu-PBT	Zn-PBT
Atom	Mn1	Fe1	Co1	Cu1	Zn1
O1	2.1426(18)	2.053(3)	2.061(3)**	2.146(3)	2.083(3)
O2	2.1460(17)	2.051(3)	2.060(3)**	2.110(3)	2.084(3)
N1	2.268(2)	2.209(3)	2.135(3)**	2.004(4)	2.145(4)
Distortion parameter					
CShM	0.32	0.22	0.09	0.17	0.07
$\Delta \cdot 10^{-4}$ ***	7.1	12.7	2.9	8.18	1.9
$\Theta/^\circ$	118.7	78.0	63.7	67.9	19.4
$\Sigma/^\circ$	40.0	26.0	18.8	25.1	55.2

[†]The given values are for 100 K diffraction data.

The bond length values of **Co-PBT at RT data are: Co1–O1 = 2.049(4) Å; Co1–O2 = 2.057(4); Co1–N1 = 2.135(5) Å.

***The values for **Co-PBT** at RT data are: CShM = 0.07; $\Delta = 4.3 \cdot 10^{-4}$; $\Sigma = 14.4^\circ$; $\Theta = 45.0^\circ$.

and Fig. S5a. In general, M–O bond distances are shorter than M–N, resulting in an elongated octahedral MO_4N_2 geometry for **Mn-PBT**, **Fe-PBT**, **Co-PBT** and **Zn-PBT**. Notably, **Cu-PBT** is the only compound where the M–O distances exceed M–N ones, suggesting a compressed CuO_4N_2 octahedra in this complex. On the other hand, a progressive shortening of M–N distances are observed across the **M-PBT** series from **Mn-PBT** to **Cu-PBT**, followed by an increase in **Zn-PBT**. In contrast, M–O distances do not follow a clear trend, with the order Mn–O > Cu–O > Zn–O > Co–O > Fe–O. This trend agrees with the cell volume across the series (Table 1), $V_{\text{Mn-PBT}} \sim V_{\text{Fe-PBT}} > V_{\text{Co-PBT}} > V_{\text{Cu-PBT}} < V_{\text{Zn-PBT}}$, suggesting that overall volume cell is sensitive to the axial coordination on the metal cations [55].

SHAPE [27] and Octadist [28] software were used to evaluate the octahedral distortion of the MO_4N_2 coordination geometry within the series (Table 3 and Fig. S5b). The SHAPE analysis provided Continuous Shape Measures (CShM), which quantify the deviation from an ideal octahedral geometry. CShM reveals that $\text{ZnO}_4\text{N}_2 \sim \text{CoO}_4\text{N}_2$ are the closer to ideal octahedra, followed by CuO_4N_2 , FeO_4N_2 and MnO_4N_2 respectively. In addition, Octadist was used to calculate Δ , Σ and Θ deviation parameters, in which Δ reflects the deviation in M–O/M–N bond lengths; Σ evaluates the deviations of the O–M–O and O–M–N *cis* bond angles from the ideal 90° ; and Θ evaluates the torsional distortion of the octahedral geometry which can be taken as a descriptor to evaluate the trigonal prismatic distortion of the octahedron (for more information see section 2.4).

The Δ parameter shows that FeO_4N_2 presents the greater difference between M–O and M–N bond length, while ZnO_4N_2 shows the most similar M–O and M–N bond distances. Meanwhile, for Σ a discontinuous trend is observed, $\text{MnO}_4\text{N}_2 > \text{FeO}_4\text{N}_2 > \text{CoO}_4\text{N}_2 < \text{CuO}_4\text{N}_2 < \text{ZnO}_4\text{N}_2$, with CoO_4N_2 presenting the lower angular deviation. On the other hand, Θ is the only parameter to follow the periodic order $\text{MnO}_4\text{N}_2 > \text{FeO}_4\text{N}_2 > \text{CoO}_4\text{N}_2 > \text{CuO}_4\text{N}_2 > \text{ZnO}_4\text{N}_2$. Since Θ can assess trigonal prismatic distortion, these values support a progressive approach to ideal octahedral geometry across the series from MnO_4N_2 to ZnO_4N_2 , in agreement with the CShM results.

Overall, the structural analysis confirms that **Cu-PBT** deviates significantly from the rest of the series due to its compressed geometry. Excluding **Cu-PBT**, the trend from **Mn-PBT** to **Zn-PBT** indicates increasing structural regularity. Despite ZnO_2N_2 showing minimal bond length deviations (Δ), it also displays the highest Θ value, suggesting a greater degree of trigonal prismatic distortion compared to the other members of the series.

Beyond the immediate coordination environment of the metal center, the **PBT** ligand adopts planar conformation evidenced by the torsion angles between the pyridine and benzothiazole rings, C9–C8C11–N2 =

177.3(4) and C7–C8–C11–S1 = 176.1(3)°, indicating both heterocycles are nearly co-planar. Additionally, the **PBT** ligands are 4.45° tilted away from the N1–Co1–N1^{#1} axis (Fig. S6a; angle between the Co1–N1 bond and the centroid of the pyridine ring belonging **PBT** ligand; #1 = 2–x, 1–y, z). Moreover, the hfac^- anions deviate from the central CoO_4 coordination plane, with an 17.46° angle between the planes defined by O1O2–Co–O1^{#1}O2^{#1} and O1–C2–C3–C4–O2 (Fig. S6b).

Notably, the conformation of the ligands in the outer coordination sphere appears to be directly influenced by intermolecular interactions within the crystal packing. In particular, the pyridine/thiazole aromatic rings and C–H groups of the **PBT** ligand, together with the F-atoms of the hfac^- anions, give rise to a variety of potential supramolecular contacts between neighboring $[\text{M}(\text{PBT})_2(\text{hfac})_2]$ units. As a result, several types of non-covalent interactions are observed in the crystal structures of the **M-PBT** complexes, as depicted in Figs. 2–3 and summarized with detailed geometrical parameters in Table 4.

For instance, two main non-covalent interactions involving $-\text{CF}_3$ groups can be identified in the crystal packing of the **M-PBT** complexes. First, (i) non-conventional C–H...F hydrogen bond formed with aromatic hydrogens atoms belonging from both pyridine (C9–H9...F2^{1#}) and benzothiazole rings (C16–H16...F2^{3#} and C14–H14...F4^{2#}), with d(D–A) ranging from ~ 3.32 to ~ 3.62 Å and extended along *a* direction. Secondly, (ii) F...F halogen-halogen interactions occur between neighboring hfac^- ligands (F6...F6^{4#}) with d(F...F) around 2.8 Å and propagating through the *c* direction (Fig. 2 and Table 4).

In addition, the axial **PBT** ligands oriented away from the $[\text{M}(\text{hfac})_2]$ displays a parallel displaced $\pi \cdots \pi$ stacked conformation along *a* direction (Fig. 3). In this offset stacked configuration, two $[\text{M}(\text{PBT})_2(\text{hfac})_2]$ units (related by an inversion center) assemble in a head-to-tail fashion forming a pair motif, in which the two **PBT** ligands interact through reciprocal pyridine-benzothiazole $\pi \cdots \pi$ contacts. Furthermore, the pendant benzothiazole rings of each pair motif engage in tail-to-tail $\pi \cdots \pi$ interactions with to adjacent $[\text{M}(\text{PBT})_2(\text{hfac})_2]$ units, adopting an almost perfectly coplanar geometry (interplanar angle $\sim 0^\circ$). These benzothiazole-benzothiazole contacts exhibit longer centroid-to-centroid distances compared to those observed for the pyridine-benzothiazole stacking (Fig. 3 and Fig. S7, Table 4).

3.3. Supramolecular interactions insights: Hirshfeld surface analysis

Hirshfeld surfaces were calculated and mapped with normalized contact distance (d_{norm}), and the corresponding 2D fingerprint plots were generated to provide detailed insights into nature and prevalence of intermolecular interactions within the crystal packing of the **M-PBT** series. Consistent with the structural description section, the crystal structure of **Co-PBT** is used as the representative model for the entire series (Table 5 and Fig. S8 and S9).

As shown in Fig. S8, red spots corresponding to short contacts are predominantly located near the F-atoms of the hfac^- ligands and the H-atoms on the aromatic rings of the **PBT** ligands, consistent with the significant H...F/F...H contributions identified in the fingerprint plots (Fig. S8a–b). The surface view along the *ab* plane (Fig. S8a) emphasizes these directional C–H...F interactions, which appear to be among the most recurrent contacts in the structure.

Additionally, the Fig. S8b highlights regions of enhanced interaction density near the thiazole moieties of **PBT**, indicating potential N...F or S...F contacts. Although weak, these contacts may play a role in orienting the **PBT** ligands within the packing, promoting directional stacking. The view along the *ac* plane (Fig. S8c) shows complementary interactions involving edge-positioned C–H donors from **PBT** engaging with neighboring F-acceptors, further contributing to the cohesion of the 3D supramolecular framework.

These observations align with the quantitative fingerprint analysis and confirm that both hfac^- and **PBT** ligands contribute cooperatively to the crystal packing, primarily through a network of weak H-bonding and dipolar interactions (Table 5). The 2D-fingerprint plots reveal that the

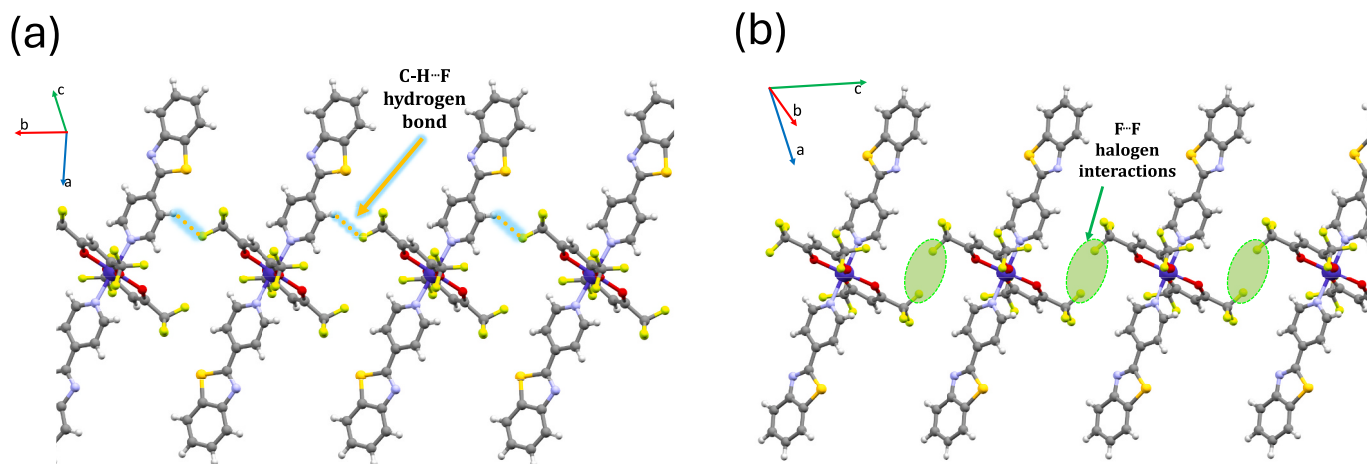


Fig. 2. (a) non-conventional C-H...F hydrogen bond and (b) F...F halogen interactions found in **M-PBT**.

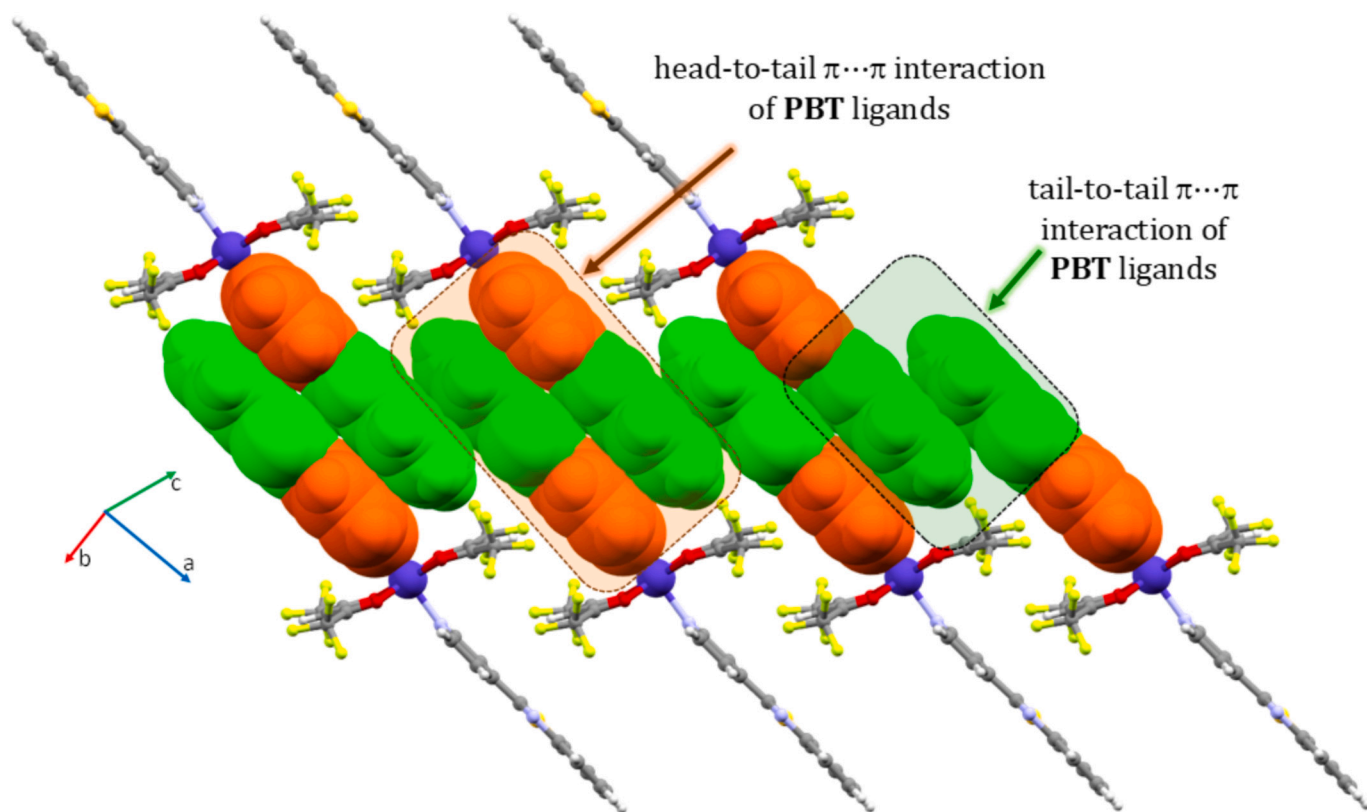


Fig. 3. $\pi\cdots\pi$ stacked conformation of $[M(PBT)_2(hfac)_2]$ complexes along *a* direction showing the head-to-tail pyridine-benzothiazole and tail-to-tail benzothiazole-benzothiazole $\pi\cdots\pi$ interactions (pyridine in green and benzothiazole in orange).

most significant interactions arise from contacts between the **PBT** heterocycles and the terminal $-CF_3$ groups of the equatorial $hfac^-$ ligands. Among these, the $F\cdots H/H\cdots F$ contacts stand out as sharp, well-defined spikes in the region of short interatomic distances (d_i and $d_e > 1.2$ – 1.8 Å), indicative of directional C-H...F hydrogen bonds. The slight asymmetry observed between the $F\cdots H$ and $H\cdots F$ plots suggests that the number and geometry of donor and acceptor atoms are not equivalent, with *H*-atoms more frequently serving as internal contacts due to their abundance on the aromatic **PBT** framework (Fig. S9a–b) [56,57]. The $C\cdots H$ and $H\cdots C$ interactions contribute significantly as well, appearing as diffuse but distinguishable regions in the fingerprint plots. These are consistent with $C-H\cdots\pi$ or $C-H\cdots S$ interactions involving the

benzothiazole and pyridyl fragments and are characterized by moderately short distances and broad distributions (Fig. S9c–d) [58]. Notably, the distinction between $C\cdots H$ and $H\cdots C$ also reflects the molecular asymmetry and the different roles of carbon atoms in the structure (as π -systems or acceptors).

In contrast, $F\cdots F$ interactions are represented by broad and dull regions, occurring at longer distances (typically >2.0 Å). These contacts are indicative of repulsive or dispersive interactions between neighboring $-CF_3$ groups, more related to close packing than to any directional affinity (Fig. S9e) [59]. Lastly, $H\cdots H$ interactions, while the most abundant, display a diffuse distribution along the diagonal of the plot, confirming their non-directional van der Waals character (Fig. S9f)

Table 4Summary of the non-covalent intermolecular interactions found in **M-PBT**.

Interaction	Geometrical parameter	Mn-PBT	Fe-PBT	Co-PBT	Cu-PBT	Zn-PBT
Non-conventional C-H...F Hydrogen bond	d(H9-F2 ^{1#})/Å	2.75	2.75	2.64	2.72	2.74
	d(C9-F2 ^{1#})/Å	3.529	3.525	3.451	3.534	3.527
	C9-H9-F2 ^{1#} /°	142.1	142.0	144.2	146.0	143.2
	d(H16-F2 ^{3#})/Å	2.67	2.63	2.57	2.62	2.60
	d(C16-F2 ^{3#})/Å	3.397	3.366	3.327	3.366	3.340
	(5)	(5)	(8)	(5)	(7)	(8)
	C16-H16-F2 ^{3#} /°	135.6	136.7	137.3	137.4	136.7
	d(H14-F4 ^{2#})/Å	2.85	2.87	2.72	2.81	2.82
	d(C14-F4 ^{2#})/Å	3.608	3.621	3.479	3.585	3.588
	(4)	(4)	(8)	(5)	(7)	(7)
Halogen-halogen F...F interaction	C14-H14-F4 ^{2#} /°	139.9	139.0	137.2	3.366 (8)	140.2
	d(F6...F6 ^{4#})/Å	2.881	2.869	2.831	2.809	2.845
Pyridine-Benzothiazole π ... π staking	Interplanar angle/°	2.297	3.762	3.766	2.316	3.306
	d(centroid-centroid)/Å	3.874	3.956	3.766	3.940	3.933
	Shift distance/Å	1.642	1.847	1.687	1.746	1.772
Benzothiazole-Benzothiazole π ... π staking	Interplanar angle/°	0	0	0	0	0
	d(centroid-centroid)/Å	4.188	4.078	3.945	4.128	4.090
	Shift distance/Å	2.362	2.136	2.073	2.240	2.193

1# = 2-x, 2-y, -z; 2# = 1 + x, 1 + y, +z; 3# = 3-x, 2-y, -1-z; 4# = 1 + x, 1 + y, 1 + z.

Table 5Summary of the H—S and 2D-fingerprint plots for intermolecular interactions in **Co-PBT**.

Contact	% Contribution	Fingerprint Shape	Interaction type
F...H/ H...F	19.9/16.1	Sharp spikes at short distances	C-H...F weak non-conventional H-bonds. Directional interactions involving CF ₃ groups
F...F	9.4	Broad and diffuse region	Dispersive-repulsive. Close packing of CF ₃ , non-directional
C...H/ H...C	8.8/7.7	Spread regions	C-H... π /C-H...S contacts. Aromatic rings and S atoms as acceptors
H...H	11.3	Broad and directional	Non-directional contacts

[60].

In summary, the Hirshfeld surface analysis highlights the dominant role of weak but directional supramolecular interactions involving both **PBT** and **hfac**[−] ligands in stabilizing the crystal packing. These include C-H...F non-conventional H-bonds, C-H... π and π ... π stacking between pyridine and benzyl, F...F halogen and diffuse H...H contacts, all of which contribute to the observed conformational arrangement of the

ligands outside the first coordination sphere. The rich network of supramolecular interactions plays a crucial role in stabilizing the crystal packing of the **M-PBT** complexes [61,62]. The near coplanarity of the **PBT** ligands and the observed in the -CF₃ **hfac**[−] anions suggest a close packing driven by these intermolecular forces. These non-covalent interactions not only influence the spatial arrangement of the ligands in the outer coordination sphere but also contribute to the overall rigidity of the crystal lattice. This is corroborated by the **M-PBT** thermal stability, with decomposition initiating between 200 and 290 °C and reaching a plateau between 300 and 450 °C (**Fig. S10**). This moderate thermal resilience underscores the structural robustness imparted by the well-organized supramolecular framework [63,64].

3.4. Global reactivity descriptors: Evaluation of electronic reactivity

As previously established, the **MN2O4** inner core in **M-BBT** series complexes show fine features dependent on the identity of the metal cation despite that exhibit isostructural crystal packing. This statement is related to with the inherent metal-ligand bonding characteristics and as consequences with the reactivity and possible applications. In this line, as was previously established, coordination complexes bearing benzothiazole scaffolds have been used for the design of novel bioactive agents [6–11]. Hence, to gather deeper insight into the structural-property relationships within the isostructural **M-PBT** complexes, Global Reactivity Indices (GRIs) from spin-polarized (unrestricted and evaluating α -spin and β -spin contributions) calculations were performed for **M-PBT** series starting from the crystal structures. The GRIs indices describe the electronic reactivity from each spin channel separately and can be useful for systems with unpaired electrons such as **Mn-PBT**, **Fe-PBT**, **Co-PBT**, **Cu-PBT**, while in the closed-shell **Zn-PBT** system the α -spin and β -spin contributions are equal. Additionally, the GRIs descriptors can offer qualitative insights into the drug-like properties, absorption, electronic flexibility and donor-acceptor tendencies of potential bioactive agents serving as complementary tools to discuss further biological responses [65–67].

In this sense, the HOMO-LUMO gap is a fundamental descriptor in molecular chemistry that provides insight into electronic stability and reactivity. In the **M-PBT** complexes (considering the α -spin), the gap values vary significantly depending on the metal center (**Fig. 4** and **Table S7** and **S8**). Therefore, the calculated descriptor suggests that **Fe-PBT**, with the smallest gap (2.500 eV), should be the most electronically reactive species among the series, implying a higher polarizability and propensity to participate in chemical reactions.

Conversely, **Zn-PBT** shows the largest gap (4.438 eV), followed closely by **Co-PBT** and **Cu-PBT** (gaps above ~4.3 eV), reflecting an enhanced electronic stability and possibly a reduced reactivity, with **Mn-PBT** showing an intermediate gap (3.809 eV) across the series. These gap trends correlate well with the known chemical characteristics of the involved cations. In the case of **Fe-PBT**, the lower gap can be related to the stabilization of the **PBT** centered LUMO (**PBT** π^* -orbitals) due to the stronger Fe(II)-pyridine metal-to-ligand charge transfer interaction. Such interactions are weaker in the other **M-PBT** complexes preventing the LUMO stabilization and consequently presenting higher HOMO-LUMO gap.

Meanwhile, the uncoordinated **PBT** ligand exhibits a smaller HOMO-LUMO gap (~1.860 eV) than the **M-PBT** complexes (**Fig. S11**). This narrower gap implies that upon coordination with transition metals, the **PBT** frontier orbitals are stabilized, with HOMO levels becoming deeper and LUMO levels shifting to lower energies. This lowering of orbital energies is associated with the delocalization of **PBT** charge density, resulting in an attenuation of its reactivity upon metal coordination. Therefore, the free **PBT** ligand retains a more reactive electronic profile in terms of frontier orbital accessibility.

On the other hand, the chemical potential μ^a indices evaluate chemical reactivity as the tendency to donate electrons, with less negative values indicating higher nucleophilicity and electronic

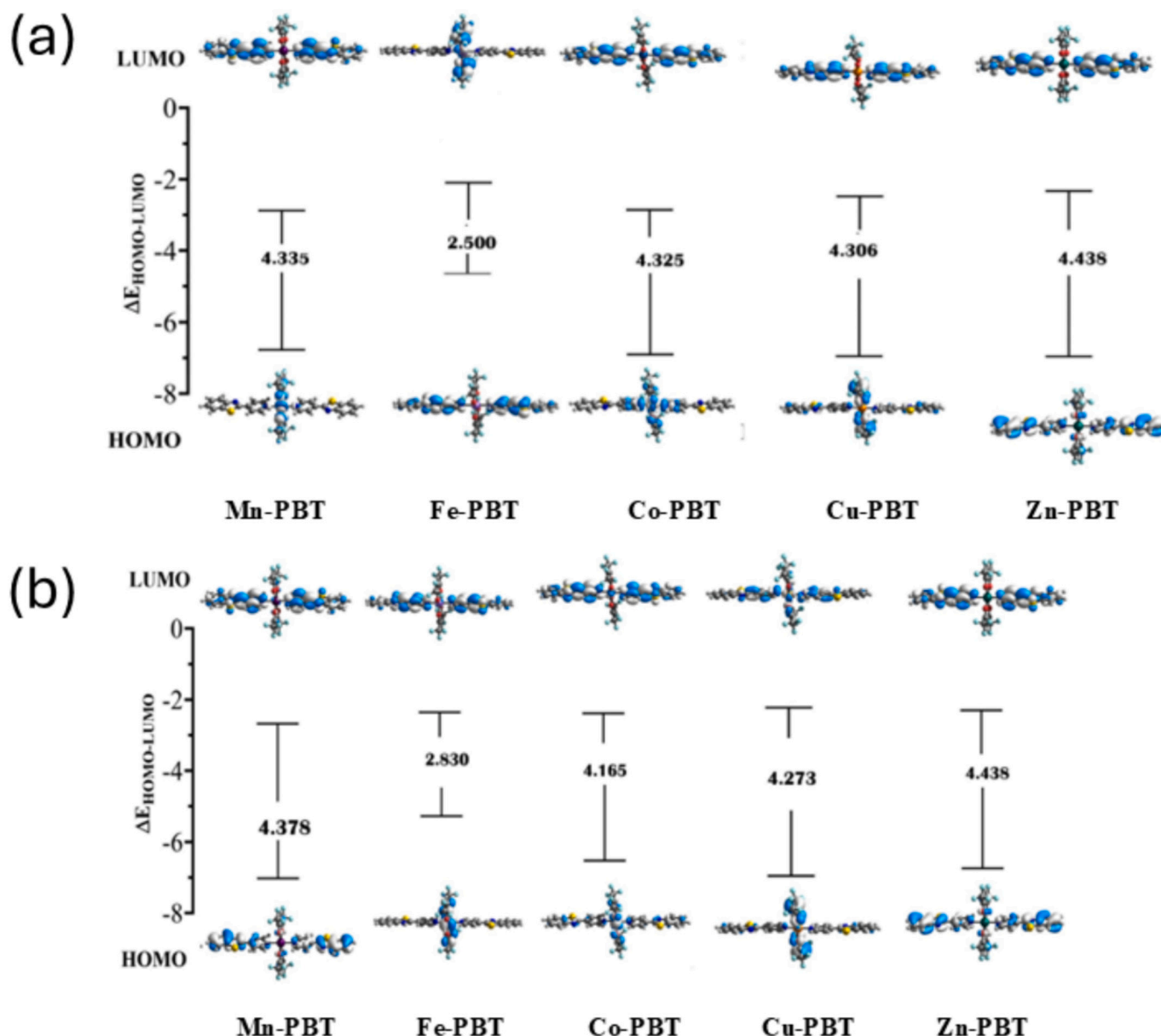


Fig. 4. HOMO and LUMO gaps for the (a) α -Spin and (b) β -Spin Channel of the **M-PBT** compounds.

reactivity. As in the case of HOMO-LUMO gap, the μ^a values vary notably across **M-PBT** series with a clear dependence on the metal cations. In accordance with the HOMO-LUMO gap results, **Fe-PBT** shows the less negative μ^a value (−3.349 eV), suggesting a strong nucleophilic and reactive character. In contrast, **Cu-PBT** and **Zn-PBT** present the most negative μ^a values (−4.957 and −4.913 eV, respectively), indicating greater resistance to electron loss and higher electronic stability, with intermediate behavior for **Co-PBT** (−4.857 eV) and **Mn-PBT** (−4.599 eV).

Moreover, the electrophilicity (ω^a) and nucleophilicity (N) indices are complementary to evaluate the tendency to accept (electrophile character) or donate (nucleophile character) electrons. The ω^a values vary within a narrow range within the series, indicating that all compounds should possess moderate to high electrophilic character. **Cu-PBT** compound showed the highest electrophilicity index (5.706 eV), followed closely by **Mn-PBT** (5.552 eV), **Co-PBT** (5.453 eV) and **Zn-PBT** (5.438 eV), with **Fe-PBT** (4.486 eV) being the least electrophilic of the group. The ω^a values align with the global nucleophilicity index (N) within **M-PBT** series (N was calculated using ferrocene as the reference;

HOMO_{Fc} = −5.10 eV), in which only the **Fe-PBT** exhibited a higher tendency to donate electrons than ferrocene (N = +0.501 eV), i.e., showing the higher nucleophilicity across the series. In contrast, the remaining complexes displayed negative N values (**Mn-PBT**, −1.403 eV; **Co-PBT**, −1.919 eV; **Cu-PBT**, −2.010 eV; **Zn-PBT**, −2.032 eV), suggesting a lower nucleophilicity than ferrocene, i.e., a more electrophilic character.

In summary, the HOMO-LUMO gap and the conceptual DFT descriptors μ^a , ω^a and N indices) provide valuable heuristic trends for comparing the isostructural **M-PBT** series. However, it should be emphasized that the physical interpretation of these parameters in open-shell transition-metal complexes (**Mn-PBT**, **Fe-PBT**, **Co-PBT**, and **Cu-PBT**) can be subtle and dependent on the choice of functional and basis set. Consequently, these calculated values serve as preliminary indicators of reactivity trends within this series rather than as definitive absolute physical constants.

Accordingly, the HOMO-LUMO gap, μ^a , ω^a and N index tendencies across the series highlight the electronic influence of the metal cation on the reactivity and to the nucleophilic or electrophilic character of the

complexes across the **M-PBT** series. Moreover the μ^{α} , ω^{α} and N trends correlate with some of the well-known redox characteristics of the metal centers within **M-PBT** complexes: Fe(II) is more disposed to donate electrons leading to the stable half-full Fe(III)- $3d^5$ configuration. Meanwhile, Zn(II) is more stable in the closed-shell $3d^{10}$ states and therefore much less propense to oxidation, while **Mn-PBT**, **Co-PBT** and **Cu-PBT** exhibit intermediate reactivity profiles. Overall, these results align with the MO_4N_2 coordination geometry analysis performed at structural analysis section. The distortion analysis revealed that **Zn-PBT** exhibits the lowest octahedral distortion parameters (CShM and Δ), indicative of higher symmetry and ligand field stabilization. These geometric features are consistent with relatively high HOMO-LUMO gaps and low reactivity indices, suggesting a direct link between minimized geometric strain and enhanced electronic stability. Conversely, **Fe-PBT** displays pronounced angular and bond length deviations, which coincide with their lower electronic hardness and higher chemical reactivity.

By comparing the α -spin and β -spin contributions among the series (Tables S7 and S8), **Fe-PBT** shows a significantly lower HOMO-LUMO gap (2.50–2.83 eV) compared to the rest of the **M-PBT** complexes (~4.2–4.4 eV). The slight difference between the α and β spin channel gaps suggest a minor spin polarization. This asymmetry in the spin channels is consistent with the electronic complexity of Fe(II) in a field of intermediate ligand strength. In contrast, the other complexes exhibit higher and more balanced electrophilicity indices, suggesting more stable and symmetrical electronic structures. The special characteristics of **Fe-PBT** reveal a greater reactivity in its frontier orbitals and a spread-out spin. Remarkably, **Fe-PBT** is the only complex in the series with a positive N index in the α -spin channel (+0.501 eV), and a positive average value (+0.133 eV), corroborating the tendency to donate electrons (a trait not observed in the other analogues complexes). On the other hand, **Mn-PBT** and **Co-PBT** show similar behavior, with moderate electrophilicity and low nucleophilicity and may serve as electronically inert platforms or controlled acceptor sites under mild redox conditions. Meanwhile, **Cu-PBT** exhibits the highest electrophilicity in the series, coupled with a very small difference between spin channels, indicating a strong electron-acceptor character and a configuration with minimal

spin delocalization, particularly useful in oxidative catalysis or electron-acceptor roles. Finally, as expected for a d^{10} closed-shell system, **Zn-PBT** displays perfectly symmetric electronic descriptors, a high HOMO-LUMO gap, and the lowest nucleophilicity. These traits are indicative of a chemically inert and electronically saturated system, which may serve as a non-reactive control or structural mimic in biological and coordination chemistry studies.

Lastly, spin density calculations provide essential insight into the electronic structure of paramagnetic species by mapping the spatial distribution of unpaired electrons within a molecule. This information is critical for quantifying the degree of spin delocalization from a metal center to the ligands. As expected for a closed-shell molecule, the isolated **PBT** ligand exhibits negligible spin density, consistent with a diamagnetic ground state with no significant participation in triplet excited states. However, upon coordination with the metal centers, the spin density maps for the **M-PBT** complexes reveal that the metal-ligand interactions induce significant spin delocalization onto the π -orbital of the **PBT** ligand. This electronic redistribution allows the **PBT** moiety to actively participate in propagating spin, a key feature for facilitating electron transfer processes.

Overall, the spin density mapping reveals varying degrees of delocalization across the metal centers and the **PBT** and hfac^- ligands, a trend that is dependent on the identity of the metal ion (Fig. 5) and consistent with GRI calculations. A detailed analysis of the **M-PBT** series reveals significant differences in the distribution of unpaired electrons. In **Mn-PBT** and **Co-PBT**, the spin density is predominantly localized on the respective metal ions. Only slight delocalization onto the coordinating atoms of the axial **PBT** and equatorial hfac^- ligands is observed, suggesting limited ligand participation in the magnetic orbitals.

Meanwhile, the **Cu-PBT** complex displays a more specific delocalization pattern, with a spin density more confined to the Cu(II) center and the immediate pyridine ring of the axial **PBT** ligand, with less delocalization onto the equatorial hfac^- ligands. This suggests a specific orbital pathway for delocalization, likely through the σ - and π -orbitals involving the pyridinic nitrogen.

In contrast, **Fe-PBT** exhibits extensive spin delocalization that spreads across the entire **PBT** ligand structure and, to a lesser extent,

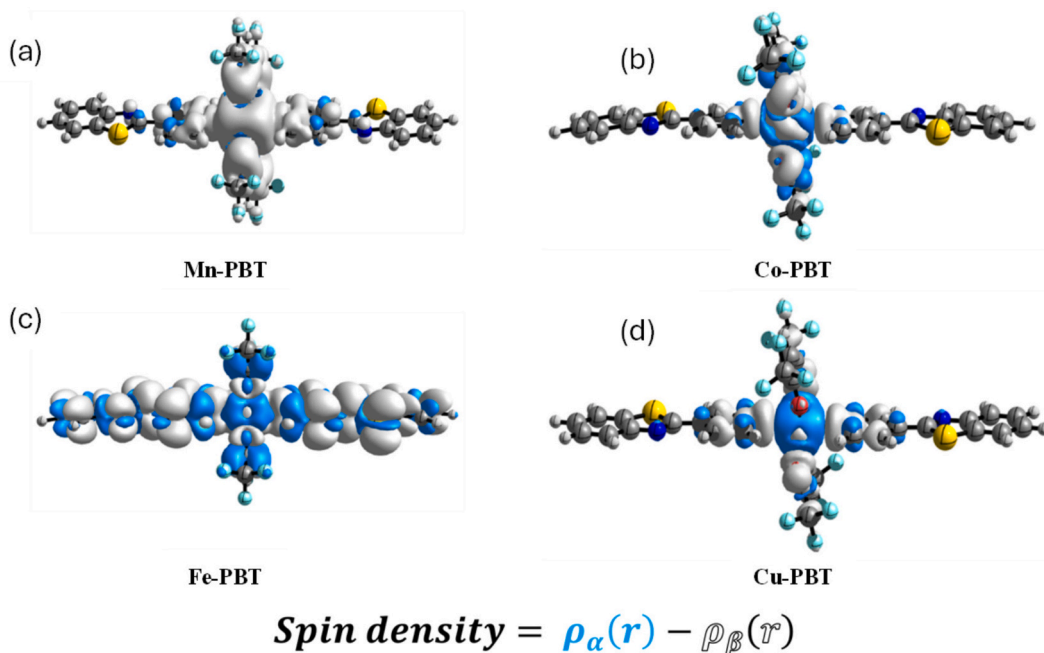


Fig. 5. Spin density distribution plots of (a) **Mn-PBT**, (b) **Co-PBT**, (c) **Fe-PBT** and (d) **Cu-PBT**. Spin density is calculated as the difference between the density of electrons with spin-up (“alpha”; α) and spin-down (“beta”; β) orbitals (Isovalue = 0.0003). Blue lobes represent positive spin density (α -spin), while white lobes correspond to negative spin density (β -spin).

onto the hfac^- ligands. This indicates strong orbital mixing between the Fe(II) d -orbitals and the **PBT** π -orbitals, leading to enhanced stabilization of the unpaired electrons via π -conjugation, a feature also revealed by the GRI calculations.

The distinct patterns of metal-ligand spin delocalization across the **M-PBT** series have important chemical and biological implications. The extensive delocalization observed in **Fe-PBT** is particularly noteworthy, implying the formation of a ligand-based radical character and significantly influencing the redox reactivity. From a bioinorganic perspective, this pronounced delocalization onto the **PBT** ligand in **Fe-PBT** could enhance its ability to interact with biological targets. For instance, the increased π -character and distributed spin could facilitate non-covalent π -stacking interactions with aromatic or electron-rich residues, thereby dictating potential biological application [65–67].

3.5. Interaction of M-PBT complexes on biological systems

Structural analysis of the **M-PBT** confirmed a non-covalent supported crystalline packing within the coordination complexes. This packing is defined by key supramolecular interactions, including C–H...F hydrogen bonds, F...F contacts, and C–H... π interactions, acting between **PBT** and hfac^- ligand fragments. The presence of these diverse contacts suggests that the **M-PBT** compounds are well-suited to form potential intermolecular interactions with a variety of substrates. Additionally, theoretical calculations provided further insight into the electronic reactivity across the **M-PBT** series, revealing clear metal-dependent trends. In particular, **Fe-PBT** was predicted to be the most nucleophilic and electronically reactive complex, with an extensive spin delocalization over the entire **PBT** ligand. Taken together, these findings highlight the **M-PBT** series as a platform for further studies with more complex systems, such as those involved in biochemical process, due to their potential supramolecular richness and the possibility of metal-dependent structure-property relationships [68–70].

In this context, to evaluate the interaction of **M-PBT** complexes with a specific biological system, the bacterium *Pseudomonas syringae* and the plant *Arabidopsis thaliana* were taken as model organisms. The *Pseudomonas* genus, which includes several ecologically and agriculturally relevant species such as *Pseudomonas fluorescens*, known for its plant growth-promoting traits, and *Pseudomonas aeruginosa*, a well-studied opportunistic human pathogen [71,72]. The genus is characterized by its remarkable metabolic versatility and capacity to thrive in diverse environments, making it a valuable model for studying microbial ecology and compound interactions. Moreover, effective control of these bacteria is crucial for both agricultural protection and public health. In our study, *Pseudomonas syringae* was cultured in media supplemented with each **M-PBT** complex to evaluate potential effects on bacterial

proliferation on culture conditions.

Fig. 6a and kinetics parameters were obtained and analyzed (Fig. 6b and S12a–d). The biologically relevant parameters from sigmoidal growth curves were extracted, including growth rate (maximum exponential increase, h^{-1}), doubling time (time required for cell population to double), number of doublings (overall population increase), doublings in log-phase (specific to exponential growth), and final yield (maximum OD_{600} reached). These parameters were used to quantify bacterial responses to each compound.

Bacterial growth was monitored over 24 h using optical density at 600 nm (OD_{600}).

All conditions displayed a sigmoidal growth pattern (Fig. 6a), with some differences across treatments. Most treatments display a similar pattern compared to the bacterial growth without any compound. However, cultures treated with the uncoordinated **PBT** ligand and the **Fe-PBT** complex exhibited increased growth rates ($p < 0.05$ and $p < 0.01$, respectively), as well as higher final yields compared to the control (Fig. 6b). In the case of **Fe-PBT**, this was accompanied by a significant reduction in doubling time, indicating a more efficient proliferation rate (Fig. S12a). Although **PBT** also showed a trend toward reduced doubling time, the difference was not statistically significant (Fig. S12a; $p = 0.123$). Interestingly, the fact that the uncoordinated **PBT** ligand alone also induced a moderate (though not statistically significant), increase in growth suggests that this scaffold possesses inherent bioactivity in *Pseudomonas syringae*. This is consistent with previous findings in *Pseudomonas putida*, which has been shown to metabolize benzothiazole derivatives, using them as carbon sources and degrading the aromatic ring structure [73]. Such metabolic capabilities are characteristic of the genus *Pseudomonas*, which is known for its remarkable adaptability to metabolic capacities [74]. Therefore, the stronger effect observed for **Fe-PBT** could result from an additive or even synergistic interaction between the bioactivity of the **PBT** ligand and the metabolic enhancement provided by iron [75]. Such synergy might arise from the combination of improved metal delivery and ligand-derived physiological modulation, leading to a more pronounced growth-promoting effect than either component alone. The other **M-PBT** complexes did not provoke statistically significant differences in any of the evaluated parameters (Fig. S12a–d). This result suggests either limited uptake or bioavailability of these metals, or a neutralizing effect due to stress responses that maintain physiological homeostasis. Notably, copper complexes are frequently associated with antimicrobial activity, yet **Cu-PBT** did not inhibit bacterial proliferation in this system, possibly due to low solubility, instability, or inefficient cellular entry.

In addition to assessing the impact of **M-PBT** complexes on bacterium development, the influence on the plant *Arabidopsis thaliana* was also performed. Seedlings of *Arabidopsis thaliana* were grown for 14 days

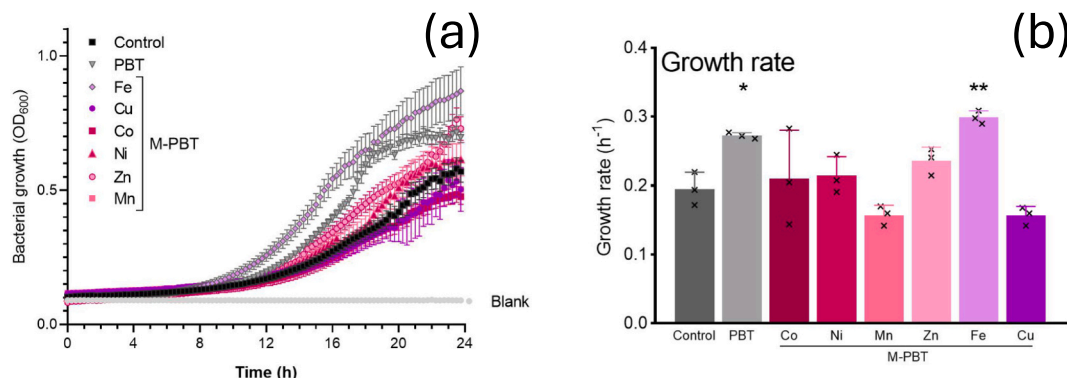


Fig. 6. Effect of **M-PBT** complexes on *Pseudomonas syringae* growth kinetics. (a) Bacterial growth curves over 24 h, measured as OD_{600} , in cultures treated with the uncoordinated ligand **PBT** or **M-PBT** complexes ($10 \mu\text{g mL}^{-1}$). Each point represents the mean $\pm$ SE of three biological replicates. Control = *P. syringae* + DMSO; Blank = medium only (no bacteria). (b) Growth rate (h^{-1}) parameter extracted from sigmoidal curve fitting. Bar plots show mean $\pm$ SD, with individual replicate values indicated ($\times$). Statistical comparisons were performed using one-way ANOVA followed by Dunnett's multiple comparisons test against the control condition (Pst). *: $p < 0.05$; **: $p < 0.01$.

on media supplemented with **M-PBT** compounds at two different concentrations. (1 and 10 $\mu\text{g mL}^{-1}$). Growth parameters including leaf area and fresh biomass were quantified.

Most **M-PBT** treatments significantly reduced seedling biomass at higher concentration (10 $\mu\text{g mL}^{-1}$; Fig. 7), with **Cu-PBT** and **Fe-PBT** producing the most pronounced inhibitory effects, followed by **Zn-PBT** and **Mn-PBT**. At 1 $\mu\text{g mL}^{-1}$, some complexes, such as **Ni-PBT**, showed no significant reduction and even a non-significant trend toward stimulation. **Co-PBT** produced moderate effects at both concentrations, while **Mn-PBT** showed a more marked effect only at the higher dose.

While seedlings treated with the uncoordinated **PBT** or **Na(hfac)** ligands displayed moderate growth reductions, the enhanced inhibitory effects observed with **M-PBT** treatments suggest a specific role of the metal coordination in modulating biological activity.

Interestingly, the uncoordinated **PBT** ligand caused substantial biomass reduction at 10 $\mu\text{g mL}^{-1}$. Nevertheless, the effect was less enhanced when **M-PBT** complexes are supplemented, indicating that metal coordination could prevent phytotoxicity [76]. Previous studies have demonstrated that 2-substituted benzothiazole derivatives can act

as plant growth regulators with both stimulatory and inhibitory effects depending on structure and concentration [77]. In our study, however, all **M-PBT** complexes showed growth-inhibitory effects, suggesting that metal coordination significantly modifies the bioactivity profile.

The observed inhibition may be linked to increased uptake, altered redox properties, or interference with key developmental pathways due to the presence of the metal cation. The stronger effects observed for **Fe-PBT**, **Zn-PBT** and **Co-PBT** could reflect differences in stability, reactivity, or intracellular interactions of the cation-ligand assembly, and are in agreement with known biological roles and toxicities of transition metals in plants [78].

Together, the effect of **M-PBT** complexes on the bacterium *Pseudomonas syringae* shows that the series of **M-PBT** complexes are metal-specific and not uniformly inhibitory or stimulatory. The fact that only **Fe-PBT** and, to a lesser extent, **PBT** enhanced bacterial proliferation emphasizes that metal identity plays a central role in modulating the biological effects of these complexes. On the other hand, **M-PBT** complexes act as bioactive agents over *Arabidopsis thaliana*, whose effects on plant growth are concentration dependent and more important, on the

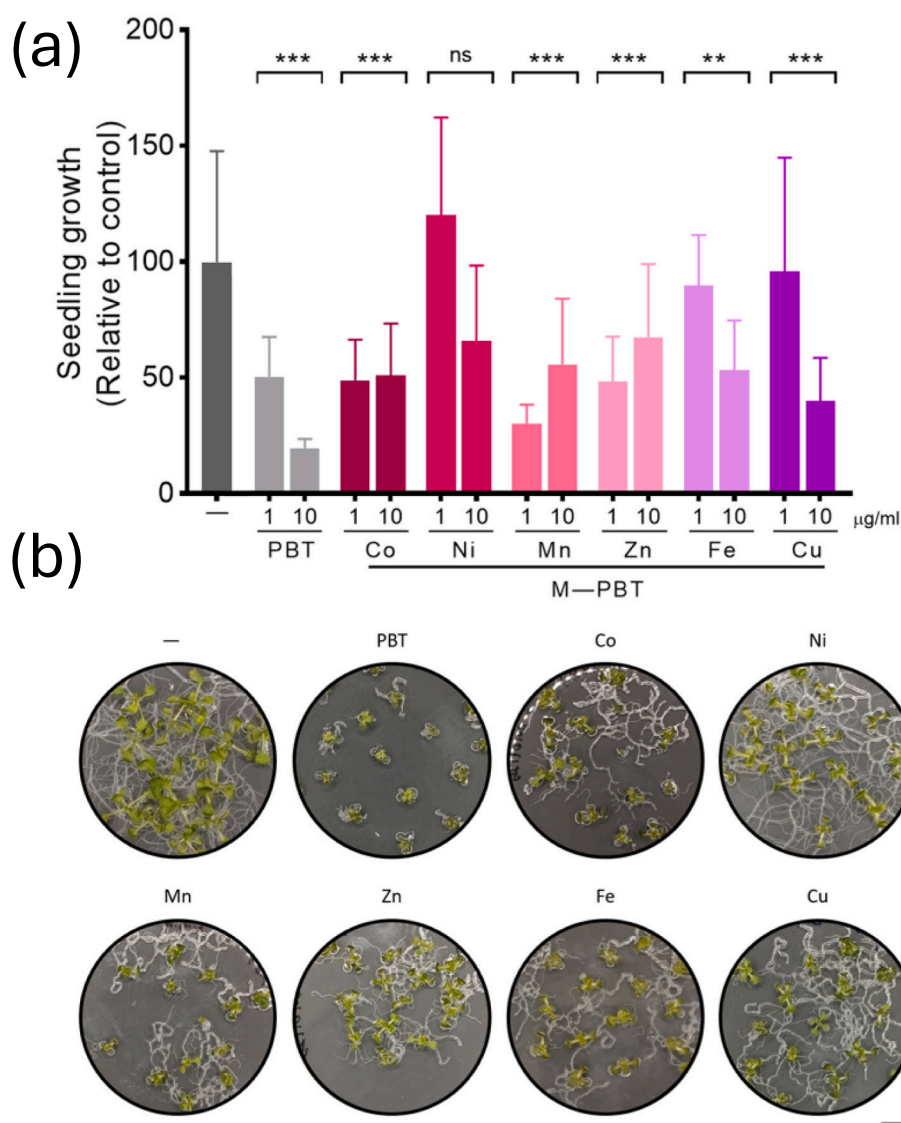


Fig. 7. Effect of **M-PBT** complexes on *Arabidopsis thaliana* seedling growth. (a) Quantification of fresh biomass after 14 days of growth in media supplemented with the uncoordinated ligand (**PBT**) or metal-benzothiazole complexes (**M-PBT**) at 1 and 10 $\mu\text{g mL}^{-1}$. Data are presented as mean $\pm$ SD ($n \geq 14$ individual seedlings per condition). Statistical significance was determined using two-way ANOVA followed by Tukey's post hoc test, comparing each treatment to the control (DMSO); ** $p < 0.01$; *** $p < 0.001$. (b) Representative images of seedlings grown on media containing each compound at 10 $\mu\text{g mL}^{-1}$, except for **Ni-PBT**, which was used at 5 $\mu\text{g mL}^{-1}$. Scale bar: 1 cm.

nature of the coordinated cation as in the case of *Pseudomonas syringae*. In the bioactivity of **M-PBT** complexes against *Arabidopsis thaliana*, rather than uniformly enhancing phytotoxicity, cation coordination appears to diversify the biological outcomes of the pyridine-benzothiazole scaffold, highlighting the relevance of cation identity in modulating plant responses.

Within the limitations of our computational model, some tendencies in the reactivity indexes can be related to the bioactivity of the **M-PBT** series. The higher nucleophilicity and electronic reactivity predicted for **Fe-PBT** align with the effect of *Arabidopsis* biomass inhibition and *Pseudomonas syringae* proliferation. This dual bioactivity may be associated with the electronic ability of **Fe-PBT** to interact with redox-active biomolecules, modulating electron transfer pathways, or promoting uptake via iron-regulated transport systems. Additionally, the observed high spin delocalization of Fe(II) in the complex could likely enhance its biochemical reactivity. Meanwhile, **Cu-PBT** also exhibited notable plant growth inhibition at high concentrations. However, this compound showed no significant effect on bacterial growth, suggesting a context-dependent bioavailability or limited uptake under the experimental conditions. Lastly, despite its electronic inertness, **Zn-PBT** still produced moderate effects on plant growth, possibly reflecting structural rather than electronic contributions to bioactivity, e.g. membrane accumulation or steric interactions with biological components.

It is important to emphasize that the biological systems assessed in this study, *Arabidopsis thaliana* and *Pseudomonas syringae*, are intrinsically distinct, differing in cellular organization and structure and metabolic functions. As such, the bioactivity of **M-PBT** complexes likely reflects not only their electronic or structural properties, but also organism-specific factors such as membrane permeability, redox environment, and transport or detoxification pathways. In particular, the observed bacterial responses are specific to *P. syringae*, a plant-associated bacterium with well-characterized metabolic plasticity. Responses to **M-PBT** compounds may vary considerably across bacterial genera or species, especially those with alternative iron acquisition strategies or limited capacity to metabolize xenobiotic compounds. Therefore, caution is warranted when extrapolating these findings beyond the *Pseudomonas* genus or to other biological systems.

4. Conclusions

In this study, we have synthesized and structurally characterized a family of isostructural transition metal complexes, $[M(PBT)_2(hfac)_2]$, combining the pyridine-benzothiazole **PBT** ligand with the fluorinated β -diketonate $hfac^-$. Single-crystal X-ray diffraction confirms a *trans*-octahedral geometry across the series, with structural distortion parameters revealing subtle but specific variations based on metal identity. A comprehensive analysis of the supramolecular landscape through Hirshfeld surfaces and fingerprint plots shows that directional interactions such as C-H...F hydrogen bonds, F...F halogen contacts, and π - π stacking play a crucial role in stabilizing the solid-state architecture.

From a theoretical perspective, the calculated reactivity indices identify **Fe-PBT** as a potentially highly reactive and nucleophilic complex within the **M-PBT** series, with significant spin delocalization and a narrow HOMO-LUMO gap. In contrast, **Cu-PBT** and **Zn-PBT** showed greater electronic stability and lower reactivity. These findings serve as heuristic data to understand the metal-dependent biological responses observed across the series and underline potential applications of **M-PBT** complexes in redox and supramolecular research.

Biological studies further highlight the functional versatility of the **M-PBT** family. All complexes exhibit robust thermal stability, while plant and bacterial assays reveal bioactivity, particularly for **Fe-PBT**. These findings demonstrate the value of strategic ligand and metal selection for modulating both solid-state and biological properties in coordination compounds. Accordingly, this work contributes to the rational design of functional metal-organic materials with potential applications in supramolecular chemistry and bioinorganics.

CRediT authorship contribution statement

Luciano Salas: Methodology, Data curation. **Benjamín Villalobos:** Methodology, Formal analysis, Data curation. **Plinio Cantero-López:** Writing – review & editing, Writing – original draft, Validation, Methodology, Formal analysis, Data curation. **Ariel Herrera-Vásquez:** Writing – review & editing, Writing – original draft, Validation, Resources, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Verónica Paredes-García:** Writing – review & editing, Validation, Supervision, Resources, Funding acquisition. **Carlos Cruz:** Writing – review & editing, Writing – original draft, Validation, Resources, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Carlos Cruz reports financial support was provided by Andrés Bello University. Carlos Cruz reports a relationship with Andrés Bello University that includes: employment. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.poly.2026.117980>.

Data availability

Data will be made available on request.

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