



Design, Synthesis and Crystal Structure Analysis of Co(II) and Cd(II) Coordination Compounds with Benzimidazole Derivative Ligands

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Two benzimidazole complexes of Cd(II) and Co(II) (**1** and **2**) were synthesized and characterized by single-crystal X-ray diffraction. The structure analysis indicates that the Cd(II) complex belongs to tetragonal P4₁2₁2 space group with $a = 0.85006$ (17) nm, $b = 0.85006$ (17) nm, $c = 2.9594$ (6) nm, $V = 2.1385$ (7) nm³, $Z = 4$. Each Cd(II) atom coordinates with two benzimidazole derivative ligands and two nitrate anions in the shape of coordination polyhedron existing between the dodecahedron and tetragonal antiprism. In the crystal structure, the adjacent coordination units were connected together through strong intermolecular N-H...O H-bonding interactions, which result in the formation of a two-dimension supramolecular structure. For the Co(II) complex with chiral ligand, the same handedness structure was formed and crystallized in the orthorhombic P2₁2₁2₁ space group with $a = 0.80052$ (6) nm, $b = 1.39487$ (8) nm, $c = 1.529340$ (10) nm, $V = 1.70769$ (16) nm³, $Z = 4$. Each Co(II) atom coordinates with one benzimidazole derivative ligand and two chlorides in distorted tetrahedron geometry.

Keywords: Crystal structure, Benzimidazole, Chiral coordination, Cd(II), Co(II).

INTRODUCTION

The design and synthesis of organic-inorganic complexes have attracted much attention in coordination chemistry not only for intriguing structural motifs, but also for their promising applications in multidisciplinary areas, such as catalysis, molecular adsorption, optics, magnetism, molecular recognition, *etc.*¹⁻⁷. Sometimes, such hybrid structures were considered as the primary structures, which can be further organized to supramolecular structures by coordination or/and hydrogen bonds or other weaker supramolecular interactions, such as strong N-H...O intermolecular H-bonding interactions⁸⁻¹⁰. For such kinds of complexes, it is important to rationally design and select the organic building blocks and metal centers with suitable coordination geometry in the self-assembly process¹¹⁻¹³. However, the structure of coordination polymers is influenced by the conformation of organic ligands and their substitute group, reactants and molar ratio, *etc.*, which makes the controllable preparation to be a great challenge¹⁴⁻¹⁷. Benzimidazole with flexible substitute groups are good N-coordination sites donors in structure chemistry, their flexible substitute groups allows the ligands to bend when it coordinates to metal ion centers, which will cause the structural diversity and may result

in novel aim structures. In recent years many coordination complexes with interesting structures constructed from flexible imidazole ligands have been successfully synthesized¹⁸⁻²⁰, while chiral coordination complexes with such organic linkers are still remain less documented²¹. As the continuing work, we present here two transition-metal (Co(II) and Cd(II)) complexes based on flexible benzimidazole ligands ((R/S)-**HBME** = (R/S)-1-(1*H*-benzimidazol-2-yl) ethanol and (S)-**HDBME** = (S)-1,2-*bis*(1*H*-benzimidazol-2-yl)ethanol) with chiral substitute groups. The two compounds were characterized by single crystal structures and spectroscopic techniques.

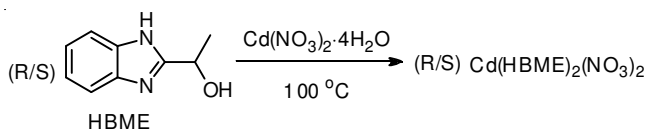
EXPERIMENTAL

NMR spectra were recorded in CDCl₃ solution on a Bruker AV 300 spectrometer at 300 MHz for ¹H. The chemical shifts were expressed in ppm (δ scale) relative to the reference compound tetramethylsilane (TMS). The synthesis of complex **1**, (S)-**HDBME** and complex **2** were shown in **Schemes I and III**, respectively.

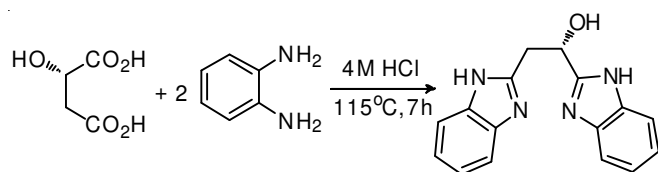
Synthesis: The reagents and solvents employed were commercially available and used as received without further purified. Ligand (R/S)-1-(1*H*-benzimidazol-2-yl) ethanol ((R/S)-**HBME**) was synthesized according to the literature²².

Synthesis of Cd[(R/S)-HBME]₂(NO₃)₂ (complex 1):

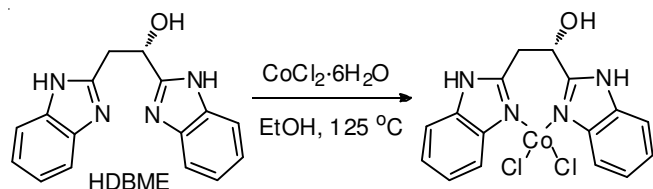
Complex **1** was prepared as shown in **Scheme-I**. In a thick-walled pyrex tube, a mixture of (R/S)-HBME (0.0162 g, 0.1 mmol), Cd(NO₃)₂·4H₂O (0.0154 g, 0.050 mmol) and 15 drops of anhydrous ethanol were frozen and sealed under vacuum, then placed inside an oven at 100 °C. The brown block-like crystals were obtained after 48 h of heating.

**Scheme-I****Synthesis of ligands (S)-1,2-bis(1H-benzimidazol-2-yl)ethanol ((S)-HDBME):**

(S)-HDBME was prepared as shown in **Scheme-II**. Benzene-1, 2-diamine (1.19 g, 11 mmol) was dissolved in hydrochloric acid (12 mL, 4 M) at 100 °C and (S)-hydroxysuccinic acid (5 mmol, 0.67 g) was added to the solution. The mixture were then heated to reflux for 7 h at 115 °C. After cooling to room temperature, the product was divided by neutralizing the mixture solution using dilute NaOH solution to make the pH 8-9. Light yellow solid product was obtained by filtration, being washed with distilled water and ethanol. The yield: 1.14 g (82 %) on the basis of (S)-(-)-hydroxysuccinic acid. ¹H NMR (CDCl₃, 300 MHz): δ 3.29 (m, 1 H), δ 3.58 (m, 1 H), 5.38 (m, 1 H), 6.22 (b, 2 H), 7.15 (m, 4 H), 7.49 (m, 4 H).

**Scheme-II****Synthesis of Co(S)-H₂dibzim(s)-HDBMECl₂ (complex 2):**

Complex **2** was prepared as shown in **Scheme-III**. In a thick-walled Pyrex tube, a mixture of (S)-(-)1,2-bis(1H-benzimidazol-2-yl)ethanol (0.0278 g, 0.1 mmol), CoCl₂·6H₂O (0.0119 g, 0.05 mmol) and 15 drops of anhydrous ethanol were frozen and sealed under vacuum, then placed inside an oven at 125 °C. The blue block-like crystals were obtained after 24 h of heating.

**Scheme-III**

Crystal structure determination: Crystallographic data of **1-2** were collected at 292 K on a Bruker SMART APEX CCD diffractometer with graphite-monochromatized MoK_α radiation (λ = 0.071073 nm). An empirical absorption correction was applied. The structures were solved by the direct method and refined using the SHELXL-97 software²³. All nonhydrogen

atoms were refined by full-matrix least-squares method on F² with anisotropy thermal parameters, while all hydrogen atoms were refined in calculated positions, assigned isotropic thermal parameters and allowed to ride their parent atoms. Crystallographic data and structure refinement results are summarized in Table-1.

TABLE-1
CRYSTALLOGRAPHIC DATA AND STRUCTURE
REFINEMENT RESULTS FOR Cd(II) AND Co(II) COMPLEXES

Compound	1	2
Empirical formula	C ₁₈ H ₂₀ N ₆ O ₈ Cd	C ₁₆ H ₁₄ N ₄ OCoCl ₂
Formular weight	560.81	408.14
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Tetragonal	Orthorhombic
Space group	P4 ₁ ,2,2	P2 ₁ ,2 ₁
Unit cell dimension		
a (Å)	8.5006(17)	8.0052(6)
b (Å)	8.5006(17)	13.9487(8)
c (Å)	29.594(6)	15.29340(10)
β (°)	90	90
Volume (Å ³)	2138.5(7)	1707.69(16)
z	4	4
ρ(calcd) (g/cm ³)	1.742	1.587
Absorption coefficient	1.081	1.328
F(000)	1128	828
Crystal size (mm)	0.10 × 0.15 × 0.20	0.25 × 0.20 × 0.16
Limiting indices	-11 ≤ h ≤ 11 -11 ≤ k ≤ 11 -38 ≤ l ≤ 38	-9 ≤ h ≤ 9 -16 ≤ k ≤ 16 -18 ≤ l ≤ 18
Reflections collected/ unique	18107 / 2533 [R _{int} = 0.0429]	14349 / 3020 [R _{int} = 0.1023]
Max. and Min. transmission	0.7230 and 0.6840	0.8156 and 0.7325
Refinement method	Full-matrix least- squares on F ²	Full-matrix least- squares on F ²
Data/restraints/parameters	2533/12/157	3020/0/211
Goodness-of-fit on F ²	1.161	1.080
Final R indices [I > 2σ(I)]	R1 = 0.0384, wR2 = 0.1324	R1 = 0.0763, wR2 = 0.1656
R indices (all data)	R1 = 0.0476, wR2 = 0.1596	R1 = 0.1055, wR2 = 0.1831
Absolute structure parameter	0.02(6)	0.05(5)

RESULTS AND DISCUSSION

The cadmium complex **1** crystallizes in the tetragonal system (space group P4₁,2,2) (Fig. 1).

Two molecules of (R/S)-HBME and two nitrate ions are bounded directly to the metal ions, as bidentate ligands, give a CdN₂O₆ chromophore which is similar to the reported results^{20,24}. Thus, Cd atom is eight-coordinated with two pyridinic like N-atoms of the benzimidazole rings [N1 and N1A] and six oxygen atoms, two from hydroxyethyl groups oxygen atoms [O1 and O1A] and four from the nitrate ions oxygen atoms [O2, O4, O2A and O4A]. The nitro groups have the same coordination modes as exhibited in the reported result^{20,24}, but two nitrate anions are quite disordered with the O2 (O4) and O2'(O4') atom, with the occupancy factors of 0.31186 and 0.68814, respectively. Selected bond distances and angle valences are given in Table-2. Cadmium-nitrogen bond distances are 2.218 (4) Å and relatively short with comparison with the literature^{20,24}. However, cadmium-oxygen distances are 2.310 (4)-2.640 (2) Å and almost in agreement with those found in

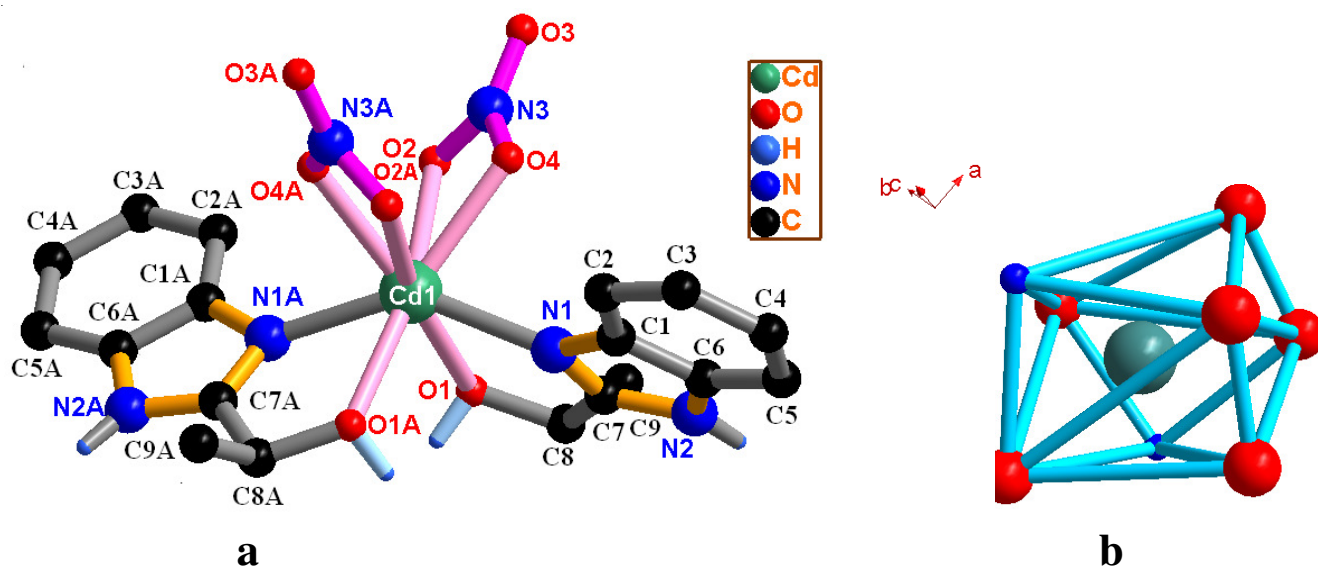


Fig. 1. A view with the atomic numbering scheme (a) and coordination polyhedron (b) of the complex **1**. Hydrogen atoms have been omitted for clarity. Symmetry code: $1-y, 1-x, 0.5-z$

the literature^{20,24}. The cadmium complex is the shape of coordination polyhedron existing between the dodecahedron and tetragonal antiprism and similar to the reported geometrical structure^{20,24}. The fused benzene and imidazole rings are nearly planar with the largest deviations from the mean plane being 0.0257 (0.0048) Å at C5. The fused ring [C1, C2, C3, C4, C5, C6, N2, C7, N1] makes an angle of 4.22(0.15)° with respect to the plane [C7, C8, O1, Cd1, N1] and they are also approximately coplanar. The C-C and C-N bond lengths within the aromatic rings are normal [C-C distances range from 1.362 (10) to 1.409(8) Å; C-N distances range from 1.308(7) to 1.415 (6) Å] (Table-2). These bond lengths are similar to those observed for other benzimidazole derivatives^{18,20,24}.

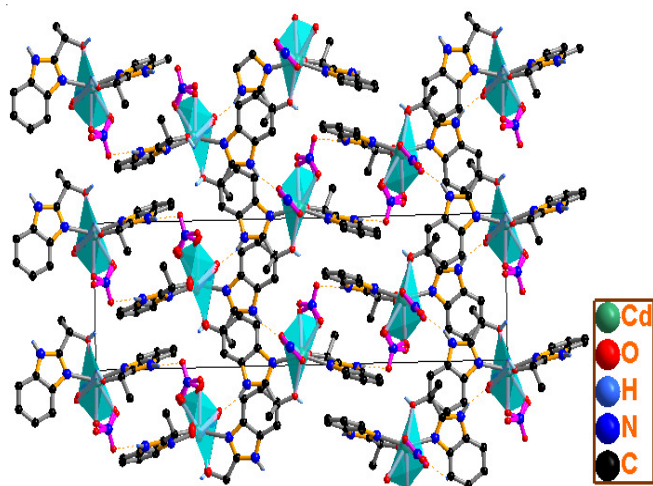


Fig. 2. A view of the 2-D hydrogen-bond network of **1** with metal atoms represented as polyhedra

D-H...A	D-H (Å)	H...A (Å)	D...A (Å)	∠DHA (°)
N2-H2A...O3 ⁱ	0.86	2.1	2.926(6)	158.9
N2-H2A...O4 ⁱⁱⁱ	0.86	2.57	3.19(2)	130.2

Symmetry codes: (i) $-x+3/2, y+1/2, -z+1/4$; (ii) $-x+3/2, y+1/2, -z+1/4$

In the crystal structure, intermolecular N-H...O interactions link the molecules into a two-dimensional network (Table-3, Fig. 2), in which they may be effective in the stabilization of the crystal packing. In the crystal structure, there are no evidence that was observed for the existence of intermolecular aromatic π - π stacking interactions in the complex.

Molecular structure of the complex 2: The cobalt complex **2** crystallizes in the orthorhombic system (space group $P2_12_12_1$). The molecular structure of four-coordinated **2** consists of distorted tetrahedron geometry in which the cobalt atom is surrounded by two chlorides and one benzimidazole ligand [(S)-HDBME] (Fig. 3). In this structure, the cobalt was coordinated with sp^2 N1 and N3 instead of sp^3 N2 and N4 in the benzimidazole ring. Selected bond distances and angle valences are given in Table-4. The Co-N1 and Co-N3 bond length are 2.006 (6) and 1.993 (7) Å, respectively, which is similar to the Co-N_{benzimidazole} length in the literature^{25,26}. Compared to the angle of ideal tetrahedron is 109.28°, while the N-Co-N and N-Co-Cl angle range from 105.3 (3) to 114.0 (2)° and the coordination environment around Co center significantly deviates from an ideal tetrahedron which can be best described as severely distorted tetrahedron. In addition, the plane formed by atoms C11-Co1-Cl2 makes an angle of 86.89 (0.21)° with respect to the plane formed by atoms N1-Co-N3

TABLE-2
SELECTED BOND LENGTHS (Å) AND BOND ANGLES (°) FOR THE Cd(II) COMPLEX

Bond	Distance (Å)	Bond	Distance (Å)	Angle (°)	Angle (°)
Cd1-N1	2.218(4)	Cd1-O2A	2.51(2)	O1-Cd1-O1A	94.3(3)
Cd1-O4	2.31(4)	O1-C8	1.397(7)	N1-Cd1-N1A	141.0(3)
Cd1-O1	2.427(5)	N1-C7	1.308(7)	N1-Cd1-O4	76.7(17)
Cd1-O4A	2.64(2)	N2-C7	1.352(6)	N1A-Cd1-O4	139.4(12)
				O4-Cd1-O4A	75(4)
				N(1)-Cd(1)-O(1)	67.23(15)
				O(4)-Cd(1)-O(1)	103(2)
				O4A-Cd1-O1	148.3(7)

and they are also not completely perpendicular. The two fused benzene and imidazole rings are nearly planar with the largest deviations from the mean plane being 0.0325 (0.0104) Å at C5 and 0.0524 (0.0079) Å at C10. These two fused ring make a dihedral angle of 16.20 (0.16)°. In addition, there are also three weak intermolecular N-H...Cl and one O-H...Cl hydrogen bond (Table-5 and Fig. 4) between the carbonyl and hydroxy groups which link the molecules into a one-dimensional network, in which they may be effective in the stabilization of the structure.

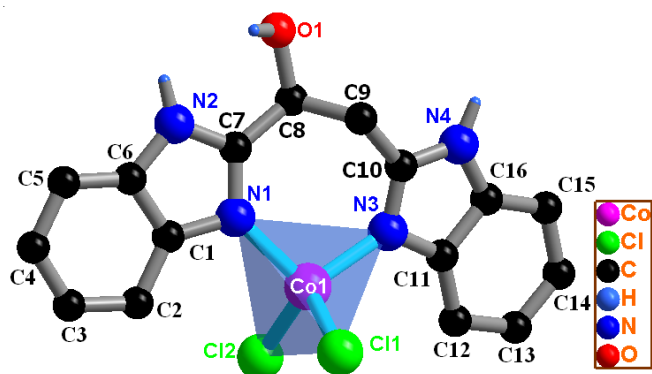


Fig. 3. View of the coordination environment of Co(II) and (S)-HDBME in complex **2**. Hydrogen atoms have been omitted for clarity

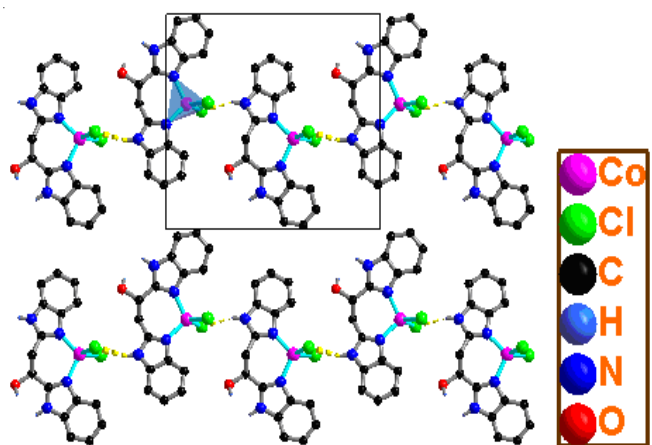


Fig. 4. Molecular one-dimensional chain hydrogen-bond structure of complex **2** viewed along the a-direction

TABLE-4
SELECTED BOND LENGTHS (Å) AND
BOND ANGLES (°) FOR Co(II) COMPLEX

Bond	Dist. (Å)	Bond	Dist. (Å)	Bond	Dist. (Å)
Co1-N3	1.993(7)	C8-O1	1.425(12)	Co1-Cl2	2.265(2)
Co1-N1	2.006(6)	C10-N3	1.308(9)	C7-N1	1.339(9)
Co1-Cl1	2.238(3)	C10-N4	1.369(11)	C7-N2	1.348(11)
Angle	(°)	Angle	(°)	Angle	(°)
N3-Co1-Cl2	114.0(2)	N1-Co1-Cl2	107.3(2)	Cl1-Co1-Cl2	107.84(10)
N1-Co1-Cl1	112.1(2)	N3-Co1-N1	105.3(3)	C9-C8-C7	116.0(10)
O1-C8-C7	111.7(9)	N3-Co1-Cl1	110.3(2)	O1-C8-C9	109.5(9)

Conclusion

Two complexes of Cd(II) and Co(II) (**1** and **2**, respectively) were successfully synthesized and characterized by single-crystal X-ray diffraction. The compounds crystallized in the space group of P4₁2₁2 and P2₁2₁2₁, respectively. There are also

TABLE-5
HYDROGEN-BOND GEOMETRY (Å, °)

D-H...A	D-H (Å)	H...A (Å)	D...A (Å)	∠DHA (°)
N4-H4B...Cl1 ⁱ	0.86	2.52	3.281(8)	147.9
N2-H2C...Cl2 ⁱⁱ	0.86	2.71	3.299(9)	126.7
N2-H2C...Cl1 ⁱⁱⁱ	0.86	2.74	3.276(10)	121.7
O1-H1A...Cl2 ⁱⁱ	0.82	2.70	3.507(13)	170.1

Symmetry codes: (i) -x+3/2, -y+1, z+1/2; (ii) x-1/2, -y+3/2, -z+2; (iii) x+1/2, -y+3/2, -z+2

a strong intermolecular H-bonding interactions which are effective in the stabilization of the structure in **1** and **2**.

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