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4,4′-Bipyridine-aided synthesis and characterization of Zn(II) and Cd(II) 2-sulfoterephthalate complexes

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ABSTRACT

Six d^{10} complexes, $[Zn_{1.5}(stp)(bpy)_{0.5}(H_2O)_2]\cdot0.5H_2O$ (**1**), $Cd_{1.5}(stp)(bpy)_{0.5}(H_2O)_2$ (**2**), $[Cd_{1.5}(stp)(bpy)(H_2O)]\cdot H_2O$ (**3**), $[Zn_{0.5}(bpy)_{0.5}(H_2O)_2][Zn(stp)(bpy)(H_2O)]\cdot0.5H_2O$ (**4**), $Cd_3(stp)_2(bpy)_3(H_2O)_3$ (**5**), $Hbpy\cdot[Zn_{0.5}(bpy)(H_2O)_2][Zn_{0.5}(stp)(H_2O)]\cdot H_2O$ (**6**) based on 2-sulfoterephthalate (stp^{3-}) and 4,4′-bipyridine (bpy) have been synthesized under hydro/solvo-thermal conditions and structurally characterized. Complex **1** exhibits a three-fold interpenetrated 3D porous architecture. Complexes **2** and **3** possess helices with different chirality arranging alternately. **4** and **6** are addition compounds, which compose of complex cation and complex anion. Complex **5** features a 3D layer-pillar framework in which a (4, 4) grid layer is constructed by stp^{3-} ligands and Cd(II) ions, and the layers are further connected by bpy pillars. The solid-state luminescent properties of the coordination polymers have also been investigated.

1. Introduction

In recent years, the investigations on how to design and synthesize metal-organic frameworks (MOFs) have been more and more extensive due to their intriguing structures and topologies as well as widespread applications in gas storage, catalysis, opticals, magnetism, and ion exchange [1,2]. It is well known that multidentate organic ligands acting as linkers are confirmed to play a vital role in the construction of MOFs. Among them, *p*-benzenedicarboxylic acid (*p*-H_2BDC) was found to be a good candidate to build various MOFs with novel topologies and properties [3]. Some reports have certified that the introduction of Lewis base groups such as amine and sulfonate groups in the neighboring site of linear *p*-BDC ligand will benefit to the assembly and decorations of porous materials or greatly increase the sorts of coordination modes of organic ligand [4]. Isoreticular porous metal-organic framework-3 (IRMOF-3), which was prepared from $Zn(NO_3)_2\cdot4H_2O$ and 2-amino-1,4-benzenedicarboxylic acid, has recently been a good example to certify the value of postsynthetic covalent modification that will develop more complex MOFs with a variety of functionalities by heterogeneous acylation of NH_2-groups [5]. While for the sulfonate group, reports about the metal 2-sulfoterephthalate (stp^{3-}) complexes are relatively rare due to hard propensity of the sulfonate group in ortho-position to interact with metal ions [6]. However, sulfonate group has intriguing properties since it has three oxygen coordination sites and is apt to adopt flexible coordination modes, which is helpful to forming helical structures or porous coordination polymers (PCPs) [7]. Kitagawa and his co-workers reported two 3D heterometallic PCPs $[CdNa(stp)(pyrazine)_{0.5}(H_2O)]\cdot H_2O$ and $[CdNa(stp)\ (dabco)_{0.5}(H_2O)]\cdot2H_2O$ and one hydroxyl-clusters PCP $[Zn_3(\mu_3\text{-}OH)_3(stp)(bpy)_{1.5}(H_2O)]\cdot EtOH\cdot2H_2O$. On one hand, the behavior that the sulfonate group tends to coordinate to alkali metal ions makes the whole stable 3D framework of heterometallic PCPs show Lewis acidic property, which benefits to confine basic guest molecules around Na(I) ions. On the other hand, when the sulfonate group is coordinatively-free in Zn(II) hydroxyl-clusters complex, the whole framework shows Lewis basic property and thus is in favor of fastening certain acidic guest molecules onto the surface of pores.

Meanwhile, it is common that bpy is often used for designing and constructing different kinds of coordination compounds [8]. It is able to play different roles in formation of the complexes when it adopts different coordination mode. It is most familiar for bpy ligand to adopt bridging coordination mode to link metal ions or metal clusters to form coordination polymers. And terminal bpy ligand affords one coordination site and acts as hydrogen bonding acceptor to construct supramolecular frameworks [9]. While for guest bpy, it often acts as template to build various structures when combined with hydrogen bondings and π–π stacking interactions [10]. It is well-known that Cd(II) and Zn(II) ions has great potential for construction of MOFs featuring interesting properties

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Table 1
Crystal data and structure refinement for complexes **1–6.**

Complex	**1**	**2**	**3**	**4**	**5**	**6**
Empirical formula	$C_{13}H_{12}NO_{9.5}SZn_{1.5}$	$C_{13}H_{11}Cd_{1.5}NO_9S$	$C_{18}H_{15}Cd_{1.5}N_2O_9S$	$C_{23}H_{21.50}N_3O_{10.50}SZn_{1.5}$	$C_{46}H_{36}Cd_3N_6O_{17}S_2$	$C_{28}H_{28}N_4O_{11}SZn$
Formula weight	464.35	525.89	603.98	638.05	1346.13	693.97
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic
space group	$C2/c$	$P2_1/c$	$C2/c$	$P\bar{1}$	$P2_1/n$	$P2_1/n$
a (Å)	25.0960(5)	11.5555(3)	14.9147(3)	7.51030(10)	17.7190(3)	10.1791(2)
b (Å)	8.6027(2)	12.3334(3)	11.9390(2)	11.2490(2)	13.8615(2)	13.9937(2)
c (Å)	18.8359(6)	12.1325(3)	22.4985(5)	16.5318(3)	19.5725(3)	19.6927(3)
α (°)	90	90	90	88.7870(10)	90	90
β (°)	130.5770(10)	111.400(2)	95.007(2)	85.2000(10)	99.7760(10)	90.4300(10)
γ (°)	90	90	90	72.3260(10)	90	90
V (Å^3)	3088.67 (14)	1609.89(7)	3990.94(14)	1326.06(4)	4737.43(13)	2805.01(8)
Z	8	4	8	2	4	4
D_c(g cm^{-3})	1.997	2.170	2.010	1.598	1.887	1.643
μ (mm^{-1})	2.540	2.179	1.774	1.508	1.505	1.022
F (0 0 0)	1872	1024	2376	651	2664	1432
R_1, wR_2 [$I > 2\sigma(I)$]	0.0382, 0.0911	0.0400, 0.0798	0.0348, 0.0667	0.0483, 0.1374	0.0402, 0.0813	0.0479, 0.1122
R_1, wR_2 (all data)	0.0567, 0.0994	0.0601, 0.0885	0.0521, 0.0736	0.0741, 0.1522	0.0638, 0.0912	0.0926, 0.1314

[11]. Based on the three coordination modes about bpy mentioned above, a reaction system composed of d^{10} metal ions, stp^{3-} and bpy with the same reaction ratio was selected. And no more than stoichiometric quantity of NaOH was added in the reaction system. In this paper we report bpy-aided syntheses of six d^{10} complexes, $[Zn_{1.5}(stp)(bpy)_{0.5}(H_2O)_2] \cdot 0.5H_2O$ (1), $Cd_{1.5}(stp)(bpy)_{0.5}(H_2O)_2$ (2), $[Cd_{1.5}(stp)(bpy)(H_2O)] \cdot H_2O$ (3), $[Zn_{0.5}(bpy)_{0.5}(H_2O)_2]$ $[Zn(stp)(bpy)(H_2O)] \cdot 0.5H_2O$ (4), $Cd_3(stp)_2(bpy)_3(H_2O)_3$ (5), Hbpy $\cdot$ $[Zn_{0.5}(bpy)(H_2O)_2][Zn_{0.5}(stp)(H_2O)] \cdot H_2O$ (6) and their structures and emission properties.

2. Experimental section

2.1. Materials and methods

All reagents were commercially available and used without further purification. The C, H, N microanalyses were carried out with a Vario EL elemental analyzer. The IR spectra were recorded in the range of 4000–400 cm^{-1} with a Nicolet Avatar 360 FT-IR spectrometer using the KBr pellet technique. The fluorescence spectra were recorded on a SHIMADZU RF-5301PC spectrofluorophotometer at room temperature. Diffraction intensities for complexes **1–6** were recorded with a Bruker SMART 1000 CCD diffractometer, employing graphite monochromated Mo-*K*α radiation (λ=0.71073 Å). Semiempirical absorption corrections were applied using the SADABS program [12]. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using SHELXS 97 and SHELXL 97 programs [13,14], respectively. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in geometrically calculated positions. Details of crystallographic data of complexes **1–6** are summarized in Table 1. Selected bond lengths and angles relevant to complexes **1–6** are listed in Table S1.

2.2. Synthesis

2.2.1. $[Zn_{1.5}(stp)(bpy)_{0.5}(H_2O)_2] \cdot 0.5H_2O$ (1)

A mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (0.015 g, 0.05 mmol), NaH_2stp (0.014 g, 0.05 mmol), bpy (0.0156 g, 0.10 mmol), NaOH solution (0.12 ml, 0.65 mol/l) and mixed solvent of 2 ml distilled water and 2 ml ethanol was sealed in a 25 ml Teflon-lined stainless steel autoclave and heated to 140 °C for 4 days. Colorless rod crystals were collected by filtration and washed by ethanol in 50.4% yield based on Zn(II). Elemental analysis (%) calcd. for $C_{13}H_{12}NO_{9.5}SZn_{1.5}$: C, 33.62; H, 2.60; N, 3.02; found: C, 33.76; H, 2.79; N, 3.02. IR data (KBr pellet, cm^{-1}): 3366(m), 1594(s), 1550(m), 1481(m), 1419(m), 1391(m), 1362(m), 1296(w), 1244(m), 1156(m), 1071(m), 1021(m), 859(m), 819(m), 781(m), 685(m), 625(m), 568(m), 525(m).

2.2.2. $Cd_{1.5}(stp)(bpy)_{0.5}(H_2O)_2$ (2)

Complex **2** was synthesized as the complex **1** except that the $Zn(NO_3)_2 \cdot 6H_2O$ was replaced by $Cd(NO_3)_2 \cdot 4H_2O$. Colorless rod crystals were collected by filtration and washed by ethanol in 79.9% yield based on Cd(II). Elemental analysis (%) calcd. for $C_{13}H_{11}Cd_{1.5}NO_9S$: C, 29.69; H, 2.11; N, 2.66; found: C, 29.67; H, 2.37; N, 2.59. IR data (KBr pellet, cm^{-1}): 3435(s), 1672(m), 1615(s), 1571(s), 1537(s), 1485(m), 1399(s), 1370(m), 1223(s), 1161(m), 1078(s), 1030(s), 847(m), 810(m), 798(m), 784(m), 687(m), 640(m), 627(s), 583(m), 562(m), 535(m), 516(m).

2.2.3. $[Cd_{1.5}(stp)(bpy)(H_2O)] \cdot H_2O$ (3)

Complex **3** was synthesized in a similar way to that for complex **1** except that $Zn(NO_3)_2 \cdot 6H_2O$ and the solvent were replaced by $Cd(NO_3)_2 \cdot 4H_2O$ and 2 ml distilled water, respectively. Colorless needle crystals were obtained and washed by ethanol in 80.0% yield based on Cd(II). Elemental analysis (%) calcd. for $C_{18}H_{15}Cd_{1.5}N_2O_9S$: C, 35.79; H, 2.50; N, 4.64; found: C, 36.07; H, 2.75; N, 4.13. IR data (KBr pellet, cm^{-1}): 3451(s), 3389(s), 1595(s), 1571(s), 1528(s), 1482(m), 1412(s), 1394(s), 1371(s), 1276(s), 1249(m), 1221(m), 1168(m), 1156(m), 1137(s), 1060(m), 986(s), 844(m), 813(m), 781(m), 772(m), 721(m), 679(m), 629(s), 583(m), 556(m), 529(m), 502(m).

2.2.4. $[Zn_{0.5}(bpy)_{0.5}(H_2O)_2][Zn(stp)(bpy)(H_2O)] \cdot 0.5H_2O$. (4)

A mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (0.015 g, 0.05 mmol), NaH_2stp (0.014 g, 0.05 mmol), bpy (0.0156 g, 0.10 mmol), NaOH solution (0.16 ml, 0.65 mol/l) and 5 ml distilled water was sealed in a 25 ml Teflon-lined stainless steel autoclave and heated to 100 °C for 4 days. Colorless rod crystals were obtained by filtration and washed by ethanol in 28.2% yield based on Zn(II). Elemental analysis (%) calcd. for $C_{23}H_{21.50}N_3O_{10.50}SZn_{1.5}$: C, 43.26; H, 3.47; N, 6.58; found: C, 42.82; H, 3.85; N, 6.36. IR data (KBr pellet, cm^{-1}): 3408(m), 1610(s), 1591(m), 1536(m), 1417(m), 1388(m), 1359(m), 1219(m), 1179(m), 1050(m), 1074(m), 1021(m), 821(m), 784(w), 683(m), 641(m).

2.2.5. $Cd_3(stp)_2(bpy)_3(H_2O)_3$ (5)

Complex **5** was synthesized as complex **4** except that $Zn(NO_3)_2 \cdot 6H_2O$ was replaced by $Cd(NO_3)_2 \cdot 4H_2O$ and the volume of distilled water was reduced to 2 ml. Colorless block crystals