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Synthesis, structures, and fluorescence properties of two d-d heterometallic cluster-based complexes constructed by *N*-(phosphonomethyl) iminodiacetic acid

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ABSTRACT

Two novel d-d heterometallic cluster-based complexes constructed by *N*-(Phosphonomethyl)iminodiacetic acid (H_4PMIDA) multifunctional ligand, $[Cu_2Zn_2(PMIDA)_2(H_2O)_3]\cdot 3H_2O$(**1**), $[ZnNi_{14}(PMIDA)_6(H_2O)_{18}]\cdot(NO_3)_6\cdot 15H_2O$(**2**), have been synthesized under hydrothermal conditions and characterized by elemental analyses, IR spectra, thermal analyses, and single-crystal X-ray diffraction. The complex 1 is one-dimensional heteronuclear molecular chain, which is further extends into a 3D supramolecular network through very extensive O–H···O hydrogen bonds. The compound 2 is a rare novel zero-dimensional heteronuclear molecular cluster, which is further extends into a 3D supramolecular network through very extensive O–H···O hydrogen bonds. Moreover, the solid-state fluorescence properties of the two complexes have also been investigated at room temperature.

1. Introduction

The design and synthesis of heterometallic coordination polymers have spurred considerable attentions because of their multiplicity in topological structures and significant physical properties including catalysis, luminescence and magnetism [1–4]. As a consequence, transition–transition (d–d) and transition–rare earth metal (d–f) heterometallic frameworks have been reported widely [5–9]. At present, much attention has been focused on heterometallic structures with nitrogen-containing carboxylate linkers, only very few reports have dealt with heterometallic coordination polymers with phosphonic acid, especially the functionalized phosphonates such as carboxyphosphonates and nitrogen-containing phosphonates used for the construction of higher dimensional heterometallic structures, because of their variety of diverse coordinating sites and modes with different affinities towards different metal centers [10–14]. Studies have suggested that assembly of Zn(II) ions and carboxylate ligands can easily generate a variety of secondary building units (SBUs) varying from Zn(II) monomers to small di-, tri-, tetranuclear clusters, and even rod-shaped chains [15]. However, Zn(II)–M(II) based on clusters (M = Cu, Ni) constructed by *N*-(phosphonomethyl)iminodiacetic acid (H_4PMIDA) are extremely rare.

Herein, we report the synthesis and crystal structures of two d-d heterometallic cluster-based complexes constructed by *N*-(Phosphonomethyl)imino-diacetic acid (H_4PMIDA), $[Cu_2Zn_2(PMIDA)_2(H_2O)_3]\cdot 3H_2O$ (1) and $[ZnNi_{14}(PMIDA)_6(H_2O)_{18}]\cdot(NO_3)_6\cdot 15H_2O$ (2).

2. Experimental

2.1. Materials and physical measurements

All the chemical reagents used in our experiments were of analytical grade and were used without further purification. The obtained samples have been characterized by elemental analyses (determined on Vario EL III Elemental Analyzer), FT-IR spectroscopy (recorded over the 400 to 4000 cm^{-1} region on a Nicolet NEXUS 670 spectrometer with KBr pellets at room temperature) and thermogravimetric analysis (TGA) (performed on a SDT Q600 thermal analyzer under a nitrogen atmosphere with a heating rate of 10 °C min^{-1}).

2.2. Synthesis of compound **1**

A mixture of $Cu(Ac)_2\cdot H_2O$ (150 mg, 0.75 mmol), $Zn(NO)_3\cdot 6H_2O$ (220 mg, 0.75 mmol), H_4PMIDA (70 mg, 0.3 mmol), and 4 mL of H_2O

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Table 1
Crystallographic data and structure refinement for 1 and 2.

Compounds	1	2
Formula	$C_{10}H_{18}Cu_2N_2O_{20}P_2Zn_2$	$C_{30}H_{102}Ni_{14}N_{12}O_{93}P_6Zn$
fw	799.98	3192.1151
T/K	293(2)	293(2)
Crystal system	Monoclinic	Trigonal
Space group	*Cc*	R-3
a/Å	11.9366(13)	26.8233(8)
b/Å	21.266(2)	26.8233 (8)
c/Å	9.5053(9)	12.0565(5)
α/°	90	90
β/°	95.511(8)	90
γ/°	90	120
V/Å^3	2401.7(4)	7512.4(4)
Z	4	3
Dc/g cm^{-3}	2.212	2.097
F(000)	1576	4776
GOF on F^2	1.068	1.031
Reflection/unique	4735/3340	7073/2917
R_1,wR_2 [$I > 2$ (I)]	0.0452, 0.1019	0.0428, 0.1058
R_1,wR_2 (all data)	0.0492, 0.1058	0.0565, 0.1117

was stirred in air for 0.5 h. The pH value of the mixture was adjusted by adding $NH_3 \cdot H_2O$ (1 M) to 3.5. The resulting solution was heated in scintillation flask at 100 °C for 7 days. After a period of approximately 48 h cooling to room temperature, the blue square single crystals were recovered by filtration, washed with deionized water and ethanol respectively, and dried in air at ambient temperature. Anal. found/calcd: C, 14.89/14.79; N, 3.46/3.45; H, 3.09/2.98 for 1. FT-IR (KBr, cm^{-1}): 3436(s), 2929(w), 2856(w), 1626(s), 1578(s), 1394 (s), 1305(m), 1075(s), 998(m), 927(w), 864(w), 747(w), 582(w), and 505 (w).

2.3. Synthesis of compound **2**

A mixture of $Ni(NO_3)_2 \cdot 6H_2O$ (220 mg, 0.75 mmol), $Zn(NO_3)_2 \cdot 6H_2O$ (220 mg, 0.75 mmol), H_4PMIDA (70 mg, 0.3 mmol), and 3 mL of H_2O was stirred in air for 0.5 h. The pH value of the mixture was adjusted by adding $NH_3 \cdot H_2O$ (1 M) to 6.0. The resulting solution was heated in scintillation flask at 100 °C for 5 days. After a period of approximately 48 h cooling to room temperature, the light green block single crystals were recovered by filtration, washed with deionized water and ethanol respectively, and dried in air at ambient temperature. Anal. Found/calcd: C, 11.27/11.29; N, 5.32/5.27; H, 3.20/3.22 for 2; FT-IR (KBr, cm^{-1}): 3435(s), 2954(w), 2914(w), 1610(s), 1385(w), 1250(w), 1122(w), 1052(m), 968(w), 729(w), 643(w), and 567(w).

2.4. Determination of crystal structures

Crystals of 1 (dimensions 0.23 × 0.15 × 0.12 mm^3) and 2 (dimensions 0.23 × 0.21 × 0.16 mm^3) were carefully selected under an optical microscope, and data collection were performed on a CrysAlisPro, Oxford Diffraction Ltd, Version 1.171.34.36 CCD automatic

Table 2
Selected bond lengths (Å) and angles (°) for 1 and 2.[a]

1			
Cu(1)–O(1)	1.870(8)	Zn(1)–O(9)	1.915(6)
Cu(1)–O(3w)	1.993(9)	Zn(1)–O(11)#1 1.928(6)	1.928(6)
Cu(1)–O(2w)	2.014(7)	Zn(1)–O(13)#1	1.974(6)
Cu(1)–O(1w)	2.251(8)	Zn(1)–N(2)#1	2.031(6)
Cu(1)–O(13)#1	2.056(6)	Zn(1)–O(10)#1	2.352(7)
Zn(2)–O(5)#1	1.909(6)	Zn(2)–O(4)	1.969(5)
Zn(2)–O(6)	1.959(6)	Zn(2)–N(1)	2.023(7)
O(1)–Cu(1)–O(3W)	160.3(4)	O(13)#1–Cu(1)–O(1W)	91.5(2)
O(1)–Cu(1)–O(2W)	96.8(3)	N(2)#1–Zn(1)–O(10)#1	87.3(3)
O(3W)–Cu(1)–O(2W)	89.3(4)	O(5)#1–Zn(2)–O(6)	105.1(3)
O(1)–Cu(1)–O(13)#1	88.3(3)	O(5)#1–Zn(2)–O(4)	87.9(2)
O(3W)–Cu(1)–O(13)#1	84.7(3)	O(6)–Zn(2)–O(4)	163.9(2)
O(2W)–Cu(1)–O(13)#1	173.8(4)	O(5)#1–Zn(2)–N(1)	171.0(3)
O(1)–Cu(1)–O(1W) 97.6(3)	97.6(3)	O(6)–Zn(2)–N(1)	83.2(3)
O(3W)–Cu(1)–O(1W)	100.9(3)	O(4)–Zn(2)–N(1)	84.5(2)
O(2W)–Cu(1)–O(1W)	91.5(3)		
2			
Zn(1)–O(2)#1	2.123(3)	O(2)#1–Zn(1)–O(2)#2	84.22(12)
Zn(1)–O(2)#2	2.123(3)	O(2)#1–Zn(1)–O(2)#3	180.00(15)
Zn(1)–O(2)#3	2.123(3)	O(2)#1–Zn(1)–O(2)	95.78(12)
Zn(1)–O(2)	2.123(3)	O(2)#2–Zn(1)–O(2)	84.22(12)
Zn(1)–O(2)#4	2.123(3)	O(2)#2–Zn(1)–O(2)#4	95.78(12)
Zn(1)–O(2)#5	2.123(3)	O(2)–Zn(1)–O(2)#4	180.00(12)
Ni(1)–O(1)	1.986(3)	O(2)#4–Zn(1)–O(2)#5	84.22(12)
Ni(1)–O(1)#1	1.986(3)	O(1)–Ni(1)–O(1)#1	101.06(13)
Ni(1)–O(1)#5	1.986(3)	O(3)–Ni(2)–O(6)#2	89.87(14)
Ni(2)–O(3)	2.059(4) 2.059(4) O(2)	O(3)–Ni(2)–O(5)	78.59(13)
Ni(2)–O(6)#2	2.085(4) 2.085(4) O(2)#1	O(6)#2–Ni(2)–O(5)	102.90(14)
Ni(2)–O(5)	2.115(4) 2.115(4) O(2)#2	O(3)–Ni(2)–N(1)	148.47(15)
Ni(2)–O(2)	2.133(3) 2.133(3) O(2)#3	O(5)–Ni(2)–N(1)	74.73(15)
Ni(2)–N(1)	2.173(4) 2.173(4) 2.173(4) 2.173(4) 2.173(4) 2.173(4) 2.173(4) O(2)	N(1)–Ni(2)–O(6)	109.12(15)
Ni(2)–O(6) 2.181(4) O(2)#4	2.181(4)	O(1W)–Ni(3)–O(3W)	90.3(2)
Ni(3)–O(1W) 2.021(5) O(1)	2.021(5)	O(1W)–Ni(3)–O(7)	92.0(2)
Ni(3)–O(5) 2.032(4) O(1)	2.032(4)	O(3W)–Ni(3)–O(7)	177.11(17)
Ni(3)–O(3W) 2.042(4) O(1)#1	2.042(4)	O(5)–Ni(3)–O(2W)	90.79(19)
Ni(3)–O(7) 2.074(4) O(3)	2.074(4)	O(7)–Ni(3)–O(2W)	86.23(19)
Ni(3)–O(2W) 2.092(4) O(3)	2.092(4)	O(5)–Ni(3)–O(3)	79.23(14)
Ni(3)–O(3) 2.113(3)	2.113(3)	O(7)–Ni(3)–O(3)	88.10(15)

1.#1) x,−y+1,z−1/2.
2.#1) −y,x−y,z; #2) x−y,x,−z+2; #3) y,−x+y,−z+2; #4) −x,−y,−z+2; #5) −x+y,−x,z.
[a] Symmetry transformations used to generate equivalent atoms.