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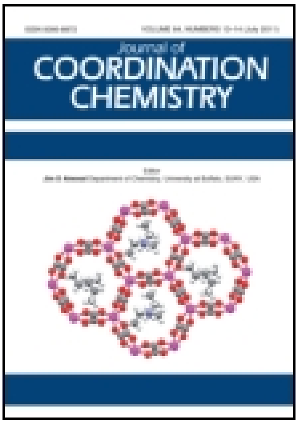

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Two photoluminescent pentanuclear homo- and hetero-metal complexes based on benzotriazole bridge

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Two photoluminescent pentanuclear homo- and hetero-metal complexes based on benzotriazole bridge

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Two new discrete Btz-bridged pentanuclear metal complexes, [HDMF][NaHg$_4$(Btz)$_6$I$_4$] (**1**) and [Zn$_5$(Btz)$_6$(L)$_3$(Ac)] · 0.5MeOH · 0.5H$_2$O (**2**) (Btz = deprotonated benzotriazole, L = *p*-aminobenzoate, HDMF = protonated DMF, and Ac = acetate), were synthesized using three-layered diffusion and natural evaporation methods, respectively. In **1**, the pentanuclear anion [NaHg$_4$(Btz)$_6$I$_4$]$^-$ is composed of a tetrahedral arrangement of four four-coordinate Hg(II) ions centered on the six-coordinate Na(I), and thereby forming a rare Btz-bridged hetero-metal complex. Compound **2** is a neutral pentanuclear homo-metal complex, consisting of a tetrahedral arrangement of four five-coordinate Zn(II) ions centered on the fifth six-coordinate Zn(II). The thermal stabilities and solid-state photoluminescence of the two complexes have been investigated.

Keywords: Pentanuclear metal complex; Benzotriazole; Crystal structure; Fluorescence; Thermal properties

1. Introduction

The development of routes and strategies for isolation of polynuclear complexes of transition metals has been a subject of interest over the last 15 years [1–5] because these compounds provide impetus for bioinorganic chemistry, solid-state physics, material science, and molecular magnetism [6–10]. The number of polynuclear transition metal complexes reported continues to grow rapidly, and novel nuclearity has been found [11]. Over the past 7 years, amine ligands have attracted special interest to construct extended metal–organic frameworks and polynuclear metal complexes. Those amine ligands cover a wide range from ammonia to 1-N heterocycles, such as pyrrole [12] and carbazole [13], 2-N derivatives, such as imidazole [14] and pyrazole, [15] and complicated spacers containing three or more nitrogens per ring. Among them, benzotriazole (HBtz), which has a special arrangement of coordinating bites and versatile coordination modes, has been extensively employed for syntheses of organic–inorganic hybrid materials [16]. As shown in scheme 1, there are three bridge modes between HBtz and metal ions; coordination modes A and B of HBtz usually link

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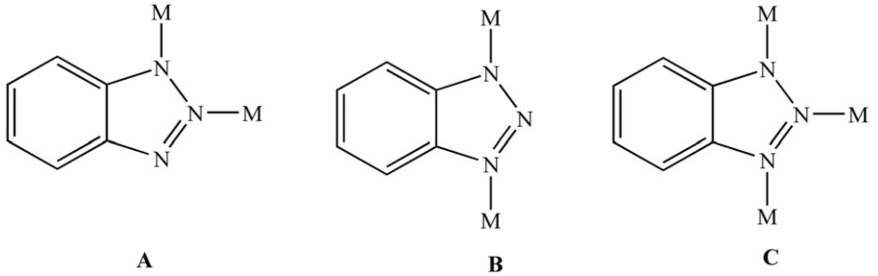

Scheme 1. Bridge coordination modes of Btz^-.

metal nodes into frameworks, while the mode C forms compact polynuclear metal complexes with the center nitrogen of HBtz linking metal ions located at the center [17]. In this article, we report syntheses, structures, and properties of two new Btz-bridged pentanuclear metal complexes, $[HDMF][NaHg_4(Btz)_6I_4]$ (**1**) and $[Zn_5(Btz)_6(L)_3(Ac)] \cdot 0.5MeOH \cdot 0.5H_2O$ (**2**) (Btz = deprotonated benzotriazole, L = *p*-aminobenzoate, HDMF = protonated DMF and Ac = acetate). In the structures of the two compounds, each deprotonated Btz in mode C forms three M–N bonds in an "arrowhead" structure motif [18]. The hetero-metal polynuclear complex **1** based on HBtz is especially rare.

2. Experimental

2.1. *Materials and physical measurements*

All chemicals were obtained commercially and used without purification. IR spectra (KBr pellets) were recorded on a Nicolet NEXUS 470 FT–IR spectrophotometer from 400 to 4000 cm^{-1}. Element analyses were performed with a Carlo-Erba 1106 elemental analyzer. The fluorescent spectra were determined in solid state at room temperature on a Hitachi F-4500 fluorophotometer. Thermal analysis curves were scanned from 35°C to 800°C under air on a STA 409 PC thermal analyzer.

2.2. *Syntheses*

2.2.1. Synthesis of $[HDMF][NaHg_4(Btz)_6I_4]$ (1). A DMF (3 mL) solution of HBtz (0.05 mmol, 6.0 mg) was carefully layered over an aqueous solution (5 mL) of HgI_2 (0.05 mmol, 22.7 mg) in a straight glass tube, and then an aqueous solution of NaOH (0.05 mol L^{-1}, 0.1 mL) as the top layer was dropwise transferred into the tube along its wall. After slow diffusion for 4 days, white crystals were obtained, washed with distilled water, and dried in air (Yield: 75%). Elemental Anal. Calcd (%) for $C_{39}H_{32}Hg_4I_4N_{19}NaO$ (2115.79): C, 22.14; H, 1.52; N, 12.58. Found (%): C, 22.41; H, 1.44; N, 12.44. IR (cm^{-1}, KBr): 3443(w), 2922(m), 1666(s), 1485(m), 1444(m), 1385(m), 1266(w), 1186(w), 1158(s), 778(m), 750(s), 640(m), 547(m).

Table 1. Crystal data and structure refinement for **1** and **2**.

Compounds	**1**	**2**
Empirical formula	$C_{39}H_{32}Hg_4I_4N_{19}NaO$	$C_{59.50}H_{48}N_{21}O_9Zn_5$
Formula weight	2115.79	1528.04
Temperature (K)	173(2)	296(2)
Crystal system	Tetragonal	Triclinic
Space group	$I\bar{4}$	$P\bar{1}$
Unit cell dimensions (Å, °)		
a	13.610(2)	15.364(4)
b	13.610(2)	15.874(7)
c	17.728(2)	17.054(4)
α	90	99.73(2)
β	90	115.98(2)
γ	90	102.49(2)
Volume (Å^3)	3283.7(7)	3482(2)
Reflections collected/unique	20236/2803 [R(int) = 0.0690]	45045/12149 [R(int) = 0.1639]
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0333$, $wR_2 = 0.0715$	$R_1 = 0.0769$, $wR_2 = 0.1773$
R indices (all data)	$R_1 = 0.0499$, $wR_2 = 0.0793$	$R_1 = 0.2374$, $wR_2 = 0.2519$
Goodness-of-fit on F^2	1.028	0.916

2.2.2. Synthesis of $[Zn_5(Btz)_6(L)_3(Ac)] \cdot 0.5MeOH \cdot 0.5H_2O$ (2). A mixture of $Zn(Ac)_2$ (0.1 mmol, 22.0 mg), BtzH (0.05 mmol, 6.0 mg), *p*-aminobenzoic acid (0.05 mmol, 6.8 mg), and methanol (8 mL) was refluxed for 30 min with vigorous stirring. After filtration, the filtrate was allowed undisturbed evaporation at ambient temperature. One week later, white crystals were collected, washed with distilled water, and dried in air (Yield: 56%). Elemental Anal. Calcd (%) for $C_{59.50}H_{48}N_{21}O_9Zn_5$ (1528.04): C, 46.77; H, 3.17; N, 19.25. Found (%): C, 46.87; H, 3.02; N, 19.55. IR (cm^{-1}, KBr): 3430(s), 1606(s), 1493(w), 1448(m), 1277(m), 1181(s), 1067(m), 785(s), 748(s), 645(w), 557(m).

2.3. *Crystal structure determination*

Suitable single crystals of **1** and **2** were selected for single-crystal X-ray diffraction analyses. The intensity data were measured on a Bruker Smart APEXII CCD imaging plate area detector with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods and expanded using Fourier techniques. All data were collected at room temperature using the ω-2θ scan technique and corrected for Lorenz-polarization effects. The non-hydrogen atoms were refined with anisotropic thermal parameters and the hydrogens were treated as idealized contributions, except those of water and the partial atoms in disordered solvent. All calculations were performed using the SHELX-97 crystallographic software package [19]. Crystal data are summarized in detail in table 1. Selected bond lengths and angles are listed in table 2.

3. Results and discussion

3.1. *Crystal structures of [HDMF][NaHg$_4$(Btz)$_6$I$_4$] (1) and [Zn$_5$(Btz)$_6$(L)$_3$(Ac)] · 0.5MeOH · 0.5H$_2$O (2)*

Complex **1** crystallizes in a non-centered space group $I\bar{4}$. The structural features of **1** are illustrated in figures 1 and 2. The asymmetric unit consists of one Hg(II),

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

1			
Hg(1)–N(2)	2.287(8)	Hg(1)–N(5)	2.288(8)
Hg(1)–N(3A)	2.336(9)	Hg(1)–I(1)	2.6089(9)
Na(1)–N(1B)	2.435(9)	Na(1)–N(1A)	2.435(9)
Na(1)–N(1)	2.435(9)	Na(1)-N(1C)	2.435(9)
Na(1)–N(4A)	2.483(11)	Na(1)–N(4)	2.483(11)
N(2)–Hg(1)–N(3A)	96.8(4)	N(2)–Hg(1)–N(3A)	96.1(3)
N(5)–Hg(1)–N(3A)	97.8(4)	N(2)–Hg(1)–I(1)	124.0(2)
N(5)–Hg(1)–I(1)	120.3(2)	N(3A)–Hg(1)–I(1)	116.3(3)
N(1B)–Na(1)–N(1A)	178.7(5)	N(1A)–Na(1)–N(1)	90.007(6)
N(1B)–Na(1)–N(1C)	90.007(6)	N(1A)–Na(1)–N(1C)	90.007(6)
N(4A)–Na(1)–N(4)	180.0		
2			
Zn(1)–O(2)	1.955(14)	Zn(1)–N(21)	1.988(9)
Zn(1)–N(15)	2.008(9)	Zn(1)–N(1)	2.013(9)
Zn(1)–O(1)	2.47(2)	Zn(2)–O(4)	1.988(9)
Zn(2)–N(18)	2.005(9)	Zn(2)–N(3)	2.028(9)
Zn(2)–N(5)	2.069(10)	Zn(2)–O(3)	2.320(11)
Zn(3)–N(19)	2.043(9)	Zn(3)–N(9)	2.059(9)
Zn(3)–N(7)	2.056(10)	Zn(3)–O(5)	2.082(11)
Zn(3)–O(6)	2.181(10)	Zn(4)–O(8)	1.989(8)
Zn(4)–N(13)	2.002(9)	Zn(4)–N(11)	2.041(9)
Zn(4)–N(16)	2.063(9)	Zn(4)–O(7)	2.339(10)
Zn(5)–N(6)	2.175(10)	Zn(5)–N(20)	2.177(8)
Zn(5)–N(10)	2.183(9)	Zn(5)–N(14)	2.183(9)
Zn(5)–N(17)	2.197(8)	Zn(5)–N(2)	2.190(9)
O(2)–Zn(1)–N(15)	112.0(6)	N(21)–Zn(1)–N(15)	100.9(4)
N(21)–Zn(1)–O(1)	94.0(5)	N(15)–Zn(1)–O(1)	107.9(5)
O(4)–Zn(2)–N(18)	120.1(4)	O(4)–Zn(2)–N(3)	132.0(4)
N(18)–Zn(2)–N(3)	101.5(4)	N(18)–Zn(2)–N(5)	98.2(4)
N(9)–Zn(3)–N(7)	99.5(4)	N(9)–Zn(3)–O(5)	142.7(5)
N(19)–Zn(3)–O(6)	154.6(4)	N(7)–Zn(3)–O(5)	111.4(5)
O(8)–Zn(4)–N(13)	130.5(4)	O(8)–Zn(4)–N(11)	122.3(4)
N(13)–Zn(4)–N(11)	101.4(4)	N(16)–Zn(4)–O(7)	157.7(4)
N(6)–Zn(5)–N(14)	177.5(4)	N(10)–Zn(5)–N(17)	90.0(3)
N(20)–Zn(5)–N(2)	90.2(3)	N(17)–Zn(5)–N(2)	90.6(3)

Symmetry transformations used to generate equivalent atoms: (**1**) A *y*, −*x*, −*z*; B −*x*, −*y*, *z*; C −*y*, *x*, −*z*.

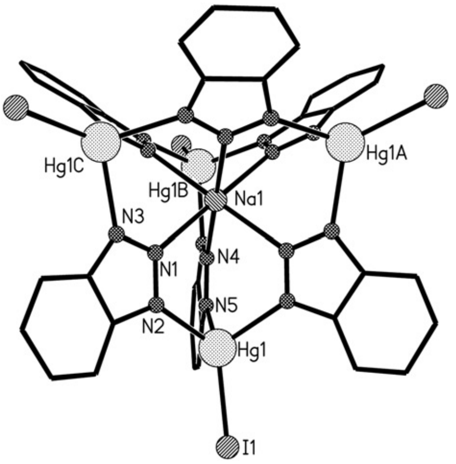

Figure 1. The structure of Btz-bridged pentanuclear **1**.

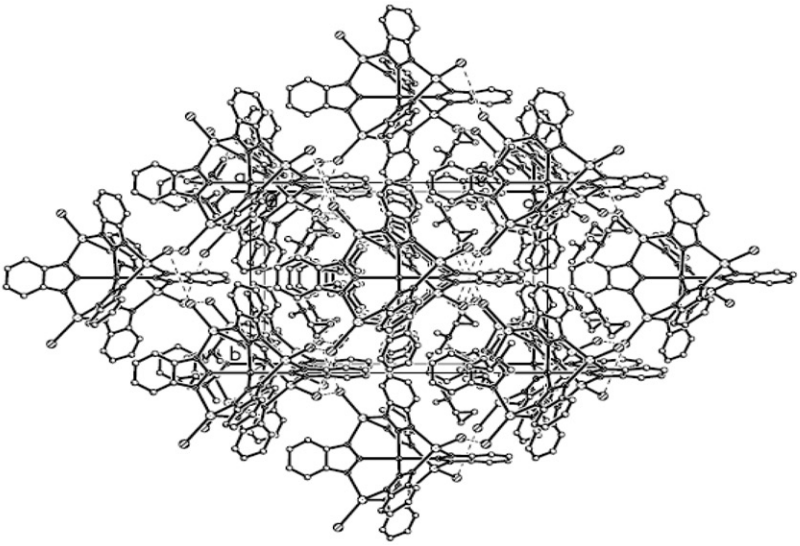

Figure 2. Packing style of pentanuclear units *via* I $\cdots$ I and C–H $\cdots$ I interactions with protonated HDMF as counterions residing in the resultant apertures.

one-quarter Na(I), one-and-a-half Btz, one I^- anion, and one-quarter HDMF cation. The composition of **1** is in good agreement with elemental analysis. The existence of protonated DMF was supported by the sensitive IR spectrum. In the IR spectrum of **1**, the strong peak centered at $1666\,\mathrm{cm}^{-1}$ is attributed to a typical adsorption of CO in DMF and the peak at $3443\,\mathrm{cm}^{-1}$ can be attributed to the vibration of N–H in the protonated DMF. Furthermore, protonated DMF are counterions as found in some other complexes, such as $(\mathrm{HDMF})_n[\mathrm{Ag}_3(\mathrm{Mo}_8\mathrm{O}_{26})(\mathrm{dmf})_4]_n$, which was also determined by X-ray single-crystallographic analysis [20]. As depicted in figure 1, the pentanuclear anion in **1** consists of a tetrahedral arrangement of four four-coordinate Hg(II) ions centered on a six-coordinate Na(I) ion, forming a novel Btz-bridged hetero-metal polynuclear complex. Each Btz anion in mode C spans an edge of the tetrahedron and is further ligated to the central Na(I) *via* its central nitrogen to form a slightly distorted NaN_6 octahedron. Each apical Hg(II) adopts a distorted tetrahedral coordination geometry bound by three nitrogens from three μ_3-Btz and one terminal I^-. The bond distances of Hg–N range from 2.287(8) to 2.336(9) Å and the Hg–I bond distance is 2.6089(9) Å. The intra-ring angles N–Hg–N cover a slight range from 96.1(3) to 97.9(3)°. For the central Na(I), the Na–N bond distances in the equatorial plane are 2.435(9) Å, while the Na–N bond distances in the axial sites are 2.483(11) Å. The in-plane and axis-transition angles of N–Na–N are 178.7(5)° and 180.0(0)°, respectively. The distortion of the tetrahedral array of Hg(II) can be measured by the separations of the apical Hg(II) ions. Four edges of the tetrahedron are 6.372 Å whereas the other two are 6.314 Å. The distances between the central Na(I) and each apical Hg(II) are 3.890 Å. The hetero-metal pentanuclear anion of **1** has S_4 symmetry with a $\bar{4}$ axis passing through the central Na(I) along the *c*-axis. *Via* I $\cdots$ I and C–H $\cdots$ I interactions, those pentanuclear anions pack with protonated DMF as counterions residing in the resultant apertures (figure 2).

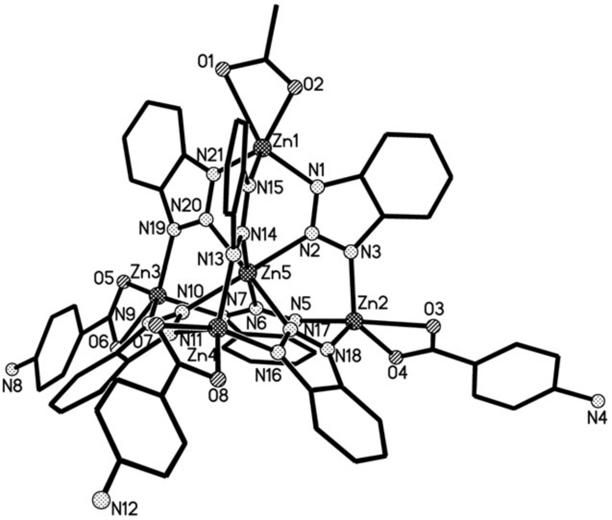

Figure 3. The structure of Btz-bridged pentanuclear **2**.

Complex **2** was synthesized from the reactions of $Zn(Ac)_2$, HL, and HBtz. In contrast to **1**, **2** crystallizes in the triclinic space group $P\bar{1}$ and each asymmetric unit consists of five Zn(II), six Btz, three L, one Ac, a-half lattice methanol, and water. The crystal structure of **2** is illustrated in figures 3 and 4. As shown in figure 3, the structural unit of **2** is also a Btz-bridged pentanuclear metal complex, but formed by the same metal. Very similar to **1**, six Btz anions in mode C link with four apical Zn(II) spanning the edges of a tetrahedron and is further ligated to the central Zn(II) *via* its central nitrogen. All apical Zn(II) ions in a N_3O_2 coordination sphere ligated by three μ_3-Btz and one chelating carboxylic group from L or Ac adopt a distorted trigonal-bipyramidal or square-pyramidal coordination symmetry (Zn–N: 1.998(9)–2.069(10) Å; Zn–O: 1.955(14)–2.47(2) Å; intra-ring angles are N–Zn–N: 93.7(4)–101.5(4)° and O–Zn–O: 54.5(6)–60.8(4)°). The central Zn5 has a slightly tetragonally distorted (4 + 2) octahedral coordination geometry with Zn–N bond distances ranging from 2.175(10) to 2.197(8) Å and the in-plane and axis-transition angles being 177.5(4)°, 178.7(4)°, and 179.3(4)°, respectively. The separations between the apical Zn(II) cover a range from 5.819 to 5.879 Å while the separations between the apical Zn(II) and the central Zn(II) range from 3.549 to 3.598 Å. As presented in figure 4(a), neutral pentanuclear units in **2** stack *via* π–π interactions between the benzotriazole rings with a centroid-to-centroid distance of 3.86(1) Å. Lattice molecules, such as methanol and water, reside in the formed cavities (shown in figure 4b).

Compared with **1** and other homo-metal compounds of Co(II), Ni(II), and Cu(II) with higher symmetry, neutral pentanuclear **2** only has C_1 symmetry [21]. Compound **1** is the first case containing μ_3-Btz-bridged hetero-metal pentanuclear anion. Compared with some homo-metal complexes of Hbtz ligands reported, such as pentanuclear complex $[Cu_5(btz)_6(trop)_4]$ [22] and 2-D frameworks $[Zn_2(btz)_4]_n$ [23] and $[Zn_4(PQCA)_4(btz)_4\text{-}(bpy)_2]_n$ [24], to some extent, the structure of **2** is very similar to that of $[Cu_5(btz)_6(trop)_4]$.

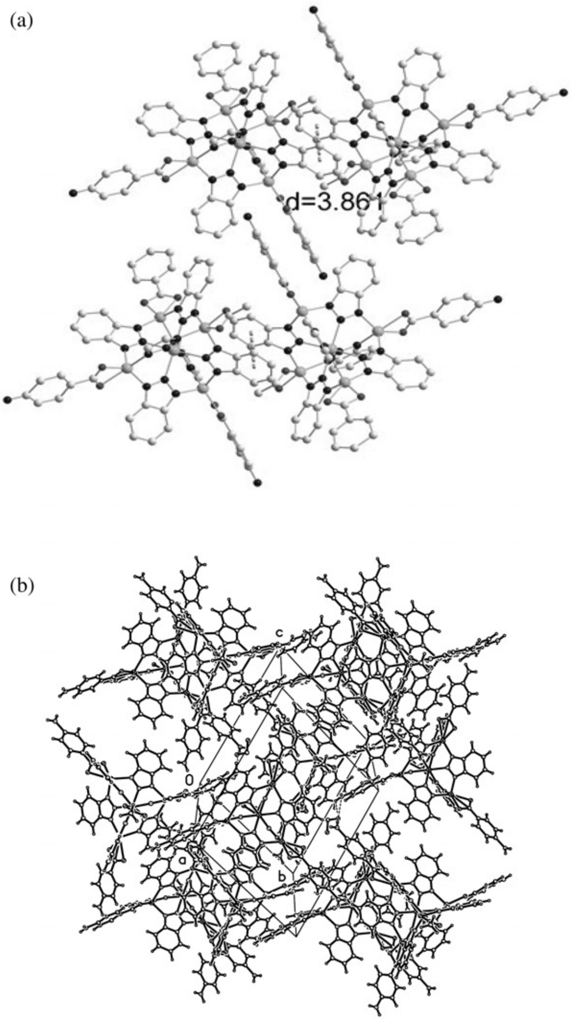

Figure 4. (a) Face-to-face π–π interactions between the benzotriazole rings, and (b) stack of neutral pentanuclear units in **2**.

3.2. *Thermogravimetric analysis*

Complexes **1** and **2** show different thermal behaviors. For **1** there is one small endothermic peak at 279.5°C and one very small exothermic peak at 571.6°C in the DSC curve, clearly two steps (Supplementary material). The first weight loss of 86.0% occurs from 184.2°C to 320°C corresponding to complete decomposition of the pentanuclear unit. The second step starts at 570–624°C with a smaller weight loss corresponding to a continuous decomposition. The 3.5% residue may be Na_2O and unburned carbon. Clearly, the pentanuclear unit in **1** is rather stabile, retaining integrity of the skeleton below 184.2°C.

For **2**, there is one small endothermic peak at 440.4°C and a small exothermic peak at 581.8°C in the DSC curve (Supplementary material). The initial weight loss of 1.64%

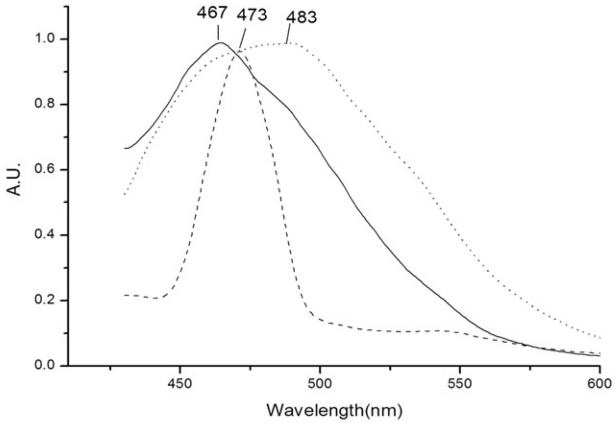

Figure 5. Solid-state photoluminescence spectra of free HBtz, **1** and **2** at room temperature (solid, dash and dot lines for HBtz, **1** and **2**, respectively).

below 100°C is ascribed to the loss of solvent occluded in the crystal lattice. Above 100°C, weight loss continues until 605°C, indicating slow decomposition of the pentanuclear unit. Finally, a white amorphous residue of ZnO remains (observed 26.56%, calculated 26.51%).

3.3. *Determination of photoluminescent properties*

Solid-state photoluminescence spectra of **1** and **2** as well as HBtz are described in figure 5 at room temperature. Compound **2** has a broad emission band at 460–500 nm with a maximum at 483 nm upon excitation at 319 nm; **1** has a similar emission with the maximum at 473 nm upon excitation at the same wavelength. Excited at 403 nm, a notable emission band with a maximum at 467 nm for free HBtz was observed. Compared with HBtz, the fluorescence intensities of **1** and **2** are slightly enhanced and their emission wavelengths slightly red shifted by 7 and 16 nm, respectively. Tentatively, emission of **1** and **2** is ascribed to metal-perturbed ligand-centered emission as found in many reported complexes of d^{10} metals and N-containing hetero-ring ligands [25].

4. Conclusions

Two complexes of Btz-bridged pentanuclear d^{10} metals were isolated and structurally determined. Complex **1** consists of a rarely-reported hetero-metal pentanuclear anion formed by μ_3-Btz, while **2** is a neutral pentanuclear homo-metal compound. HBtz can form extended frameworks in hydro(solvo)thermal conditions while it can construct pentanuclear complexes through traditional solution methods, such as in our case. The coordination of the central nitrogen of HBtz with a metal directs the formation of polynuclear complexes, playing a key role in dimensional control. This is a strategy to design polynuclear complexes through coordination direction of ligands as exemplified in the literature [26]. In addition, both complexes can emit photoluminescence; thermogravimetric analyses show their pentanuclear units have stability.

Supplementary material

Crystallographic information of **1** and **2** has been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 801627 and 801628. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

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References

[1] R.E.P. Winpenny. *Dalton Trans*., 1 (2002).

[2] E. Libby, K. Folting, C.J. Huffman, J.C. Huffman, G. Christou. *Inorg. Chem*., **32**, 2549 (1993).

[3] G.L. Abbati, A. Cornia, A.C. Fabretti, A. Caneschi, D. Gatteschi. *Inorg. Chem*., **37**, 1430 (1998).

[4] G. Aromi, P.C. Berzal, P. Gamez, O. Roubeau, H. Kooijman, A.L. Spek, W.L. Driessen, J. Reedijk. *Angew. Chem. Int. Ed*., **40**, 3444 (2001).

[5] S. Herold, S.J. Lippard. *Inorg. Chem*., **36**, 50 (1997).

[6] S.J. Lippard, J.M. Berg. *Principles of Bioinorganic Chemistry*, University Science Books, Mill Valley, CA (1994).

[7] R.M. Cinco, A. Rompel, H. Visser, G. Aromi, G. Christou, K. Sauer, M.P. Klein, V.K. Yachandra. *Inorg. Chem*., **38**, 5988 (1999).

[8] D. Gatteschi, R. Sessoli, A. Cornia. *Chem. Commun*., 725 (2000).

[9] G. Christou, D. Gatteschi, D.N. Hendrickson, R. Sessoli. *MRS Bull*., **25**, 1 (2000).

[10] E. Coronado, C.J. Gómez-Garcia. *Chem. Rev*., **98**, 273 (1998).

[11] E.K. Brechin, A. Graham, A. Parkin, S. Parsons, A.M. Seddon, R.E.P. Winpenny. *Dalton Trans*., 3242 (2000).

[12] M. Ganesan, C.D. Berube, S. Gambarotta, G.P.A. Yap. *Organometallics*, **2**, 1707 (2002).

[13] K. Müller-Buschbaum, C.C. Quitmann. *Z. Inorg. Allg. Chem*., **629**, 1610 (2003).

[14] W.J. Evans, G.W. Rabe, J.W. Ziller. *Inorg. Chem*., **33**, 3072 (1994).

[15] G.B. Deacon, A. Gitlits, B.W. Skelton, A.H. White. *Chem. Commun*., 1213 (1999).

[16] (a) L.F. Jones, E.K. Brechin, D. Collison. *Chem. Commun*., 2974 (2002); (b) D.M. Low, L.F. Jones, E.K. Brechin. *Angew. Chem. Int. Ed*., **42**, 3781 (2003); (c) L.F. Jones, E.K. Brechin, D. Collison. *Inorg. Chem*., **42**, 6971 (2003); (d) L.F. Jones, G. Rajaraman, D. Collison. *Chem. Eur. J*., **10**, 5180 (2004); (e) L.F. Jones, J. Raftery, S.J. Teat, D. Collison. *Polyhedron*, **24**, 2443 (2005); (f) J. Tabernor, L.F. Jones, D. Collison. *Dalton Trans*., 975 (2004).

[17] E.K. Brechin, A. Graham, A. Parkin, S. Parsons, A.M. Seddon, R.E.P. Winpenny. *Dalton Trans*., 3242 (2000).

[18] J. Handley, D. Collison, C.D. Garner, M. Helliwell, R. Docherty, J.R. Lawson, P.A. Tasker. *Angew. Chem. Int. Ed*., **32**, 1036 (1993).

[19] G.M. Sheldrick. *SHELX-97, Program for the Solution and Refinement of Crystal Structures*, University of Göttingen, Germany (1997).

[20] H. Abbas, A.L. Pickering, D.L. Long, P. Kögerler, L. Cronin. *Chem. Eur. J*., **11**, 1071 (2005).

[21] (a) Y.L. Bai, J. Tao, R.B. Huang, L.S. Zheng. *Angew. Chem. Int. Ed.*, **47**, 5344 (2008); (b) E. Diamantopoulou, C.P. Raptopoulou, A. Terzis, V. Tangouls, S.P. Perlepes. *Polyhedron*, **21**, 2117 (2002); (c) P. Tasker, A. Parkin, T.C. Higgs, S. Parsons, D. Messenger. *Private Communication* (2005).

[22] M. Murrie, D. Collison, C.D. Garner, M. Helliwell, S.S. Turner. *Polyhedron*, **17**, 3031 (1998).

[23] R.F. Hu, J. Zhang, Y. Kang, Y.G. Yao. *Inorg. Chem. Commun.*, **8**, 828 (2005).

[24] Y.C. Shen, Z.J. Li, J.K. Cheng, Y.Y. Qin, Y.G. Yao. *Inorg. Chem. Commun.*, **10**, 888 (2007).

[25] (a) Y. Wang, M.C. Hu, Q.G. Zhai, S.N. Li, Y.C. Jiang, W.J. Ji. *Inorg. Chem. Commun.*, **12**, 283 (2009); (b) X.R. Meng, S.Z. Jin, H.W. Hou, C.X. Dua, S. W. Ng. *Inorg. Chim. Acta*, **362**, 1524 (2009); (c) X.Y. Zhou, Y.Q. Huang, W.Y. Sun. *Inorg. Chim. Acta*, **362**, 1403 (2009).

[26] (a) H. Hou, Y. Wei, Y. Song, L. Mi, M. Tang, L. Li, Y. Fan. *Angew. Chem. Int. Ed.*, **44**, 6067 (2005); (b) X.Q. Shen, H.C. Yao, R. Yang, Z.J. Li, H.Y. Zhang, B.L. Wu, H.W. Hou. *Polyhedron*, **27**, 203 (2008); (c) S. Zhu, X.M. Sun, Y.Z. Li, B.L. Wu, H.Y. Zhang. *J. Coord. Chem.*, **63**, 4236 (2010).