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Syntheses, structures and luminescent properties of a dimer and an one-dimensional chain coordination polymer with the flexible bis(triazole) and hydroxybenzoate ligands

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Abstract

Two novel complexes $[Zn(phba)_2(btp)]_2$ (**1**) and $[Cd(phba)_2(btp)(H_2O)]_n$ (**2**) have been synthesized by using 1,3-bis(1,2,4-triazol-1-yl)propane (btp) and 4-hydroxybenzoate (phba). **1** contains the neutral dimer $Zn_2(btp)_2$ metallacycle, while **2** forms the one-dimensional zigzag chain structure. **1** and **2** exhibit blue luminescent emissions at 402 and 394 nm, respectively, excited at 340 nm in the solid state at room temperature.

Keywords: 1,3-Bis(1,2,4-triazol-1-yl)propane; Hydroxybenzoate; Zinc complex; Cadmium complex; Dimeric complex; One-dimensional chain

1. Introduction

The design and construction of the coordination polymers and polynuclear complexes has attracted great attention in recent years for their potential application as well as the variety of architectures and topologies [1–9]. The selection of the ligands is undoubtedly the key point in the synthesizing of the coordination polymers and polynuclear complexes.

1,2,4-Triazole and its derivatives are very interesting ligands because they combine the coordination geometry of both pyrazole and imidazole with regard to the arrangement of their three heteroatoms. A large number of mononuclear, oligonuclear and polynuclear transition metal complexes of 1,2,4-triazole derivatives have been synthesized and characterized due to their magnetic properties and novel topologies [10–15]. However the complexes of the flexible bis(triazole) ligands have not been well exploited up to now [16–19]. Our interest is to study the coordination chemistry of 1,2,4-triazole and its derivatives together with their potential application in the material science. Recently, we reported the crystal structures of a series of transition metal coordination polymers with the flexible bis(triazole) ligands such as 1,2-bis(1,2,4-triazol-1-yl)ethane [20–23] and 1,4-bis(1,2,4-triazol-1-ylmethyl)benzene [24,25].

On the other hand, although salicylate has been widely employed for the synthesis of the coordination compounds [26,27]. 4-Hydroxybenzoate, the isomer of salicylate, was rarely studied to date [28]. The combination of the flexible ligand 1,3-bis(1,2,4-triazol-1-yl)propane (btp) and 4-hydroxybenzoate (phba) can give rise to novel complexes. In the present paper, we report the preparation, crystal structure and luminescent properties of a dimer $[Zn(phba)_2(btp)]_2$ (**1**) and an one-dimensional zigzag chain coordination polymer $[Cd(phba)_2(btp)(H_2O)]_n$ (**2**).

2. Experimental

2.1. Materials and general methods

The flexible ligand 1,3-bis(1,2,4-triazol-1-yl)propane (btp) was synthesized according to the literature method

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[18]. All other reagents and solvents employed were commercially available and used as received without further purification. The C, H, N microanalyses were carried out with a Perkin-Elmer 240C analyser. IR spectra were obtained for KBr pellets on a Nicolet 170SX FT-IR spectrophotometer in the 4000–400 cm^{-1} region. The luminescence measurements were carried out in the solid state at room temperature and the spectra were collected with a Perkin-Elmer LS50B spectrofluorimeter.

2.2. Preparation of the complexes

2.2.1. *[Zn(phba)$_2$(btp)]$_2$ (**1**)*

A 25 mL water/MeOH solution (1:1 v/v) of $Zn(NO_3)_2 6H_2O$ (0.5 mmol) was added to one leg of an "H-shaped" tube, and a 25 mL water/MeOH (1:1 v/v) solution of 1,3-bis(1,2,4-triazol-1-yl)propane (btp) (0.5 mmol) and sodium 4-hydrogenbenzoate (1.0 mmol) was added to the other leg of the tube. Colourless crystal **1** (yield: 37%) were obtained after about two months. Anal. Calcd. for $C_{42}H_{40}N_{12}O_{12}Zn_2$ (**1**): C, 48.71; H, 3.89; N, 16.23%. Found: C, 48.57; H, 3.74; N, 16.01. IR data (cm^{-1}): 3241 m, 3141 m, 1605 s, 1536 s, 1505 m, 1454 m, 1397 s, 1273 m, 1243 m, 1219 m, 1165w, 1135 m, 1095w, 996w, 857w, 787 m, 671w, 641 m, 417w.

2.2.2. *[Cd(phba)$_2$(btp)(H$_2$O)]$_n$ (**2**)*

The synthesis procedure of **2** was similar to the synthesis of **1**, except that $Cd(NO_3)_2.6H_2O$ was instead of $Zn(NO_3)_2 6H_2O$. Anal. Calcd. for $C_{21}H_{22}CdN_6O_7$ (**2**): C, 43.28; H, 3.80; N, 14.42%. Found: C, 43.21; H, 3.74; N, 14.35. IR data (cm^{-1}): 3386s, 3118vs, 1698w, 1598s, 1528s, 1505s, 1443m, 1389s, 1281s, 1243s, 1165m, 1104m, 1034w, 934w, 857m, 795m, 749m, 702w, 656m, 625m, 548w.

2.3. X-ray crystallography

All data collections were performed at the temperature of 193(2) K on a Rigaku Mercury CCD diffractometer with the ω-scan technique. The structures were solved by direct methods and refined with the full-matrix least-squares technique using the SHELXS-97 and SHELXL-97 programs [29]. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The hydrogen atoms from btp and phba ligands were generated geometrically. The hydrogen atoms from water molecules were obtained from difference Fourier maps. The crystallographic data for 1 and 2 are listed in Table 1. The selected bond lengths and angles for 1 and 2 are listed in Table 2.

3. Results and discussion

In the IR spectra, the conspicuous carboxylate stretching at 1605, 1505, 1454 and 1397 cm^{-1} in **1**, 1598, 1505, 1443 and 1389 cm^{-1} in **2**. **1** and **2** both present two groups of the antisymmetric ν_a(COO) and symmetric stretching

Table 1
Crystallographic data for **1** and **2**

Empirical formula	$C_{42}H_{40}N_{12}O_{12}Zn_2$	$C_{21}H_{22}CdN_6O_7$
Formula weight	1035.60	582.85
Temperature (K)	193(2)	193(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
a (Å)	10.750(2)	9.9743(12)
b (Å)	19.234(3)	11.0238(7)
c (Å)	11.432(3)	11.2144(9)
α	90	66.090(8)
β (°)	114.071(4)	77.431(9)
γ	90	83.062(9)
V (Å^3)	2158.3(7)	1099.51(17)
Z	2	2
F(000)	1064	588
ρ[g.cm^{-3}]	1.594	1.760
μ[mm^{-1}]	1.191	1.051
Crystal size [mm]	$0.38 \times 0.31 \times 0.19$	$0.40 \times 0.28 \times 0.15$
θ range for data collection (°)	3.05–25.34	3.17–25.35
Index ranges	$-12 \leqslant h \leqslant 12$, $-22 \leqslant k \leqslant 23$, $-13 \leqslant l \leqslant 12$	$-10 \leqslant h \leqslant 12$, $-12 \leqslant k \leqslant 13$, $-13 \leqslant l \leqslant 13$
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Independent reflections	3940[R(int) = 0.0337]	3981[R(int) = 0.0180]
Parameter	308	324
Max. and min. transmission	0.8053 and 0.6603	0.8582 and 0.6785
Goodness of fit S	1.095	1.014
Final R_1 and wR_2 [$I > 2\sigma(I)$]	0.0366 and 0.0855	0.0204 and 0.0519
R_1 and wR_2 indices (all data)	0.0419 and 0.0884	0.0225 and 0.0532
Largest diff. Peak and hole (e Å^{-3})	0.330 and −0.471	0.578 and −0.444

Table 2
Selected bond lengths (Å) and angles (°) for **1** and **2**

1			
Zn(1)–O(1)	2.153(2)	Zn(1)–O(2)	2.152(2)
Zn(1)–O(4)	1.9839(17)	Zn(1)–N(3)	2.066(2)
Zn(1)–N(6*A*)	2.064(2)		
O(2)–Zn(1)–O(1)	60.74(8)	O(4)–Zn(1)–O(1)	100.54(8)
O(4)–Zn(1)–O(2)	161.02(8)	N(6A)–Zn(1)–O(1)	143.96(8)
N(6*A*)–Zn(1)–O(2)	91.61(8)	O(4)–Zn(1)–N(6A)	103.95(8)
N(3)–Zn(1)–O(1)	107.80(8)	N(3)–Zn(1)–O(2)	92.86(9)
O(4)–Zn(1)–N(3)	96.37(8)	N(6A)–Zn(1)–N(3)	95.36(8)
2			
Cd(1)–O(1)	2.4841(14)	Cd(1)–O(2)	2.3054(14)
Cd(1)–O(4)	2.2916(14)	Cd(1)–O(7)	2.4502(17)
Cd(1)–N(3)	2.2574(16)	Cd(1)–N(6A)	2.2572(16)
O(2)–Cd(1)–O(1)	54.57(5)	N(3)–Cd(1)–O(1)	142.67(5)
N(6*A*)–Cd(1)–O(1)	95.41(5)	N(3)–Cd(1)–O(2)	91.03(5)
N(6*A*)–Cd(1)–O(2)	149.95(5)	N(3)–Cd(1)–N(6A)	117.27(6)
O(4)–Cd(1)–O(7)	159.74(6)	O(4)–Cd(1)–O(1)	82.38(5)
O(4)–Cd(1)–O(2)	88.28(5)	N(3)–Cd(1)–O(4)	113.75(6)
N(6*A*)–Cd(1)–O(4)	89.07(6)	O(7)–Cd(1)–O(1)	79.28(6)
O(2)–Cd(1)–O(7)	88.08(6)	N(3)–Cd(1)–O(7)	86.24(6)
N(6*A*)–Cd(1)–O(7)	84.17(6)		

Symmetry codes: A $-x+1, -y+1, -z+1$ for **1**; A $x, y, z-1$ for **2**.