Synthesis and Crystal Structure of a Green Photoluminescent 1D Cobalt(II) Coordination Polymer Constructed from 2,2′ Bibenzimidazole

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Hydrothermal reaction of $Co(NO_3)_2 \cdot 6H_2O$ with H_2bibm and H_4cta at 120 °C yielded a novel 1D Co(II) coordination polymer, $[Co(H_2bibm)(cta)]_n \cdot nH_2O$ (**1**) [H_2bibm = 2,2′-bibenzimidazole, cta = citrate], in which distorted CoN_2O_4 octahedra are linked by the cta ligands in a tetradentate bridging mode to construct a zigzag chain with Co···Co distances of 7.510(1) Å. A 2D supramolecular network is formed by π-π stacking with a face-to-face distance of 3.55 Å between the imidazole rings of the 2,2′-bibenzimidazole ligands and interchain O-H···O and N-H···O hydrogen bond interactions. Complex **1** displays strong green fluorescence emissions at 538 nm in the solid state upon photoexcitation at 395 nm at room temperature.

Key words: Cobalt(II) Complex, Crystal Structure, Fluorescence

Introduction

The field of crystal engineering has attracted great interest from chemists, and considerable efforts have been focused on the design, synthesis and characterization of supramolecular structures [1 – 6], not only because of their intriguing variety of architectures, but also for their versatile potential application in the areas of absorption, catalysis, nonlinear optics, molecular magnetization and others [7 – 15]. The bidentate chelating ligand 2,2′-bibenzimidazole (H_2bibm) with four nitrogen donor sites, which can undergo reversible protonation and deprotonation [16 – 19], can be used not only for the coordination to a transition metal ion in nondeprotonated (neutral, H_2bibm), mono-deprotonated (monoanion, $Hbibm^-$) and di-deprotonated (dianion, $bibm^{2-}$) forms, but simultaneously complementary intermolecular hydrogen bonds can also be constructed in supramolecular assemblies [20 – 21]. The two nitrogen donors of neutral 2,2′-bibenzimidazole in coplanar rings can coordinate to a transition metal ion *via* a chelating mode of *syn* orientation. The nondeprotonated H_2bibm with the residual N–H entities can form complementary intermolecular hydrogen bonds of the N–H···O type with counter ions and solvent molecules in crystals. As a versatile flexible bridging ligand, citric acid (citric acid = H_4cta) with up to seven O donor atoms has been extensively studied for designing new inorganic-organic hybrid materials [22], in which the combinations of the coordination versatility and the high coordination numbers available to transition metal cations can stabilize different sorts of coordination polymers. However, the synthesis of coordination polymers involving H_4cta and H_2bibm simultaneously as bridging and terminal ligands to the best of our knowledge has not been reported until now. Herein, we report the synthesis, structural characterization and photoluminescence properties of the zigzag-like 1D coordination polymer $[Co(H_2bibm)(cta)]_n \cdot nH_2O$. Significant intermolecular hydrogen bonding and π-π stacking interactions extend the 1D arrangement into a 2D supramolecular framework.

Results and Discussion

The crystal structure of complex **1** consists of 1D $[Co(H_2bibm)(cta)]_n$ zigzag-like chains and free water molecules. The crystallographic analysis has revealed that complex **1** crystallizes in the centrosymmetric space group $P2_1/c$. The asymmetric unit of **1** contains one crystallographically unique Co(II) ion, one 2,2′-

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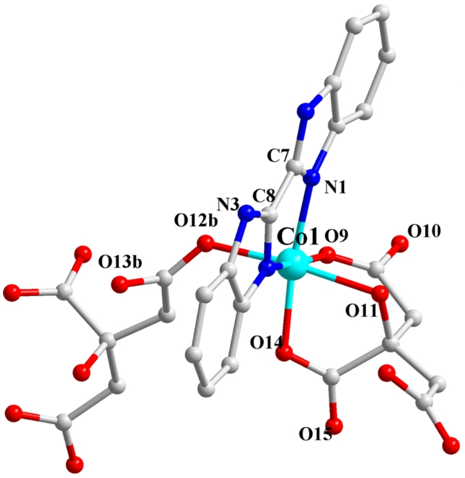

Fig. 1 (color online). The Co(II) coordination environment in the molecular structure of **1** (hydrogen atoms are omitted for clarity).

bibenzimidazole ligand, two citrate anions and one guest water molecule (Fig. 1). The coordination geometry of the Co^{2+} center is best described as distorted $\{CoN_2O_4\}$ octahedral comprising three carboxyl and one hydroxyl oxygen atoms from two different citrate anions and two nitrogen atoms from a nondeprotonated bidentate 2,2′-bibenzimidazole. The equatorial positions are occupied by O12b, O9, O11 and N3, and the axial positions are occupied by N1 and O14. The Co–N bond lengths are 2.093(2) and 2.154(3) Å, comparable to those detected in $[Co(phen)(oba)]_n \cdot 0.5nH_2O$ [phen =1,10-phenanthroline, oba = 4,4′-oxybis(benzoate)] [23] and slightly shorter than the apical distances [2.141(2)–2.176(2) Å] in $[Co_2(H_2O)(TATP)_2(oba)_2]_n \cdot 2nH_2O$ [TATP =1,4,8,9-tetranitrogen-trisphene] [23]. The Co–O bond lengths fall in the range from 2.043(2) to 2.126(2) Å (Table 1). The N–Co–N angle is 78.96(10)°, whereas the O–Co–O angles formed by carboxyl and hydroxyl oxygen atoms range between 78.73(8)° and 171.94(9)° (Table 1).

Two adjacent six-coordinated Co^{2+} ions are linked by the cta ligands in a tetradentate bridging mode to form an infinite zig-zag chain along the [001] direction with the Co–Co separations at 7.510(1) Å stacked with the sequence ···ABAB··· of the cta ligands. The chains are decorated with H_2bibm ligands alternately in an outward fashion, connected by the nitrogen atoms in a chelating μ_1-(η_2-N_1, N_2) mode.

In crystals of complex **1** there exist interesting supramolecular interactions. Along the [010] direction, hydrogen bonding is observed. The O-H···O hydrogen bonds are between two carboxyl oxygen atoms (O10 and O15, Fig. 1) from two difference citrate anions with O···O separations of 2.540(3) and 2.561(4) Å, and between carboxyl oxygen atoms (O15 and O12b) and guest water molecule oxygen atoms (O16W) with O···O separations of 2.993(11) and 2.801(11) Å (Table 2). The N–H groups of each bibenimidazole molecule are involved in hydrogen bonds with carboxyl oxygen atoms. The N2-H2A···O13^j distance

Table 1. Selected bond lengths (Å) and angles (deg) for complex **1**[a].

Co(1)–O(9)	2.124(2)	Co(1)–N(1)	2.093(2)
Co(1)–O(11)	2.126(2)	Co(1)–N(3)	2.154(3)
Co(1)–O(14)	2.043(2)	Co(1)–O(12b)	2.102(2)
O(9)–Co(1)–O(11)	81.66(9)	O(14)–Co(1)–N(1)	169.78(10)
O(9)–Co(1)–O(14)	88.44(9)	O(14)–Co(1)–N(3)	95.51(9)
O(9)–Co(1)–N(1)	96.24(10)	O(12b)–Co(1)–O(14)	94.84(8)
O(9)–Co(1)–N(3)	172.98(9)	N(1)–Co(1)–N(3)	78.96(10)
O(9)–Co(1)–O(12b)	93.41(9)	O(12b)–Co(1)–N(1)	93.96(9)
O(11)–Co(1)–O(14)	78.73(8)	O(12b)–Co(1)–N(3)	92.04(10)
O(11)–Co(1)–N(1)	92.91(9)	N(1)–C(7)–C(8)	118.2(3)
O(11)–Co(1)–N(3)	93.40(9)	N(3)–C(8)–C(7)	118.5(3)
O(11)–Co(1)–O(12b)	171.94(9)		

[a] Symmetry code: (b) x, $3/2-y$, $z-1/2$.

Table 2. Hydrogen bond geometry (Å, deg) for complex **1**[a].

D-H···A	D-H	H···A	D···A	D–H···A
N2-H2A···O13^j	0.86	1.88	2.726(4)	167.8
N4-H4A···O12^j	0.86	1.99	2.806(3)	158.8
O10-H10A···O15^c	0.93	1.61	2.540(3)	177.8
O11-H11A···O13	0.90	1.77	2.561(4)	146.1
O16-H16C···O12^f	0.85	2.21	2.993(11)	153.7
O16-H16D···O15	0.85	1.95	2.801(11)	179.0

[a] Symmetry codes: (c) $1-x$, $1/2+y$, $3/2-z$; (f) $1-x$, $2-y$, $2-z$; (j) $-x$, $1/2+y$, $3/2-z$.

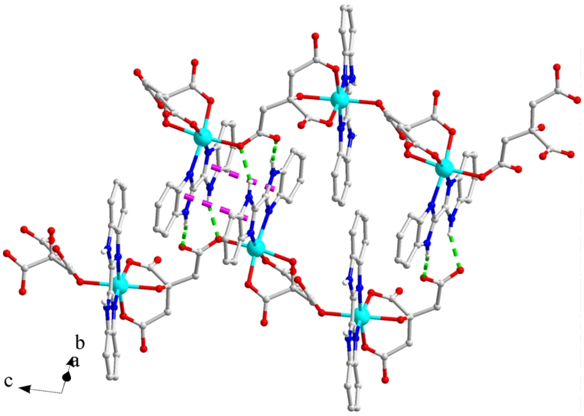

Fig. 2 (color online). N–H···O hydrogen bond interactions (thin dashed lines; green) and π-π stacking interactions (thick dashed lines; crimson) between two nearest zigzag chains in the crystal structure of **1** (for the atom color code used see Fig. 1).

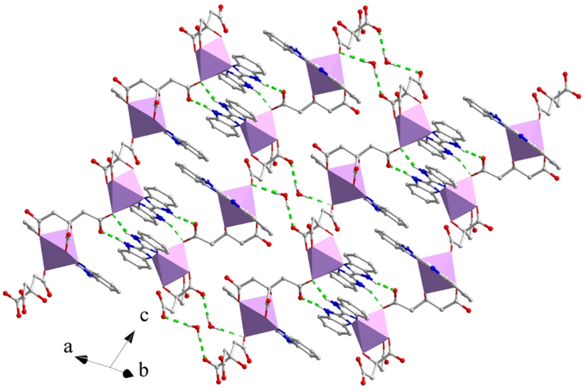

Fig. 3 (color online). The two-dimensional network formed in the crystal structure of **1**.

of 2.726(4) Å and the N4-H4A···O12[j] (symmetry code (j) $-x$, $1/2+y$, $3/2-z$) distance of 2.806(3) Å correspond to strong interactions (Fig. 2, Table 2). Furthermore, there also exist moderate aromatic π-π stacking interactions parallel to the *bc* plane with face-to-face distances of 3.55 Å between the imidazole rings in the 2,2′-bibenzimidazole molecules as depicted in Fig. 2. As a consequence, the π-π interactions and the interchain hydrogen bond interactions all help stabilizing the two-dimensional framework (Fig. 3).

In the IR spectrum, the strong and broad absorption band at 3466 cm^{-1} is assigned to ν(OH) stretching vibrations of hydrogen bonds. According to the literature [25], as described by M. McCann *et al.*, the difference $\Delta\nu$ of the stretching vibrations ν_{as} and ν_s of the carboxyl group can indicate the coordination mode of the citrate group to the metal atom. The shift $\nu_{as}(\text{OCO}^-)$ (1656 cm^{-1}) $-$ $\nu_s(\text{OCO}^-)$ (1545 cm^{-1}) = 111 cm^{-1} suggests that the carboxyl groups are coordinated in a chelating mode [19]. Fig. 4 shows the fluorescence emission spectra of **1** in the solid state at r. t. Upon excitation at 395 nm, complex **1** exhibits a strong green emission band at 538 nm, which is 39 and 3 nm red-shifted and 42 nm blue-shifted, respectively, compared to the free ligand H_2bibm, which upon excitation at 491 nm shows emission bands at 499, 535, 580 nm [26]. This phenomenon is also observed in H_2bibm-metal analogs [24], which show hypsochromic shifts of 45, 81 and 126 nm in $[\text{Zn}(H_2\text{bibzim})(\text{BDC})]_n$ (BDC =1,4-benzenedicarboxylate) (λ_{em} = 454 nm, λ_{ex} = 365 nm), but hypsochromic shifts of 57, 93 and 138 nm or 19, 55 and 100 nm in $[\text{Cd}(H_2\text{bibzim})(\text{BDC})]_n$ (λ_{em} = 442 and 480 nm, λ_{ex} = 365 nm) compared to the free ligand H_2bibm (λ_{em} = 499, 535 and 580 nm, λ_{ex} = 491 nm). This different shift of the emission bands is ascribed to the phenyl chromophore of the BDC ligand.

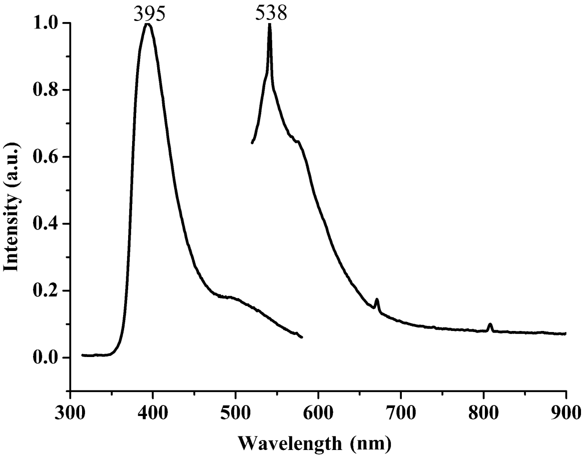

Fig. 4. Solid-state excitation and emission spectra of **1** at r. t.

Because the emission bands of the free H_2bibm are assigned to intraligand π-π^* transitions [26], we assign the emissions described above for **1** to LLCT bands. The strong green-fluorescent emission of complex **1** could be of potential application in advanced materials.

Conclusion

In summary, a novel Co(II) complex with 2,2′-bibenzimidazole and citrate ligands has been synthesized under hydrothermal conditions, and its luminescence properties were investigated. The intricate hydrogen bonding and π-π stacking interactions in the supramolecular framework were discussed. The strong green-fluorescent emission of complex **1** could be of potential application in advanced materials.

Experimental Section

All reagents were bought from commercial sources and used without further purification. The elemental analysis was carried out on a PE 1700 CHN auto elemental analyzer. The infrared spectrum (IR) (KBr pellet) was recorded in the 400 – 4000 cm^{-1} range using a Bruker IFS66V vacuum-type FT-IR spectrophotometer. Fluorescence measurements were performed on a Model FL3-P-TCSPC spectrofluorimeter. The crystal structure was determined by a Bruker APEX area detector diffractometer employing the SHELXTL crystallographic software.

The ligand 2,2′-bibenzimidazole (H_2bibm) was prepared according to the method described by Lane [27].

Table 3. Crystal data and data collection and refinement details for complex **1**.

Empirical formula	$C_{20}H_{18}CoN_4O_8$
M_r	501.32
Crystal color	dark red
Crystal dimens., mm^3	$0.30 \times 0.20 \times 0.20$
Crystal system	monoclinic
Space group	$P2_1/n$
a, Å	13.0899(2)
b, Å	11.8677(2)
c, Å	13.3587(3)
β, deg	108.6430(10)
V, Å^3	1966.34(6)
Z	4
T, K	296(2)
Calcd. density, Mg m^{-3}	1.69
μ(Mo$K\alpha$), cm^{-1}	9.3
F(000), e	1028
$2\theta_{max}$, deg	50.50
Total reflns. collected / unique	11674 / 3554
Ref. parameters	300
$R1$ [$I \geq 2\sigma(I)$] / $wR2$ (all data)	0.0429 / 0.1487
GOF (F^2)	0.891
Peak / hole, e Å^{-3}	1.00 / −0.86

Synthesis of [Co(H$_2$bibm)(cta)]$_n$ · nH$_2$O

For the hydrothermal reaction of $Co(NO_3)_2 \cdot 6H_2O$ (0.5 mmol), H_2bibm (0.25 mmol), H_4cta (0.25 mmol), and water (15 mL), the mixture was stirred for 20 min in air, then transferred and sealed into a 23-mL Teflon reactor, which was heated at 120 °C for three days and then cooled to r. t. Red needle-shaped crystals were obtained (yield 36 % based on Co), filtered off, washed with distilled water and dried in air. – $C_{20}H_{18}CoN_4O_8$ (501.32): calcd. C 47.92, H 3.62, N 11.18; found C 47.59, H 4.01, N 10.81. – IR (KBr pellet, cm^{-1}): ν = 3466, 2992, 2877, 1656, 1545, 1401, 1243, 1020, 793, 744, 711.

Crystal structure determination

The diffraction data were collected on a Bruker Smart Apex CZN diffractometer with graphite-monochromatized MoK_α radiation (λ = 0.71073 Å) at 296 K. An absorption correction was applied using SADABS [28]. The structure was solved by Direct Methods and refined with full-matrix least-squares techniques using SHELXTL [29]. All non-hydrogen atoms were refined with anisotropic displacement parameters. The crystal data, details on the data collection and refinement are summarized in Table 3, and selected bond lengths and angles are presented in Table 1. The hydrogen bond lengths and bond angles are listed in Table 2. Fig. 1 – 3 illustrate the molecular and crystal structure of **1**.

CCDC 773502 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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