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Structural and property studies on metal–organic compounds with 3-D supramolecular network

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ABSTRACT

Two carboxylato-bridged allomeric compounds, $\{[Cu_2(dbsa)_2(hmt)\ (H_2O)_4]_{1/2}\cdot 2H_2O\}_n$ (**1**), $\{[Ni(dbsa)(H_2O)_2]_{1/2}[Ni(dbsa)(hmt)(H_2O)_2]_{1/2}\cdot 2H_2O\}_n$ (**2**) (H_2dbsa=meso-2,3-dibromosuccinic acid, hmt=hexamethylenetetramine) have been synthesized and characterized by X-ray structral analyses. The metal ions have two kinds of coordination fashion in one unit, and bridged by carboxylate and hmt ligands along with weak interactions existing in the solid structure, forming a 3-D supramolecular network. Variable-temperature magnetic property studies reveal the existence of antiferromagnetic interactions in **1** and **2** with $g=2.2$, $J_1=-3.5\ cm^{-1}$, $J_2=-2.8\ cm^{-1}$ for **1**, and $g=2.1$, $J=-3.5\ cm^{-1}$ for **2**.

1. Introduction

Metal–organic frameworks (MOFs) represent one of the most active and attractive research fields in materials science [1,2], because of their structural diversity and interesting properties, which lead to applications in gas (especially hydrogen) storage [3–5] and separation [6], non-linear optics [7], chemical sensor [8], luminescence [9], magnetism [10], catalysis [11], or biomedicine [12]. Aromatic multi-carboxylates often act as building block to construct porous coordination framworks owing to their versatile coordination modes, such as monodentate, chelate, monatomic bridge, bi- and tri-dentate bridges, and also multiple bridges [13–15]. In contrast to the ragid aromatic multi-carboxylate anions, the aliphatic α, ω-dicarboxylate ligands such as succinic acid that act as important flexible spacer ligands, due to their conformational and coordination versatility, tend to bridge transition metal ions to form coordination polymers with a variety of interesting structures [16–18].

Here, two polymers constructed by meso-2,3-dibromosuccinic acid (H_2dbsa) and hexamethylenetetramine (hmt) were reported. Compared with succinic acid, the electrophilic and steric effect of bromine atom in H_2dbsa give rise to the difficulty in the formation of metal–oxygen coordination bond, and the crystal structures with direct metal–carboxylate coordination bond reported are limited [19,20]. Two allomeric compounds $\{[Cu_2(dbsa)_2(hmt)\ (H_2O)_4]_{1/2}\cdot 2H_2O\}_n$ (**1**) and $\{[Ni(dbsa)(H_2O)_2]_{1/2}[Ni(dbsa)(hmt)(H_2O)_2]_{1/2}\cdot 2H_2O\}_n$ (**2**) were synthesized using hmt as weak base, adjusting the pH value to 6 in the reaction system. In compound **1**, the metal ions are bridged by the carboxylate oxygen atoms of dbsa and the nitrogen atoms of hmt, forming a 2-D layered structure. While in compound 2, there are only weak interactions between Ni(2) and N(2) atoms. The layers are further constructed into a 3-D network due to the weak interactions of hydrogen bonds, Ni(II)···N and O···Br. The super-exchange coupling interactions between the metal ions were also investigated using variable-temperature magnetic susceptibility measurement.

2. Experimental

2.1. Materials and physical methods

All of the chemicals were commercially available and used without further purification. Infrared spectra were recorded on a Bruker EQUINOX-55 FTIR spectrometer as KBr pellets. Variable-temperature magnetic susceptibility measurement was performed with a quantum Design MPMS XL-5 SQUID system at an applied field of 1Koe from 2 to 300 K. The experimental susceptibilities were corrected for the diamagnetism of the constituent atoms (Pascal's constants). Thermogravimetric analysis was carried out under N_2 condition on a Q600 analyzer.

2.2. Preparation of the title compounds

$\{[Cu(dbsa)(hmt)]_{1/2}[Cu(dbsa)(hmt)(H_2O)_2]_{1/2}\cdot 3H_2O\}_n$ (**1**). A mixture of H_2dbsa (0.5 mmol, 0.136 g), copper(II) perchlorate (0.5 mmol, 0.124 g) and html (1 mmol, 0.140 g) in aqueous/methanol solution

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(2:1, 20 ml) was adjusted to pH 6 with 5% NaOH aqua solution under stirring. After stirring for 1 h, the mixture was filtered and standing at room temperature. Green crystals were obtained after two days and washed with methanol solution (yield: 80%). *Anal. Calc.* for $C_{10}H_{22}Br_2CuN_4O_8$ (%): C, 21.8; H, 3.9; N, 10.2. Found (%): C, 21.6; H, 3.8; N, 10.0. IR data (KBr, cm^{-1}): 3520 ws, 2971 s, 1636 s, 1461 s.

$\{[Ni(dbsa)(hmt)]_{1/2}[Ni(dbsa)(hmt)(H_2O)_2]_{1/2}\cdot 3H_2O\}_n$ (**2**). Compound **2** was prepared by the same procedure as **1**, except for the use of $Ni(OAc)_2$ (0.1244 g, 0.5 mmol) instead of $Cu(ClO_4)$. Blue–green crystals were obtained after two day (yield: 85%). *Anal. Calc.* for $C_{10}H_{22}Br_2Ni\ N_4O_8$ (%): C, 22.0; H, 4.1; N, 10.3. Found (%): C, 21.6; H, 4.3; N, 10.1. IR data (KBr, cm^{-1}): 3393 ws, 2974 s, 1594 s, 1389 s.

2.3. *X-ray structural studies*

The single-crystal X-ray diffraction data for the title compounds were carried out on a Bruker Apex II CCD diffractometer with graphite monochromated Mo*K*α radiation (λ=0.71073 Å) at 293 K. Cell parameters were retrieved using SMART software and refined with SAINT on all observed reflections. The data were corrected for Lorentz and polarization effects. Semi-empirical absorption corrections were applied by SADABS [21]. The structures were solved by direct methods using SHELXS program of the SHELXL package and refined with SHELXL program [22,23]. The heavy atoms were located from the E-maps and other non-H atoms in successive difference Fourier syntheses. The final refinements were performed by full-matrix least-squares methods with anisotropic thermal parameters for all non-H atoms on F^2. Hydrogen atoms were generated by the riding model in idealized geometries and refined with isotropic temperature factors. Crystallographic data and structure refinement for the compounds are summarized in Table 1.

3. Result and discussion

3.1. *Structural descriptions*

Compounds **1** and **2** are allomeric, and the bond distances in the two compounds are similar as listed in Table 2. In Compound **1**, the hmt ligans are bidentate, linking to two metal ions, while the carboxylate groups of the dbsa ligand only play mono-dentate coordination fashion (Fig. 1a). The equatorial squar plane of Cu (1) is completed by two oxygen atoms from two dbsa ligands and two nitrogen atoms from two hmt ligands (mean deviation: 0.000), and two oxygen atoms from two aqua molecules are in the axial direction with much long bond distances due to the Jahn–Teller effect [24–26] (Cu(1)–O(6)=2.481 Å). The Cu(2) center is six—coordinated by two oxygen atoms from two dbsa ligands, two oxygen atoms from two aqua molecules in the equatorial plane (mean deviation: 0.000), and two nitrogen atoms from two hmt ligands at the Jahn–Teller axial of Cu(2) with the weak Cu–N separations of 2.606 Å. The bond lengths of Cu(1)–O (1) and Cu (2)–O(3) are 1.964(4) Å and 1.955(4) Å respectively, similar to the correspongding values (1.961 Å and 1.9562 Å) in the Cu(II)-succinate system reported by Mao [27]. In coumpund **2**, the major part of the unit is composed of two chains, $[Ni(dbsa)(H_2O)_2]_n$ and $[Ni(dbsa)(hmt)(H_2O)_2]_n$, taking no account of the weak

Table 1
Crystal data and structural refinement for complexes **1** and **2**.

Complex	**1**	**2**
Empirical formula	C10 H22 Br2 Cu N4 O8	C20 H44 Br4 Ni2 N8 O16
M_r	549.68	1089.69
Crystal system	Triclinic	Triclinic
space group	*P*−1	*P*−1
a (Å)	7.6973(15)	7.7001(8)
b (Å)	9.6448(19)	9.6322(11)
c (Å)	12.544(2)	12.5444(14)
α (°)	88.337(3)	88.507(2)
β (°)	87.697(4)	87.750(2)
γ (°)	72.322(3)	72.256(2)
V ($Å^3$)	886.4(3)	885.36(17)
Z	2	1
D_{calc} ($Mg\ m^{-3}$)	2.059	2.044
μ(mm^{-1})	5.787	5.656
F(0 0 0)	546	544
Goodness-of-fit on F^2	1.011	1.083
R_1 [$I>2\sigma$]	0.0557	0.0605
wR_2 (all data)	0.1448	0.1337
Largest diff. peak and hole (e. $Å^{-3}$)	1.247 and −0.872	1.048 and −0.541

$^aR_1=\sum||F_o-|F_c||/\sum|F_o|\times{}^bwR2=[\sum w(|F_0|-|F_c|)^2]^{1/2}$; $w=[\sigma^2(F_o)^2+(0.1(\max(F_o^2,0)+2F_c^2)/3)^2]^{-1}$

Table 2
Selected bond distances (Å) and angles (°) for the title complexes.

Complex **1**			
Bond	Bond distance (Å)	Bond	Bond distance (Å)
Cu(1)–O(1)	1.964(4)	Cu(1)–N(1)	2.157(5)
Cu(1)–O6	2.481(4)	Cu(2)–O(3)	1.955(4)
Cu(2)–O(5)	1.951(4)	Cu(2)–N(2)	2.606(4)
Br(1)· · ·Br(2)$^{\#1}$	3.6286(11)	O(2)· · ·Br(2)$^{\#1}$	3.536(4)
O(2)· · ·Br(1)$^{\#3}$	3.388(4)	O(4)· · ·Br(2)$^{\#4}$	3.508(4)
Bond	Bond angle (°)	Bond	Bond angle (°)
O(1)–Cu(1)–N(1)	92.41(16)	O(1)–Cu(1)–N(1)$^{\#1}$	87.59(16)
O(1)$^{\#1}$–Cu(1)–N(1)$^{\#1}$	92.41(16)	O(1)$^{\#1}$–Cu(1)–N(1)	87.59(16)
O(1)–Cu(1)–O(6)	84.52(15)	O(1)$^{\#1}$–Cu(1)–O(6)	95.48(15)
N(1)–Cu(1)–O(6)	84.62(15)	N(1)$^{\#1}$–Cu(1)–O(6)	95.38(15)
O(1)$^{\#1}$–Cu(1)–O(1)	180.0(2)	N(1)$^{\#1}$–Cu(1)–N(1)	180.0
O(5)–Cu(2)–O(3)	87.49(16)	O(5)$^{\#2}$–Cu(2)–O(3)	92.51(16)
O(5)$^{\#2}$–Cu(2)–O(3)$^{\#2}$	87.49(16)	O(5)–Cu(2)–O(3)$^{\#2}$	92.51(16)
O(5)–Cu(2)–N(2)	91.14(15)	O(5)$^{\#2}$–Cu(2)–N(2)	88.86(15)
O(3)$^{\#2}$–Cu(2)–N(2)	91.62(16)	O(3)–Cu(2)–N(2)	88.38(16)
O(3)–Cu(2)–O(3)$^{\#2}$	180.0	O(5)–Cu(2)–O(5)$^{\#2}$	180.00(18)
Complex **2**			
Bond	Bond distance (Å)	Bond	Bond distance (Å)
Ni(1)–O(1)	1.966(5)	Ni(1)–N(1)	2.149(6)
Ni(1)–O(6)	2.483(5)	Ni(2)–O(3)	1.962(5)
Ni(2)–O(5)	1.950(5)	Ni(2)· · ·N(2)	2.604(6)
Br(1)· · ·Br(2)$^{\#1}$	3.6309(13)	O(2)· · ·Br(1)$^{\#3}$	3.383(5)
O(2)· · ·Br(2)$^{\#1}$	3.537(6)	O(4)· · ·Br(2)$^{\#4}$	3.491(6)
Bond	Bond angle (°)	Bond	Bond angle (°)
O(1)–Ni(1)–N(1)	92.3(2)	O(1)–Ni(1)–N(1)$^{\#2}$	87.7(2)
O(1)$^{\#2}$–Ni(1)–N(1)$^{\#2}$	92.3(2)	O(1)$^{\#2}$–Ni(1)–N(1)	87.7(2)
O(1)–Ni(1)–O(6)	95.16(19)	O(1)$^{\#1}$–Ni(1)–O(6)	84.84(19)
N(1)–Ni(1)–O(6)	95.6(2)	N(1)$^{\#2}$–Ni(1)–O(6)	84.4(2)
O(1)$^{\#2}$–Ni(1)–O(1)	180.000(1)	N(1)–Ni(1)–N(1)$^{\#2}$	180.000(1)
O(5)–Ni(2)–O(3)	88.0(2)	O(5)–Ni(2)–O(3)$^{\#1}$	92.0(2)
O(5)$^{\#1}$–Ni(2)–O(3)$^{\#1}$	88.0(2)	O(5)$^{\#3}$–Ni(2)–O(3)	92.0(2)
O(5)–Ni(2)–O(5)$^{\#1}$	180.000(1)	O(3)$^{\#1}$–Ni(2)–O(3)	180.000(1)

Symmetry codes for **1**: #1 $-x+1, -y, -z+1$; #2 $-x+1, -y, -z$; #3 $-x+1, -y-1, -z+1$; #4 $-x+1, -y+1, -z$. For **2**: #1 $-x+1, -y+2, -z+1$; #2 $-x+1, -y+2, -z+2$; #3 $-x+1, -y+1, -z+2$; #4 $-x+1, -y+3, -z+1$; #5 $x+1, y, z$; #6 $-x+2, -y+2, -z+1$.