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ORIGINAL PAPER

Synthesis, Crystal Structure and Luminescence Property of a Chiral Magnesium (II) Mixed-ligand Complex $[Mg(H_2O)_2(phen)(HBDC)_2](phen)$

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Abstract A new mixed-ligand complex of $[Mg(H_2O)_2(phen)(HBDC)_2](phen)$ (phen = 1, 10-phenanthroline, H_2BDC = 1,3-benzene dicarboxylic acid) has been synthesized and its crystal structure determined by single-crystal X-ray diffraction. It is noteworthy that this complex was formed from achiral reactants, and found to crystallize in the chiral space group *C*2. Structure analysis shows that each Mg(II) ion is coordinated by the two nitrogen atoms of phen, one oxygen atom from each of the two 1,3-HBDC molecules and one oxygen atom from each of the two water molecules, leading to a distorted octahedral geometry. The mixed-ligand complexes are assembled into a two-dimensional supramolecular network through the formation of intermolecular hydrogen bonds. The luminescence property and thermal stability behavior of the complex were also investigated. The complex shows a strong blue luminescence emission. Crystal data: $a = 24.5856(16)$, $b = 10.1598(6)$, $c = 7.1460(4)$ Å, $\beta = 105.226(2)^\circ$, $V = 1722.30(18)$Å^3, $Z = 2$, $R_1 = 0.0367$, $wR_2 = 0.0833$ $[I>2\sigma(I)]$.

Keywords Chiral complex · Mg(II) ion · Crystal structure · Luminescence

Introduction

The design and synthesis of novel chiral crystals has attracted intense interest owing to the realization of their potential use as functional materials in nonlinear optical devices [1, 2], asymmetric catalysis [3, 4], and enantioselective synthesis [5, 6]. Most chiral complexes are assembled from chiral molecules, while chiral complexes synthesized from completely achiral molecules are less common [7, 8]. Up to now, the design and control over coordination compounds has been mainly focused on the incorporation of transition metal ions as coordination centers, whereas less attention has been paid to the main group metal ions [9–12].

In this report, a new chiral crystal $[Mg(H_2O)_2(phen)(HBDC)_2](phen)$ was synthesized using magnesium(II) as the center ion, coordinated by achiral organic ligands, 1,10 phenanthroline (phen) and 1,3-benzene dicarboxyate (1,3-HBDC), and water. The luminescence property of $[Mg(H_2O)_2(phen)(HBDC)_2](phen)$ was investigated and found to show a strong blue luminescence emission.

Experimental Section

Materials and Physical Measurements

All reagents were commercially available and used as received. Infrared spectra were recorded on a Bruker Equinox-55 spectrophotometer in the 500–4000 cm^{-1} region using $[Mg(H_2O)_2(phen)(HBDC)_2](phen)$ in KBr pellet form. Elemental analysis (CHNO) was determined using a Thermo Flash EA 1112-Elmer elemental analyzer. The luminescence property was measured using a HITACHI F-4500 luminescence spectrophotometer and the thermal analysis was performed using a NETZSCH STA449C analyzer.

Synthesis of $[Mg(H_2O)_2(phen)(HBDC)_2](phen)$

$Mg(NO_3)_2 \cdot 6H_2O$ (1.0 mmol), phen (1.0 mmol), 1, 3-H_2BDC (1.0 mmol) were reacted together in methanol/H_2O

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(10 mL/20 mL), and the resulting solution was left to stand at 70 °C for several days, where after colourless block-like crystals were formed. Yield: 42% (based on Mg). Anal. Calcd. for $C_{40}H_{30}N_4O_{10}Mg$ (%): C, 63.97; H, 4.01; N, 7.46; O, 21.30. Found: C, 64.05; H, 3.97; N, 7.43; O, 21.39. IR spectrum (cm^{-1}): 1702(s), 1609(ms), 1557(s), 1423(ms), 1395(s), 929(ms), 868(d) and 842(ms).

X-ray Crystallography

Crystallographic data for the crystal is summarized in Tables 1, 2 and 3. The data were collected using MoKα radiation ($\lambda = 0.71073$ Å) on an R-Axis Spider diffractometer at 153(2) K. The cell dimensions and space group were determined according to established procedures [13]. The structures were solved by direct methods using the SHELXTL program and refined by full-matrix least-squares techniques. The non-hydrogen atoms were assigned anisotropic displacement parameters in the refinement. The hydrogen atoms were obtained from difference Fourier maps and a riding model was used.

Table 1 Crystallographic data and structure refinement for $[Mg(H_2O)_2(phen)(HBDC)_2](phen)$

Empirical formula	$C_{40}N_4O_{10}H_{30}Mg$
Formula weight	750.99
Crystal system	Monoclinic
Space group	*C*2
a, (Å)	24.5856 (2)
b, (Å)	10.1598 (6)
c, (Å)	7.1460 (4)
β, (°)	105.226 (2)
V, (Å^3)	1722.30 (2)
Z	2
Dc (g cm^{-1})	1.448
Abs coef. (mm^{-1})	0.122
Crystal size (mm)	0.63 × 0.25 × 0.23
T(K)	153 (2)
F_{000}	780
Reflections collected	8528
Unique reflections	3905
Range (°)	3.26–27.48
Flack parameter	−0.1(4)
R [$I > 2(I)$]	$R_1 = 0.0367$, $wR_2 = 0.0833$

Table 2 Selected bond lengths (Å) and angles (°) for compound

Mg(1)–O(1)	2.0538(2)	Mg(1)–N(1)	2.219(2)
Mg(1)–O(5)	2.0651(2)		
O(1)^a–Mg(1)–O(1)	102.07(1)	O(1)^a–Mg(1)–O(5)	89.25(7)
O(1)^a–Mg(1)–N(1)	165.66(8)	O(5)–Mg(1)–O(5)^a	178.08(1)
O(5)–Mg(1)–N(1)	85.83(8)	N(1)–Mg(1)–N(1)^a	75.23(1)

Symm code: ^{a} $-x, y, -z + 1$

Table 3 Hydrogen bond lengths (Å) and angles (°) in compound

	D–H	H···A	D–A	∠DHA
O(5)−H(5A)···O(2)^a	0.84	1.95	2.731(3)	154.5
O(5)–H(5WA)···N(2)^b	1.15(7)	1.84(7)	2.899(3)	150(5)

Symm code: ^{a} $-x, y, -z + 1$; ^{b} $x - 1, y, z$

Results and Discussion

The coordination environment of the Mg(II) ion in $[Mg(H_2O)_2(phen)(HBDC)_2](phen)$ is shown in Fig. 1. The compound crystallizes in the monoclinic chiral space group *C*2. The Flack parameter was found to be −0.1(4), confirming that the absolute structure could be determined [14]. Each Mg(II) ion is coordinated by the two nitrogen atoms of phen, one oxygen atom from each of the two 1,3-HBDC molecules and one oxygen atom from each of the two water molecules, leading to a distorted octahedron geometry. Bond lengths of Mg(1)–N (1), Mg(1)–O(5) and Mg(1)–O(1) are 2.219(2) Å, 2.0651(2) Å, 2.0538(2) Å. The basal plane is formed by O(1), O(1A), N(1), N(1A), and the axial sites are occupied by O(5) and O(5A). Bond angles of O(5)–Mg(1)–O(1), O(5)–Mg(1)–N(1), O(5)–Mg(1)–O(5A) are 91.96(7)°, 85.83(8)°, 178.0(8)°, respectively. The complexes are assembled into a two-dimensional supramolecular network through the formation of intermolecular hydrogen bonds, as shown in Fig. 2.

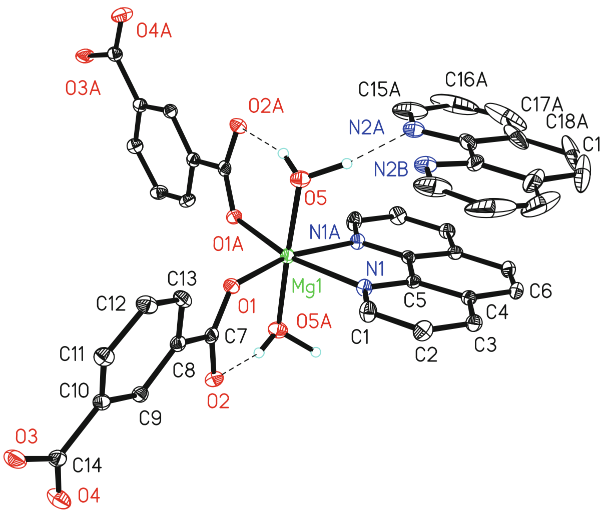

Fig. 1 The coordination environment of the Mg(II) ion in $[Mg(H_2O)_2(phen)(HBDC)_2](phen)$ in 30% probablility

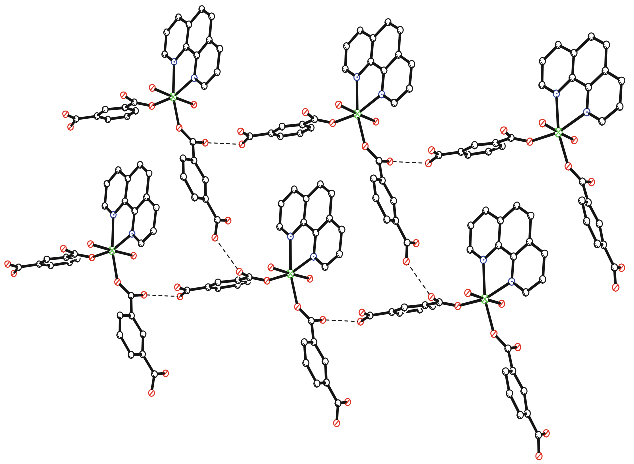

Fig. 2 The two-dimensional hydrogen bonded network viewed along the *c*-axis, and the *a*-axis is horizontal

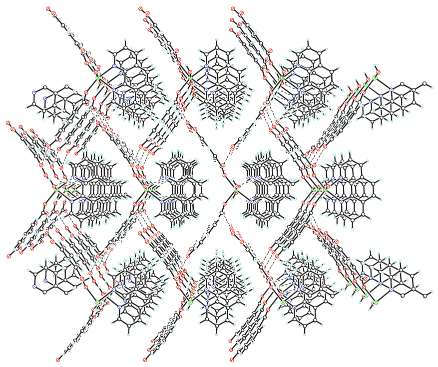

Fig. 3 The three-dimensional network viewed along *c*-axis in the complex, and the *b*-axis is horizontal

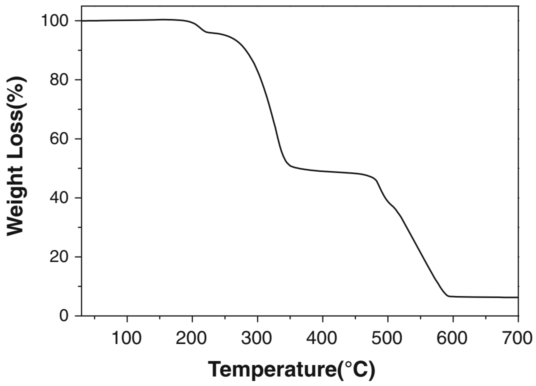

Fig. 4 TGA curve for $[Mg(H_2O)_2(phen)(HBDC)_2](phen)$

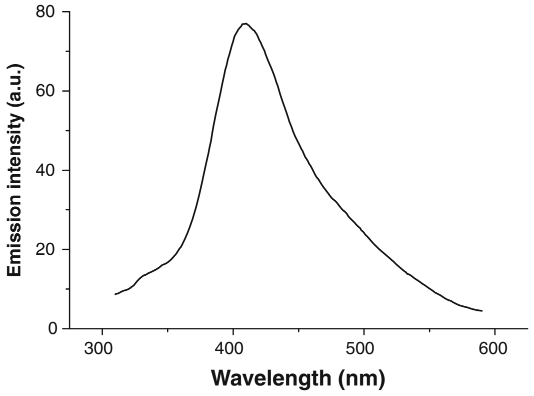

Fig. 5 Solid-state emission spectra for $[Mg(H_2O)_2(phen)(HBDC)_2](phen)$ at room temperature

The structures contain a phen ligand attached to magnesium have been reported by Zhang, Skogareva, etc. [15–22], and three structures have a cocrystalized phen ligands hydrogen bound to water in the same manner as the structure in the report [15–17]. The non-coordinated phen is some disordered due to the fact that the ligand is not locked into place as tightly as the coordinate phen. Hydrogen bond length of O(5)–H(5A)···O(2)^A, O(5)–H(5WA)···N(2)^B are 2.731(3) Å, 2.899(3) Å and bond angles are 154.5°, 150.5°.The parallel distance between the uncoordinated and coordinated phen ligands is 3.465 and 3.517 Å, respectively, indicating that there are strong π–π stacking interactions between the phen ligands, as shown in Fig. 3.

Thermogravimetric analysis of the complex was carried out to examine its thermal stability. In the complex, the first weight loss of 4.45% from 190 to 220 °C was attributed to the loss of water molecules from the complex (calcd. 4.80%). Increasing the temperature to 355 °C led to further decomposition, resulting in the second weight loss of 46.33%, corresponding to the loss of phenanthroline molecules from the complex (calcd. 47.99%). The last weight loss of 43.08% from 480 to 590 °C corresponded to the loss of H_2BDC molecules from the complex (calcd. 39.98%). The final pyrolysis product was MgO, as shown in Fig. 4.

The luminescence property of the complex was investigated in the solid state at room temperature, as shown in Fig. 5. The complex exhibited a luminescence emission with a maximum at 409 nm upon excitation at 300 nm, which is attributed to ligand-based emissions [5]. The blue emission of the complex in the solid state implies that the complex may be potentially applicable as a material for blue light-emitting diode devices.

Supplementary Data

CCDC 706400 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033.

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