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Synthesis and characterization of binuclear manganese(IV,IV) and mononuclear cobalt(II) complexes based on 2-(2-hydroxyphenyl)-1H-benzimidazole

Ming-Yue Duan^a; Jun Li^a; Yun Xi^a; Xiang-Fei Lü^a; Jing-Zhou Liu^a; Giuseppe Mele^b; Feng-Xing Zhang^a

^a Department of Chemistry, Key Laboratory of Synthetic and Natural Functional Molecule Chemistry of Ministry of Education, Northwest University, Shaanxi 710069, P.R. China ^b Dipartimento di Ingegneria dell'Innovazione, Università del Salento, 73100 Lecce, Italy

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Synthesis and characterization of binuclear manganese(IV,IV) and mononuclear cobalt(II) complexes based on 2-(2-hydroxyphenyl)-1H-benzimidazole

MING-YUE DUAN[†], JUN LI^{*†}, YUN XI[†], XIANG-FEI LÜ[†], JING-ZHOU LIU[†], GIUSEPPE MELE[‡] and FENG-XING ZHANG[†]

[†]Department of Chemistry, Key Laboratory of Synthetic and Natural Functional Molecule Chemistry of Ministry of Education, Northwest University, Xian, Shaanxi 710069, P.R. China

[‡]Dipartimento di Ingegneria dell'Innovazione, Università del Salento, Via Arnesano 73100 Lecce, Italy

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The bidentate benzimidazolic hpbm (**1**), [2-(2-hydroxyphenyl)-1H-benzimidazole], was obtained under mild conditions, and its corresponding metal complexes, di- μ -oxo dimanganese(IV,IV) [Mn₂O₂(hpbm)₄·2Py·5H₂O] (**2**), and mononuclear complex [Co(hpbm)₂] (**3**), were prepared and characterized. The crystal structures of **2** and **3** have been established by X-ray diffraction. Complex **2** consists of two six-coordinate manganese(IV) coordinated to two hpbm ligands and bridged by two O²⁻ with a Mn–Mn distance of 2.777 Å. For **3**, a Co(II) is coordinated to two deprotonated hpbm in a nearly tetrahedral environment. Hydrogen bonds play pivotal roles in constructing the dimensional structures of both the compounds.

Keywords: 2-(2-Hydroxyphenyl)-1H-benzimidazole; Di- μ -oxo dimanganese(IV,IV) complex; Cobalt(II) complex; Crystal structure

1. Introduction

Metal complexes containing imidazole-based ligands have rich coordination chemistry and a number of established applications [1–4]. The 2-(2-hydroxyphenyl)benzimidazole (hpbm) is an *N,O*-bidentate ligand with two donor groups of relevance to metal centers in biological systems, phenolate (tyrosine), and imidazole (histidine). Hpbm has been studied theoretically as laser dyes and fluorescent probes [5, 6], but its metal complexes are limited, especially crystal structures [5, 7, 8].

We obtained trinuclear Ni(II) and mononuclear Cu(II) complexes with hpbm [9, 10] and a mononuclear Mn(III) complex with 2-(5-bromine-2-hydroxyphenyl) benzimidazole (Br-hpbm) [11]. Hpbm exhibited variable coordination with Ni(II), Cu(II), and Mn(III). Continuing, we report here the structures of mononuclear Co(II) and dinuclear Mn(IV,IV) complexes.

*Corresponding author. Email: junli@nwu.edu.cn

2. Experimental

2.1. Material and physical measurements

The following commercially available chemicals were of analytical grade and used without purification: $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{Co}(\text{OAc})_2 \cdot 6\text{H}_2\text{O}$, NaOH , $\text{CH}_3\text{CH}_2\text{OH}$, pyridine, salicylic acid, and *o*-phenylenediamine. Elemental analysis was performed on a Vario EL-III CHNOS instrument. FT-IR spectra were recorded using KBr from 4000 to 400 cm^{-1} employing a BEQ UZNDX-550.

2.2. Synthesis of 2-(2-hydroxyphenyl)benzimidazole (hpbm) (1)

Hpbm was synthesized in correspondingly high yield by one-step condensation of *o*-phenylenediamine (2.05 g, 19 mmol in 25 mL EtOH) with salicylaldehyde (2.32 g, 19 mmol in 15 mL EtOH) at 80°C under stirring without using any catalyst. The resulting orange solution was refluxed for 2 h and then cooled to room temperature. After 12 h of refrigeration (-4°C), the orange solution was filtered and 15 mL ethyl ether was added. Needle-shaped orange crystals appeared after 2 days in the open air and were filtered, washed with ethanol, and recrystallized from methanol. Yield 65%. m.p. = $240\text{--}241^\circ\text{C}$. IR spectrum (KBr; cm^{-1}): 1593[$\nu(\text{C}=\text{C})$], 1488[$\nu(\text{C}=\text{N})$], 1265[$\nu(\text{C}-\text{O})$], 2800–2500[H bond]. Anal. Calcd for $\text{C}_{13}\text{H}_{10}\text{N}_2\text{O}$ (%): C, 74.29; H, 4.76; N, 13.33. Found (%): C, 74.27; H, 4.59; N, 13.18.

2.3. Synthesis of $[\text{Mn}_2\text{O}_2(\text{hpbm})_4 \cdot 2\text{Py} \cdot 5\text{H}_2\text{O}]$ (2)

Hpbm (0.210 g, 1 mmol) and NaOH (0.04 g, 1 mmol) were dissolved in 10 mL methanol and then a solution of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (0.1 g, 0.5 mmol) in methanol was added slowly under stirring. After 1 h brown precipitate was obtained by filtration, presumed to be $\text{Mn}(\text{III})[(\text{hpbm})_2\text{Cl}]\text{CH}_3\text{OH}$ according to the elemental analysis. The brownish solid was dissolved in pyridine and black crystals were formed through ethyl ether vapor diffusion after 20 days, during which air oxidized the Mn^{3+} and formed a rare oxo-bridged binuclear $\text{Mn}(\text{IV})$ complex. This reaction indicates that $\text{Mn}(\text{II})$ or $\text{Mn}(\text{III})$ can be easily oxidized to $\text{Mn}(\text{IV})$ in air when coordinated by hpbm. Yield 15%. IR spectrum (KBr; cm^{-1}): 1621[$\nu(\text{C}=\text{N})$], 1260[$\nu(\text{C}-\text{O})$], 635[$\nu(\text{Mn}-\text{O}-\text{Mn})$]. Anal. Calcd for $\text{C}_{62}\text{H}_{56}\text{N}_{10}\text{Mn}_2\text{O}_{11}$ (%): C, 57.77; H, 7.86; N, 10.82. Found (%): C, 57.81; H, 7.59; N, 11.01.

2.4. Synthesis of $[\text{Co}(\text{hpbm})_2]$ (3)

A solution of $\text{Co}(\text{OAc})_2 \cdot 6\text{H}_2\text{O}$ (0.5 mmol) in water was added to the solution of hpbm in ethanol. After the pH was adjusted to 6–7, the mixture was transferred into a 25 mL PTFE pot after 1 h reaction under stirring. Dark purple crystals were obtained after 4 days of heating at 160°C under hydrothermal condition with cooling at 10°C h^{-1} to room temperature. Yield 63%. IR spectrum (KBr; cm^{-1}): 3093[$\nu(\text{N}-\text{H}, \text{O}-\text{H})$], 1603[$\nu(\text{C}=\text{C})$], 1528[$\nu(\text{C}=\text{N})$], 1249[$\nu(\text{C}-\text{O})$]. Anal. Calcd for $\text{C}_{26}\text{H}_{18}\text{N}_4\text{O}_2\text{Co}$ (%): C, 65.41; H, 3.77; N, 11.7. Found (%): C, 65.11; H, 3.95; N, 11.94.

2.5. X-ray crystallography

The single crystals of **2** and **3** of suitable size were mounted in a SMART APEX CCD diffractometer equipped with Mo-K α radiation. Absorption corrections were applied using SADABS [12]. The structures were solved by direct methods and refined by full-matrix least-squares using SHELXS-97 [13]. Organic hydrogens were generated in ideal positions. Anisotropic thermal parameters were applied to all non-hydrogen atoms. Crystallographic parameters and basic information pertaining to data collection and structure refinement for **2** and **3** are summarized in table 1. Selected bond distances and angles are given in table 2.

3. Results and discussion

3.1. Synthesis

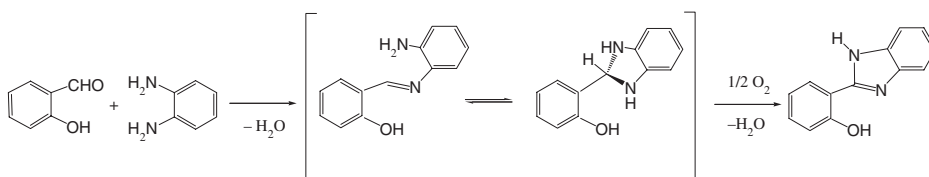
Traditionally, 2-(2-hydroxyphenyl) benzimidazole (hpbm) is prepared from salicylic acid and *o*-phenylenediamine in concentrated polyphosphoric acid at 190–210°C in low yield [14]. Takashi *et al.* [15] have obtained it via photolysis of [N,N'-*o*-phenylenebis-(salicylideneaminato)] diaquamanganese(III) with a 40% yield, however under harsh conditions. Later Yuka *et al.* [16] synthesized it with stirring at 120°C in the presence of activated carbon in xylene. Kiumars *et al.* [17] employed ceric ammonium nitrate as catalyst in the presence of H₂O₂ for the preparation of hpbm and a series of 2-substituted benzimidazole at 50°C with short reaction times and excellent yields (above 90%), by far the most efficient method for the synthesis

Table 1. Crystal data and structure refinement details for **2** and **3**.

	2	3
Empirical formula	C ₆₂ H ₅₆ N ₁₀ Mn ₂ O ₁₁	C ₂₆ H ₁₈ N ₄ O ₂ Co
Formula weight	1227.05	477.37
Temperature (K)	298(2)	273(2)
Color	Black	Dark purple
Crystal system	Orthorhombic	Monoclinic
Space group	<i>Pbcn</i>	<i>P2(1)/n</i>
Unit cell dimensions (Å, °)		
<i>a</i>	16.520(2)	10.1905(19)
<i>b</i>	14.162(2)	10.0322(9)
<i>c</i>	24.043(4)	21.3639(18)
β	90	94.3700(10)
Volume (Å ³), <i>Z</i>	5625.2(14), 4	2177.7(3), 4
Calculated density (g cm ⁻³)	1.449	1.456
<i>F</i> (000)	2544	980
Crystal size (mm ³)	0.22 × 0.16 × 0.11	0.22 × 0.13 × 0.11
θ range for data collection (°)	1.69–25.35	1.91–28.26
Reflections collected	27,869	13,387
Independent reflections	5142	5270
Data completeness	1.0000	0.976
Data/restraints/parameters	5142/5/413	5270/0/304
<i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)]	0.0426	0.0322
<i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0984	0.0891
Goodness-of-fit on <i>F</i> ²	0.852	1.108

Table 2. Selected bond lengths (Å) and angles (°) of **2** and **3**.

2			
Mn(1)–O(1)	1.811(2)	Mn(1)–O(3)	1.943(2)
Mn(1)–N(3)	1.990(2)	Mn(1)–Mn(2)	2.7772(9)
O(1)–Mn(1)–O(1)#1	80.11(11)	O(1)#1–Mn(2)–O(1)	79.92(11)
O(1)–Mn(1)–O(3)	173.11(8)	O(1)#1–Mn(2)–O(2)#1	172.39(8)
O(1)#1–Mn(1)–O(3)	94.21(8)	O(1)–Mn(2)–O(2)#1	93.66(8)
O(1)–Mn(1)–O(3)#1	94.21(8)	Mn(1)–O(1)–Mn(2)	99.98(47)
3			
Co(1)–O(1)	1.9154(12)	Co(1)–O(2)	1.9190(12)
Co(1)–N(3)	1.9637(13)	Co(1)–N(1)	1.9677(13)
O(1)–Co(1)–O(2)	114.09(6)	O(1)–Co(1)–N(3)	112.40(5)
O(2)–Co(1)–N(3)	94.12(5)	O(1)–Co(1)–N(1)	94.52(5)

Symmetry code #1: $-x, y, -z + 1/2$.Scheme 1. A possible mechanism forming 2-(2-hydroxyphenyl) benzimidazole (**1**).

of benzimidazole derivatives. The main advantage of our method is that it is environmentally benign without any catalyst or other reagent. Schiff bases are prepared by the condensation of aromatic carboxaldehydes with polyamines. However, closed-ring production may occur under conditions of proper molar ratio, reaction temperature, and solvent. The possible reaction mechanism (scheme 1) may be an intramolecular nucleophilic attack resulting in unsaturated heterocyclic rings and then the corresponding closed-ring product with the participation of oxygen in the reaction. Therefore, it is an environmentally friendly, simple, and relatively high-yielding method to synthesize hpbm [5, 7].

We found that single crystals of transition metal complexes are difficult to obtain due to their insolubility in organic solvent. Fortunately, X-ray-quality crystals of two neutral molecules, **2** and **3** were obtained using solvent diffusion and hydrothermal methods, respectively.

3.2. Crystal structures of **2**

Compound **2** consists of two six-coordinate manganese(IV) bridged by two O^{2-} ; the Mn_2O_2 bridging unit is planar (figure 1). Each manganese is additionally ligated to two hpbm through one nitrogen on the imidazole ring and one oxygen of the deprotonated phenol. Although d^3 is not subject to Jahn–Teller distortion, the Mn(IV) ions are in a distorted octahedral environment, probably because of steric crowding around manganese centers. The Mn–Mn distance is 2.777 Å in the range of Mn–Mn bonds (2.625–2.780 Å) observed for other structurally characterized complexes with a Mn_2O_2 unit [18–20]. The planar hpbm is strongly twisted when coordinated with dihedral angles of 16.60 and 19.96°, respectively, between the benzimidazole ring

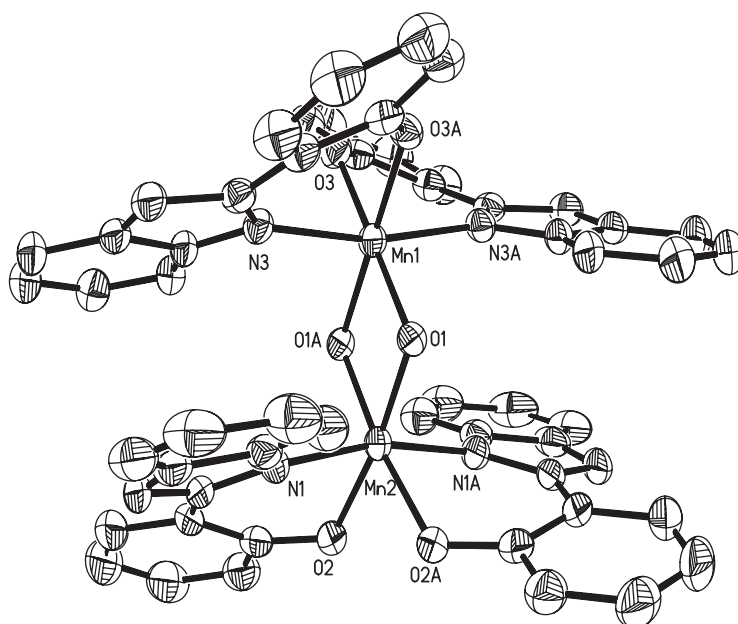


Figure 1. The crystal structure of **2**. H atoms of C–H are omitted for clarity.

and phenol ring. This twisting is largely due to the octahedral environment and formation of six-member rings.

The overall structure is highly solvated with two pyridines as well as five water molecules, four around the fifth in the center, forming a distorted tetrahedron (figure 2). Four hydrogen bonds in the structure are: (1) the nitrogen of two pyridines accept protons of two water molecules to form O–H...N hydrogen bonds (N–O distance is 2.831 Å); (2) O–H...O hydrogen bonds between four H₂O molecules and the fifth one in the center (O–O distances are 2.969 and 2.905 Å); (3) four H₂O molecules at the vertices donate protons to oxygen in ligands of neighboring molecules (O–O distances are 2.837 and 2.799 Å, respectively); (4) four H₂O molecules at the vertices accept protons of uncoordinated –NH– in ligands of neighboring molecules (N–O distances are 2.846 and 2.814 Å, respectively). The latter three hydrogen bonds form an infinite arrangement with water playing a vital role in constructing a 2-D structure (figure 3). The Mn together with the fifth water in the center are on the two-fold axes of space group *Pbcn*. Packing along the two-fold axes is well organized giving room for the H-bonding between the ligand oxygens and water. The numbers and orientations of interaction sites, counteranions, and solvents, and the hydrogen bonds are the main factors holding the subunits together [21].

3.3. Crystal structures of **3**

Compound **3** (figure 3) involves a Co(II) coordinated to two deprotonated hpbm's, through oxygen and nitrogen from phenol and imidazole in a slightly twisted tetrahedron with dihedral angles between the plane defined by N(1)–Co(1)–O(1) and

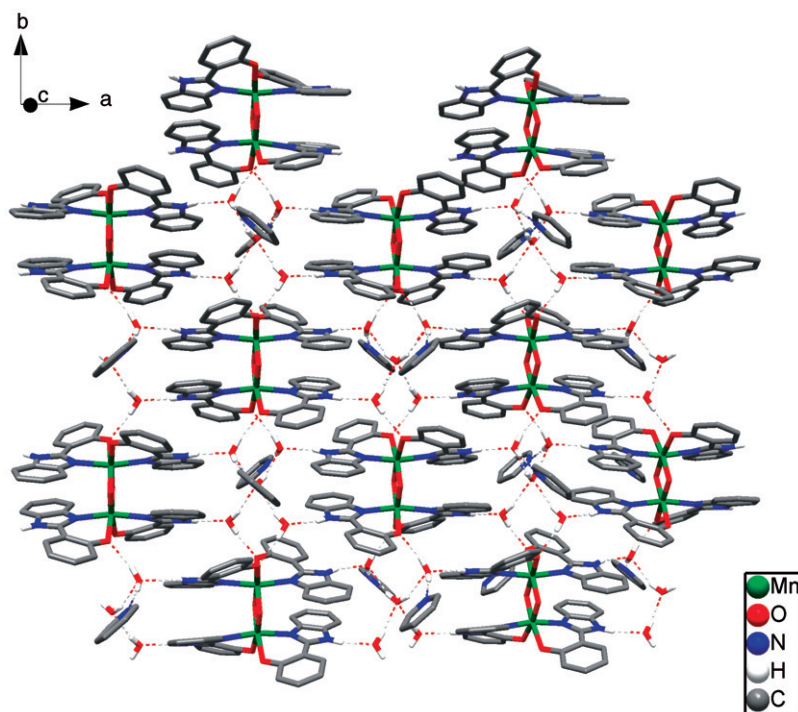


Figure 2. 2-D arrangement of 2 via H-bonds. Hydrogens of C–H are omitted for clarity.

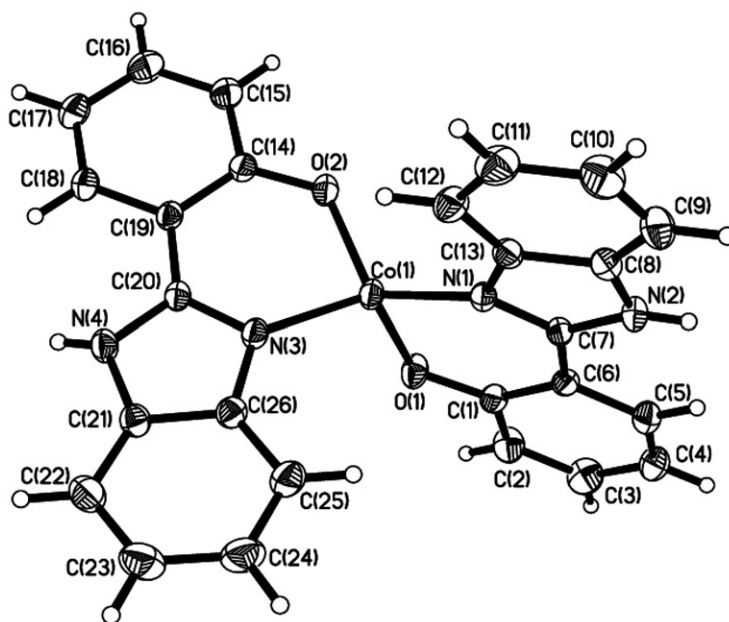


Figure 3. ORTEP diagram of 3.

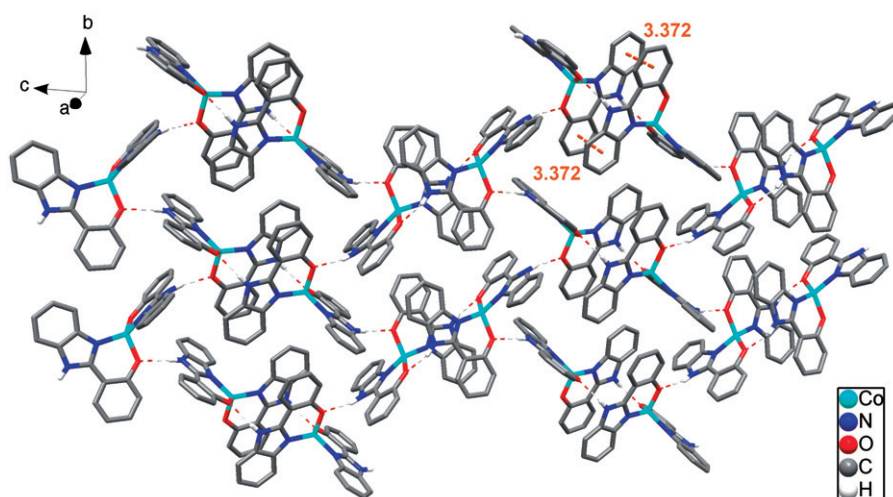


Figure 4. 2-D arrangement of **3** as a result of intermolecular N–H...O bonds and π – π stacking. Hydrogens of C–H are omitted for clarity.

N(3)–Co(1)–O(2) of 89.73° . The coordinated ligands are almost planar with dihedral angles of 6.15 and 5.92° , respectively, between benzimidazole and phenol. Proton from uncoordinated –NH– in benzimidazole and oxygen of the deprotonated phenol have a strong intermolecular hydrogen bond N–H...O with neighboring molecules to form a 2-D supermolecular structure (figure 4). The N–O bond distances are 2.818 and 2.830 Å, respectively. π – π stacking is also found between different layers at 3.372 Å. In $\text{Co}(\text{C}_{13}\text{H}_9\text{N}_2\text{O})_2 \cdot 2\text{DMF}$ [22], Co(II) was also ligated to two hpbm, but possessing two more DMF molecules compared with **3**; two DMF molecules were on each side of hpbm forming hydrogen bonds between the oxygen of DMF and uncoordinated nitrogen of benzimidazole twisting hpbm, resulting in a more distorted tetrahedral geometry with smaller dihedral angles (75.4°) than **3**. The Co–N length was slightly longer than in **3**, while the Co–O length was the same as **3**. Coordination between Co(II) and phenol was not affected by the hydrogen bond.

A Zn complex of hpbm [5] resembles the Co(II) complex, isostructural in monoclinic and $P2(1)/n$ space group with $Z=4$; though the unit cell volume for the Zn(II) complex ($2169.2(3)$ Å³) is slightly smaller than that of Co(II) ($2177.7(3)$ Å³), the unit cell similarity index π was calculated to be 0.00075 [23], quite near to zero, indicating considerable similarity in their 3-D array. For a Cu(II) [10] complex the dihedral angle between two hpbm is $47.3(3)^\circ$, much smaller than that of Co(II) and Zn(II); perhaps a compromise between the trend of Cu(II) to adopt square planar geometry, the special hindrance of hpbm, and hydrogen bond forces between the solvent and ligands. The trinuclear Ni(II) complex [9] is much more complicated in structure, probably due to the relatively small ion radius creating hindrance, and the bridging oxygens in μ_3 and μ_2 form making the flexible structure possible. For **2**, the instability of Mn(III) in the solution exposed to air leads to a di- μ -oxo dinuclear structure.

The nature of ligands, and the radii and nature of metals, play significant roles in determining the structure and properties of metal coordination complexes. Though no general approach predicts and controls the structure of metal complexes,

investigation into relationships between the structures of complexes and properties of metals, rigidity, and spacial hindrance of ligand increases understanding.

4. Conclusion

In summary, an environmental friendly, simple, and relatively high-yield method was used to synthesize 2-(2-hydroxyphenyl)benzimidazole (**1**) and two transition metal complexes, $[\text{Mn}_2\text{O}_2(\text{hpbm})_4 \cdot 2\text{Py} \cdot 5\text{H}_2\text{O}]$ (**2**) and $[\text{Co}(\text{hpbm})_2]$ (**3**). In **2**, two Mn(IV) ions in distorted octahedral environment are bridged by two O^{2-} with a Mn–Mn distance of 2.777 Å. The hpbm planes are strongly twisted when coordinated with dihedral angles 16.60 and 19.96° between the benzimidazole and phenol. In **3**, Co(II) is coordinated to two hpbm anions in a tetrahedron. The coordinated ligands have dihedral angles of 6.15 and 5.92° between benzimidazole and phenol. The two structures were compared with the reported Zn(II), Cu(II), and Ni(II) complexes with hpbm, and suggest that metal ions play significant roles in determining the structure and properties of metal coordination complexes. Hydrogen bonds are observed in both complexes playing a significant role in 2-D structures.

Supplementary material

CCDC 715036, 697335, and 697336 contain the supplementary crystallographic data for **1**, **2** and **3**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223-336-033; or Email: deposit@ccdc.cam.ac.uk.

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