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A series of divalent metal complexes with mixed 5-(imidazol-1-ylmethyl)isophthalic acid and N-donor ligands: Synthesis, characterization and property

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ABSTRACT

Eight complexes with different 3d metal centers and auxiliary ligands, [Cu(L)(py)] (**1**), [Cu(L)(bpy)]·1.5H_2O (**2**), [Mn(L)] (**3**), [Mn(L)(pybim)]·3H_2O (**4**), [Ni(L)(bpy)]·2H_2O (**5**), [Ni(L)(phen)]·2H_2O (**6**), [Ni(L)(bpe)(H_2O)]·2H_2O (**7**) and [Zn(L)(bpy)]·2H_2O (**8**) [H_2L = 5-(imidazol-1-ylmethyl)isophthalic acid, py = pyridine, bpy = 2,2′-bipyridine, pybim = 2-(pyridin-2-yl)-1H-benzo[d]imidazole, phen = 1,10-phenanthroline, bpe = 1,2-di(pyridin-4-yl)ethylene] were obtained under hydrothermal conditions and characterized by single crystal and powder X-ray diffractions, IR, elemental and thermogravimetric analyses. Complex **1** is a 3-connected uninodal 2D network with (4.8^2) topology, while **2**, **4**, **6** and **7** display 3-connected uninodal 2D network with (6^3) **hcb** topology, **3** exhibits a (5,5)-connected binodal 3D net with (4^5)(6^5) topology, **5** and **8** have 1D double-chain structures. The influence of metal centers and auxiliary ligands on the structures of resultant complexes is discussed. Magnetic property of **3** and luminescence of **8** were investigated.

1. Introduction

The assembling strategies of coordination architectures involve the deliberate design of organic building blocks and the adept employment of metal centers [1]. Hitherto, a lot of researches have been carried out to manage influential factors, including the coordination geometry of metal center, the intrinsic nature of organic ligand, and other experimental conditions such as acidic or basic media for the reaction system, reaction solvent, and temperature as well as the ratio of metal-to-ligand, to construct coordination supramolecular compounds for their fascinating structures and potential applications in gas storage, chemical sensors, ion exchange, microelectronics, magnetism, nonlinear optics, and heterogeneous catalysis etc. [2–5]. Among the above mentioned influential factors, the nature of organic ligand has been documented as crucial roles in the formation of coordination supramolecular compounds [6]. Therefore, the design of organic ligands is undoubtedly decisive in assembly of complexes. Among the well employed organic ligands, N- and/or O-donor multidentate ligands, such as isonicotinic acid, 4-(pyridin-4-yl)benzoic acid, and imidazole-4, 5-dicarboxylic acid, are always regarded as excellent building blocks for construction of desirable frameworks and have been well employed in coordination chemistry due to their fine coordinating capacities and variable coordination modes [7].

In our previous studies, we ever used a series of imidazole-containing ligands, for example 1,3,5-tris(imidazol-1-yl)benzene and 1,3,5-tris(imidazol-1-ylmethyl)benzene, and mixed N- and O-donor containing ligands like 4-(imidazol-1-yl)benzoic acid and 3,5-di(imidazol-1-yl)benzoic acid to construct coordination supramolecular compounds [8]. Based on the previous studies, we have been recently focusing our attention on the utilization of the semi-rigid ligand 5-(imidazol-1-ylmethyl)isophthalic acid (H_2L) as organic building blocks to react with varied metal salts under appropriate synthetic conditions. The H_2L ligand possesses two carboxylate groups and one flexible imidazol-1-ylmethyl arm which can rotate freely. Hence, it could potentially adopt different conformation in assembly reaction *via* the adjustment of external experimental conditions. The H_2L ligand can form series cadmium(II) and zinc(II) complexes with alkaline reagent dependent structural diversity; moreover, five cobalt(II) polymers from the H_2L ligand were assembled and their structural diversity was achieved by the presence of auxiliary ligands and the alteration of metal-to-ligand ratio [9]. Based on the consideration of fact that functional properties of complexes are largely dependent on their architectures, more experimental conditions, including trying

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more types of auxiliary ligands and metal salts, were tried to further pursue structural diversity of complexes for the exploration of new crystalline materials.

In this paper, we report the preparation and structural characterization of a series of divalent 3d metal complexes: [Cu(L)(py)] (**1**), [Cu(L)(bpy)]·1.5H_2O (**2**), [Mn(L)] (**3**), [Mn(L)(pybim)]·3H_2O (**4**), [Ni(L)(bpy)]·2H_2O (**5**), [Ni(L)(phen)]·2H_2O (**6**), [Ni(L)(bpe)(H_2O)]·2H_2O (**7**) and [Zn(L)(bpy)]·2H_2O (**8**) [H_2L = 5-(imidazol-1-ylmethyl)isophthalic acid, py = pyridine, bpy = 2,2′-bipyridine, pybim = 2-(pyridin-2-yl)-1H-benzo[d]imidazole, phen = 1,10-phenanthroline, bpe = 1,2-di(pyridin-4-yl)ethylene]. The influential factors of synthetic strategies on structures will be discussed. In addition, magnetic property of **3** and luminescence of **8** were examined.

2. Experimental

2.1. Materials and measurements

All commercially available chemicals and solvents are of reagent grade and were used as received without further purification. The ligand H_2L was prepared according to the previously reported method [9]. Elemental analyses of C, H, and N were taken on a Perkin-Elmer 240C elemental analyzer. Infrared spectra (IR) were recorded on a Bruker Vector22 FT-IR spectrophotometer by using KBr pellets. Thermogravimetric analyses (TGA) were performed on a simultaneous SDT 2960 thermal analyzer under nitrogen atmosphere with a heating rate of 10 °C min^{-1}. Powder X-ray diffraction (PXRD) patterns were measured on a Shimadzu XRD-6000 X-ray diffractometer with Cu Kα (λ = 1.5418 Å) radiation at room temperature. The magnetic measurement in the temperature range of 1.8–300 K was carried out on a Quantum Design MPMS7 SQUID magnetometer in a field of 2000 Oe. Diamagnetic corrections were made with Pascal's constants. The luminescence spectra for the powdered solid samples were measured on an Aminco Bowman Series 2 spectrofluorometer with a xenon arc lamp as the light source. In the measurements of emission and excitation spectra the pass width is 5 nm, and all the measurements were carried out under the same experimental conditions.

2.2. Preparation of [Cu(L)(py)] (*1*)

Reaction mixture of $Cu(NO_3)_2$·3H_2O (24.1 mg, 0.1 mmol), H_2L (24.6 mg, 0.1 mmol) and 1 mL pyridine in 10 mL H_2O was sealed

Table 1
Crystal data and structure refinements for complexes **1**–**8**.

Compound	**1**	**2**	**3**	**4**
Empirical formula	$C_{17}H_{13}N_3O_4Cu$	$C_{44}H_{38}N_8O_{11}Cu_2$	$C_{12}H_8N_2O_4Mn$	$C_{24}H_{23}N_5O_7Mn$
Formula weight	386.84	981.90	299.14	548.41
Crystal system	orthorhombic	triclinic	monoclinic	triclinic
Space group	*Pbca*	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a (Å)	17.406(4)	9.5885(6)	8.8274(12)	8.753(8)
b (Å)	8.758(2)	9.8352(6)	16.682(2)	10.165(10)
c (Å)	20.774(7)	13.9055(9)	7.8691(11)	14.819(14)
α (°)	90.00	71.4010(10)	90.00	96.430(15)
β (°)	90.00	80.9910(10)	100.689(3)	91.546(15)
γ (°)	90.00	66.1990(10)	90.00	110.753(14)
T (K)	200	293(2)	293(2)	293(2)
V (Å^3)	3166.9(16)	1136.58(12)	1138.7(3)	1222(2)
Z	8	1	4	2
D_{calc} (g cm^{-3})	1.623	1.435	1.745	1.490
μ (mm^{-1})	1.408	1.003	1.171	0.595
F(000)	1576	504	604	566
θ Range (°)	3.05–27.49	1.55–26.00	2.35–27.00	1.39–28.00
Reflections collected	25700	6242	6508	8609
Unique reflections	3623	4373	2472	5845
Goodness-of-fit (GOF) on F^2	1.092	1.074	1.367	1.053
R_1[a], wR_2[b] [$I > 2\sigma(I)$]	0.0416, 0.1076	0.0565, 0.1631	0.0995, 0.1815	0.0505, 0.1207
R_1, wR_2 (all data)	0.0538, 0.1134	0.0631, 0.1692	0.1022, 0.1825	0.0694, 0.1304
Compound	**5**	**6**	**7**	**8**
Empirical formula	$C_{22}H_{20}N_4O_6Ni$	$C_{24}H_{20}N_4O_6Ni$	$C_{24}H_{24}N_4O_7Ni$	$C_{22}H_{20}N_4O_6Zn$
Formula weight	495.13	519.15	539.18	501.79
Crystal system	triclinic	triclinic	monoclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a (Å)	9.5783(7)	10.448(4)	9.9659(19)	9.4978(6)
b (Å)	10.1593(7)	14.664(4)	28.894(6)	10.2376(7)
c (Å)	13.0962(14)	15.179(4)	10.6565(14)	13.3159(13)
α (°)	97.7380(10)	79.215(10)	90.00	100.4420(10)
β (°)	100.3690(10)	78.396(13)	122.320(12)	98.5720(10)
γ (°)	116.8360(10)	85.013(11)	90.00	115.7140(10)
T (K)	293(2)	200	293(2)	293(2)
V (Å^3)	1084.19(16)	2234.9(11)	2593.2(9)	1108.70(15)
Z	2	4	4	2
D_{calc} (g cm^{-3})	1.517	1.543	1.381	1.503
μ (mm^{-1})	0.942	0.919	0.797	1.154
F(000)	512	1072	1120	516
θ Range (°)	1.63–25.99	3.06–27.48	2.37–28.00	1.61–26.00
Reflections collected	6015	21127	16051	6137
Unique reflections	4178	10109	6138	4274
Goodness-of-fit (GOF) on F^2	0.960	1.058	1.065	0.972
R_1[a], wR_2[b] [$I > 2\sigma(I)$]	0.0319, 0.0682	0.0437, 0.1144	0.0489, 0.1605	0.0507, 0.1263
R_1, wR_2 (all data)	0.0394, 0.0708	0.0582, 0.1212	0.0625, 0.1668	0.0656, 0.1339

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[b] $wR_2 = |\Sigma w(|F_o|^2 - |F_c|^2)|/\Sigma|w(F_o)^2|^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$. $P = (F_o^2 + 2F_c^2)/3$.