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pH- and metal-dependent structural diversity from mononuclear to two-dimensional polymers based on a flexible tricarboxylate ligand

Chengjuan Li [a], Yanqiang Peng [a], Suna Wang [a,b,*], Xianxi Zhang [a], Yizhi Li [b], Jianmin Dou [a,**], Dacheng Li [a]

[a] School of Chemistry and Chemical Engneering, Liaocheng University, Liaocheng 252059, PR China
[b] State Key Laboratory of Coordination Chemistry, Nanjing 210093, PR China

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ABSTRACT

Six complexes based on a flexible tripodal ligand H_3TTTA (2,2′,2″-[1,3,5-triazine-2,4,6-triyltris(thio)]-tris-acetic acid) have been hydrothermally synthesized and structurally characterized. X-ray single-crystal diffractions reveal that they have rich structural chemistry: mononuclear, $[Zn(HTTTA)(2,2'\text{-bpy})(H_2O)_3]_n$ (**1**); dimeric metallamacrocycle, $[Zn(HTTTA)(2,2'\text{-bipy})(H_2O)]_n$ (**2**) and $[Cd(HTTTA)(2,2'\text{-bipy})(H_2O)\cdot H_2O]_n$ (**3**); two-dimensional networks with binodal (3,6)-connected CdI_2 topology based on linear trinuclear $M_3(\mu^2\text{–}CO^2)_4(\mu_2\text{–}CO_2)_2$ SBUs (Secondary Building Units), $[M_3(TTTA)_2(2,2'\text{-bipy})_2(H_2O)_m\cdot nH_2O]_n$ (M=Zn·**4**, m=0, n=4; Cd·**5** and Mn·**6**, m=2; n=2). The value of pH and the metal ions has large influences on the resulting structures. The flexible tricarboxylic acid exhibits four coordination modes from monodentate to μ^6-bridge. Fluorescence and magnetic properties of the complexes have also been investigated in details.

1. Introduction

Supramolecular coordination assemblies attract much interest in recent years, stemming from the potential applications in the areas including gas storage, molecular sieves, ion-exchange, catalysis, magnetism and optoelectronics, as well as their intriguing variety of architectures and topologies, such as molecular grids, bricks, herringbones, ladders, rings, boxes, diamondoids and honeycombs [1–16]. Of great interest is the construction of supramolecular architectures based on rigid or flexible carboxylic acid ligands [17–27]. Rigid ligands with comparably predictable coordination conformations are also employed in predesigned syntheses. Flexible ones, however, can adopt different conformations to decrease the geometric constrain and steric hindrance, so may form unpredictable intriguing topologies and properties. In addition, various kinds of intermolecular weak interactions, such as O–H···O (N) hydrogen bonds, weak C–H···X (X=O, N, π) and $\pi\cdots\pi$ stacking interactions, are always observed [28–36]. They can cooperate with metal–ligand coordination bonding, leading to interesting supramolecular architectures.

We are interested in the latter and their extended structures. Systematic investigation has been made on the coordination chemistry of a series of tripodal acid ligands containing the $-OCH_2-$, $-NHCH_2-$ and amide groups [37–40]. In our recent manuscript, the lanthanide chemistry of H_3TTTA ligand (2,2′,2″-[1,3,5-triazine-2,4,6-triyltris(thio)]tris-acetic acid) with $-SCH_2-$ group has revealed that three types of structures from three-dimensional networks, one-dimensional chains to metallamacrocycle molecules are observed from light metal ions to heavy ones [41]. The synergistic effect of lanthanide contraction and flexible tripodal ligands should be responsible for the progressive change of these complexes.

For further investigation on coordination chemistry of this ligand with transition metal centers, six complexes were obtained: mononuclear, $[Zn(HTTTA)(2,2'\text{-bipy})(H_2O)_3]_n$ (**1**); metallamacrocycles, $[Zn(HTTTA)(2,2'\text{-bipy})(H_2O)]_n$ (**2**) and $[Cd(HTTTA)(2,2'\text{-bipy})(H_2O)\cdot H_2O]_n$ (**3**); two-dimensional binodal (3,6)-connected CdI_2 networks, $[M_3(TTTA)_2(2,2'\text{-bipy})_2(H_2O)_m\cdot nH_2O]_n$ (M=Zn·**4**, m=0, n=4; Cd·**5** and Mn·**6**, m=2; n=2). The multicarboxylic acid exhibits different deprotonation modes ($HTTTA^{2-}$ and $TTTA^{3-}$) and coordination conformations (monodentate, bisdentate and μ^6-bridge). For mono- and metallamacrocycle complexes, the non-covalent interactions between the molecules induce different packing modes to form diverse supramolecular networks. Fluorescence properties of these complexes have been also investigated.

2. Experimental section

2.1. General methods

The H_3TTTA ligand was prepared according to the previous procedure [40]. All the other reagents were commercially

* Corresponding author at: School of Chemistry and Chemical Engneering, Liaocheng University, Liaocheng 252059, PR China. Fax: +86 635 8239001.
** Corresponding author.
E-mail addresses: wangsuna@lcu.edu.cn (S. Wang), jmdou@lcu.edu.cn (J. Dou).

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Table 1
Crystal data and refinement of the complexes.

Complex	**1**	**2**	**3**
Empirical formula	$C_{19}H_{21}N_5O_9S_3Zn$	$C_{38}H_{34}N_{10}O_{14}S_6Zn_2$	$C_{38}H_{38}N_{10}O_{16}S_6Cd_2$
Formula weight	624.96	1177.85	1307.94
Space group	$P21/n$	$C2/c$	$C2/c$
a (Å)	7.6656(10)	20.733(2)	21.796(11)
b (Å)	33.813(4)	10.5492(9)	10.584(5)
c (Å)	10.403(2)	21.9589(18)	22.132(11)
α (deg.)	90.00	90.00	90.00
β (deg.)	111.586(2)	104.089(2)	108.221(8)
γ (deg.)	90.00	90.00	90.00
V (Å^3)	2507.5(7)	4658.4(7)	4849.55(3)
Z	4	4	4
$D_{calcd.}$ (g cm^{-3})	1.655	1.679	1.791
μ (mm^{-1})	1.289	1.376	1.215
$R1$, $wR2$[a] [$I>2\sigma(I)$]	0.0347, 0.0819	0.0360, 0.0688	0.0785, 0.2179
GOF	1.007	1.019	1.069
Complex	**4**	**5**	**6**
Empirical formula	$C_{38}H_{36}N_{10}O_{16}S_6Zn_3$	$C_{38}H_{36}N_{10}O_{16}S_6Cd_3$	$C_{38}H_{36}N_{10}O_{16}S_6Mn_3$
Formula weight	1277.24	1418.33	1245.95
Space group	$P-1$	$P-1$	$P-1$
a (Å)	8.883(3)	9.3334(7)	9.4300(6)
b (Å)	11.713(4)	11.0008(8)	10.7611(7)
c (Å)	12.813(4)	13.0536(5)	13.0175(8)
α (deg.)	111.027(4)	108.19 (4)	107.80(5)
β (deg.)	108.443(4)	107.53 (3)	108.68(3)
γ (deg.)	92.013(5)	94.23 (6)	93.26(2)
V (Å^3)	1163.7(7)	1193.01(2)	1173.80(2)
Z	1	1	1
$D_{calcd.}$ (g cm^{-3})	1.823	1.974	1.763
μ (mm^{-1})	1.886	1.669	1.144
$R1$, $wR2$[a] [$I>2\sigma(I)$]	0.0582, 0.1412	0.0532, 0.0937	0.0686, 0.1506
GOF	0.943	1.040	1.090

[a] $R_1=\sum\||F_o|-|F_c|\|/|F_o|$, $wR_2=[\sum w(\sum F_o^2-F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

Table 2
Geometrical parameters of hydrogen bonds in the complexes.

D–H···A	d(H···A)	d(D···A)	∠(DHA)	Symmetry codes
Complex 1				
O(2W)–H(2WA)···O(2)	2.06	2.691(3)	130.2	
O(6)–H(6)···O(4)[a]	1.76	2.573(3)	168.9	$x-1/2, -y+3/2, z+1/2$
O(2W)–H(2WB)···O(4)[b]	1.93	2.691(3)	147.6	$-x+2, -y+2, -z+1$
O(3W)–H(3WA)···O(3)[b]	2.17	2.762(3)	126.2	$-x+2, -y+2, -z+1$
O(3W)–H(3WB)···N(3)[c]	2.38	2.949(3)	124.9	$-x+2, -y+2, -z+2$
O(1W)–H(1WB)···O(3)[d]	2.04	2.802(3)	148.6	$-x+1, -y+2, -z+1$
Complex 2				
O(1W)–H(1WA)···O(2)[d]	1.97	2.755(3)	152.8	$-x+1, -y+2, -z+1$
O(1W)–H(1WA)···O(1)[a]	1.94	2.784(3)	172.0	$-x, -y, -z$
O(1W)–H(1WC)···O(5)[b]	2.22	2.783(3)	124.2	$x, y-1, z$
O(3)–H(3)···O(2)	1.79	2.602(3)	169.7	
C(17)–H(17)···O(4)[c]	2.68	3.290(4)	123.5	$-x+1/2, y+1/2, -z+1/2$
C(6)–H(6B)···N(2) [d]	2.41	3.377(4)	171.0	$-x+1/2, y-1/2, -z+1/2$
C(13)–H(13)···O(6) [e]	2.64	3.277(5)	126.4	$x+1/2, y-1/2, z$
Complex 3				
O(3)–H(3)···O(2)	1.89	2.640(10)	150.9	
O(2W)–H(2WC)···O(4)	2.11	2.787(14)	136.1	
O(1W)–H(1WA)···O(6)[a]	2.03	2.702(9)	135.3	$x, y-1, z$
O(1W)–H(1WA)···O(1)[b]	2.34	3.037(9)	139.3	$-x+2, -y+1, -z+2$
O(1W)–H(1WB)···O(2W)[c]	2.01	2.850(14)	167.2	$x, -y+1, z+1/2$
O(2W)–*H*(2WB)···O(5)[d]	2.51	2.934(17)	111.9	$-x+2, y-1, -z+3/2$
Complex 4				
O(1W)–H(1WA)···O(2W)[a]	2.33	3.005(6)	137.0	$x, y, z+1$
O(1W)–H(1WC)···O(6)[b]	2.33	2.847(4)	119.3	$-x, -y+1, -z+1$
O(2W)–H(2WD)···O(1W)[c]	2.45	3.028(6)	125.5	$-x+1, -y+1, -z+1$