



Structures, photoluminescence and heterogeneous catalysis of five metal complexes constructed by a flexible tricarboxylate ligand



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ABSTRACT

Five isostructural complexes constructed with H_3TTTA and 4,4'-bpy, namely $Co(H_2TTTA)_2(4,4'-bpy)_2$ (**1**), $Ni(H_2TTTA)_2(4,4'-bpy)_2$ (**2**), $Mn(H_2TTTA)_2(4,4'-bpy)_2$ (**3**), $Cd(H_2TTTA)_2(4,4'-bpy)_2$ (**4**) and $Cu(H_2TTTA)_2(4,4'-bpy)_2$ (**5**) ($H_3TTTA = 2,2', 2''-[1,3,5\text{-triazine-2,4,6-triyltris(thio)}]$ tris-acetic acid, 4,4'-bpy = 4,4'-dipyridine), have been synthesized and characterized by elemental analysis, IR, XRD and single crystal X-ray diffraction. The strong $O-H \cdots N$ and $O-H \cdots O$ stacking interactions link the molecules into a 2D network. Moreover, these 2D networks are connected into 3D frameworks through $C-H \cdots O$ and $C-H \cdots N$ stacking interactions, which seem to be effective in stabilizing the crystal structures. Complexes **1–5** have been tested for their catalytic properties. The results indicate that all the complexes show good catalytic activities for the cyanosilylation of benzaldehyde, whilst the Mn complex (**3**) shows a much better conversion for the cyanosilylation of acetophenone than the other complexes. The fluorescence properties of the complexes have also been investigated in detail.

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1. Introduction

In recent years metal complexes of carboxylate containing ligands have been significantly studied because they have different structural topologies and wide practical use as dyes, extractants, drugs, pesticides, catalysts, magnetic materials and in host-guest chemistry [1]. Exploring highly symmetrical multi-topic ligands and suitable metal salts to construct supramolecular architectures is of great interest [2]. Rigid ligands with various coordination modes can be adjusted to satisfy the requirements of the assembly process and interesting structural motifs may result, while flexible ones can adopt different conformations to decrease the geometric constrain and steric hindrance, and thus may form interesting topologies and structures. In addition, various kinds of intermolecular weak interactions, such as $O-H \cdots O$ (N) hydrogen bonds, weak $C-H \cdots X$ ($X = O, N, \pi$) and $\pi \cdots \pi$ stacking interactions, are always observed [3]. Multiple carboxylate ligands have been widely used as bridging ligands to build metal complexes [4]. Dicarboxylate ligands, tricarboxylate ligands and tetracarboxylate ligands have been widely used in the past two decades due to their various coordination modes and the possibility of the construction of supramolecular structures with their roles as H-bond acceptors and donors.

Among various applications of metal complexes, one possibility would be the preparation of solid catalysts. The design and synthesis

of metal complexes for cyanosilylation of carbonyl compounds is of current interest in synthetic chemistry [5]. The cyanohydrins produced are very useful synthetic intermediates for homochiral products, pharmaceutical compounds and natural products [6].

To obtain functional coordination polymers for cyanosilylation of carbonyl compounds, we introduce a flexible ligand, H_3TTTA ($2,2',2''-[1,3,5\text{-triazine-2,4,6-triyltris(thio)}]$ tris-acetic acid). The sulfide atom can function as an electron acceptor, forming $S \cdots H-O$ hydrogen bonds or non-covalent $S \cdots S$ weak interactions. In addition, due to the large distortion of the S atom itself, the additional $-SCH_2-$ group may exhibit more flexible characteristics in comparison with $-OCH_2-$ and $-NHCH_2-$, and lead to more versatile conformations in the assemblies [7]. Therefore, five isostructural mixed ligated complexes were synthesised. The single crystal structures, powder X-ray diffraction (PXRD), thermogravimetric analysis, fluorescence and role as catalysts of the complexes have also been investigated in detail.

2. Experimental

2.1. General methods

The ligand was prepared according to the previously reported procedure [7]. The other reagents were commercially available and used as purchased. The elemental analysis was carried out with a Perkin-Elmer 240C elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range $4000-400\text{ cm}^{-1}$ on a

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Nicolet FT-170SX spectrometer. Thermal analyses were performed on a Tan integrated thermal STA 449C analyzer, heated from room temperature to 800 °C with a heating rate of 10 °C/min under flowing nitrogen, and the data are consistent with the structures. Photoluminescence analysis was performed on a Cary Eclipse fluorescence spectrometer. Powder X-ray diffraction (XRD) patterns were collected on a Rigaku D/max2500VB3+/PC diffractometer equipped with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$).

2.2. Syntheses of the complexes

2.2.1. Preparation of $\text{Co}(\text{H}_2\text{TSTA})_2(4,4'\text{-bpy})_2$ (**1**)

A mixture of the ligand (0.035 g, 0.1 mmol), 4,4'-bpy (0.031 g, 0.2 mmol) and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.047 g, 0.2 mmol) in H_2O (3 mL) was

placed in a Parr Teflon-lined stainless steel vessel and heated to 80 °C for 1 day. The reaction system was cooled to room temperature slowly and then crystals of **1** were obtained. After filtration, the crystals were washed with water and dried in air. Yield: 64% based on H_2TSTA . *Anal. Calc.* for $\text{C}_{38}\text{H}_{32}\text{CoN}_{10}\text{O}_{12}\text{S}_6$ (1072.03): C, 42.53; H, 2.98; N, 13.06. Found: C, 42.95; H, 2.54; N, 13.34%. IR (cm^{-1} , KBr pellet): 3073(w), 2965(w), 2912(w), 1677(s), 1603(s), 1478(s), 1414(w), 1390(w), 1269(m), 1230(m), 1060(m), 846(m), 818(m), 786(w), 720(m), 652(m), 551(s), 482(w), 446(w).

2.2.2. Preparation of $\text{Ni}(\text{H}_2\text{TSTA})_2(4,4'\text{-bpy})_2$ (**2**)

Complex **2** was obtained in a method similar to **1**, except using $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (0.052 g, 0.2 mmol). Yield: 47% based on H_2TSTA . *Anal. Calc.* for $\text{C}_{38}\text{H}_{32}\text{NiN}_{10}\text{O}_{12}\text{S}_6$ (1071.81): C, 42.54; H, 2.98; N, 13.06.

Table 1

Crystal data and structure refinement for complexes 1–5.

Complex	1	2	3	4	5
Formula	$\text{C}_{38}\text{H}_{32}\text{CoN}_{10}\text{O}_{12}\text{S}_6$	$\text{C}_{38}\text{H}_{32}\text{NiN}_{10}\text{O}_{12}\text{S}_6$	$\text{C}_{38}\text{H}_{32}\text{MnN}_{10}\text{O}_{12}\text{S}_6$	$\text{C}_{38}\text{H}_{32}\text{CdN}_{10}\text{O}_{12}\text{S}_6$	$\text{C}_{38}\text{H}_{32}\text{CuN}_{10}\text{O}_{12}\text{S}_6$
Formula weight	1072.03	1071.81	1068.04	1125.50	1076.64
Crystal system	triclinic	triclinic	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
<i>a</i> (Å)	8.5877(17)	8.5886(17)	8.6072(17)	8.6000(17)	8.6000(17)
<i>b</i> (Å)	8.6985(17)	8.6701(17)	8.7442(17)	8.8000(18)	8.9000(18)
<i>c</i> (Å)	15.161(3)	15.189(3)	15.216(3)	15.388(3)	14.900(3)
α (°)	98.79(3)	98.92(3)	98.75(3)	99.31(3)	76.40(3)
β (°)	106.18(3)	106.21(3)	106.10(3)	106.14(3)	74.00(3)
γ (°)	99.01(3)	98.75(3)	99.72(3)	99.50(3)	83.30(3)
D_{calc} (g cm^{-3})	1.694	1.695	1.673	1.736	1.680
<i>Z</i>	1	1	1	1	1
<i>F</i> (000)	549	550	547	570	551
Reflections collected	9115	8793	9367	8848	9048
Unique reflections	3638	3624	3679	3688	3710
μ (mm^{-1})	0.785	0.839	0.684	0.875	0.885
Goodness-of-fit (GOF) on F^2	0.987	1.039	0.993	1.174	0.985
R_1 [$I > 2\sigma(I)$]	0.0247	0.0280	0.0257	0.0317	0.0527
wR_2 [$I > 2\sigma(I)$]	0.0684	0.0794	0.0657	0.0840	0.1099
R_1 (all data)	0.0273	0.0315	0.0297	0.0344	0.0783
wR_2 (all data)	0.0698	0.0847	0.0676	0.0988	0.1270
$(\Delta\rho)_{\text{max}}$ (e \AA^{-3})	0.319	0.319	0.379	0.588	0.388
$(\Delta\rho)_{\text{min}}$ (e \AA^{-3})	0.318	−0.675	0.251	0.674	0.565

Table 2

Selected bond lengths (Å) and angles (°) for complexes 1–5.

Complex 1					
Co1–O1 ^{#1}	2.0930(13)	Co1–O4 ^{#1}	2.1338(13)	Co1–N2 ^{#1}	2.1523(15)
O1 ^{#1} –Co1–O1	180.00(6)	O1 ^{#1} –Co1–O4 ^{#1}	85.47(6)	O1–Co1–O4 ^{#1}	94.53(6)
O1 ^{#1} –Co1–N2 ^{#1}	92.52(5)	O1–Co1–N2 ^{#1}	87.48(5)	O4 ^{#1} –Co1–N2 ^{#1}	85.65(5)
O4–Co1–N2 ^{#1}	94.35(5)	N2–Co1–N2 ^{#1}	180.00(6)		
Complex 2					
Ni1–O1 ^{#2}	2.0761(17)	Ni1–O3 ^{#2}	2.1008(17)	Ni1–N2 ^{#2}	2.1004(19)
O1 ^{#2} –Ni1–O1	180.00(1)	O1 ^{#2} –Ni1–N2 ^{#2}	92.68(7)	O1–Ni1–N2 ^{#2}	87.32(7)
O1 ^{#2} –Ni1–O3	93.72(7)	O3–Ni1–N2 ^{#2}	94.92(7)	O3–Ni1–N2	85.08(7)
O1–Ni1–O3	86.28(7)	N2 ^{#2} –Ni1–N2	180.00(8)		
Complex 3					
Mn1–O1 ^{#2}	2.1773(14)	Mn1–O4 ^{#2}	2.1837(14)	Mn1–N4 ^{#2}	2.2806(15)
O1 ^{#2} –Mn1–O1	180.00(1)	O1 ^{#2} –Mn1–O4	95.87(6)	O1–Mn1–O4	84.13(6)
O1 ^{#2} –Mn1–N4	86.99(5)	O1–Mn1–N4	93.01(5)	O4–Mn1–N4	85.94(5)
O4 ^{#2} –Mn1–N4	94.06(5)	N4–Mn1–N4 ^{#2}	180.00(5)		
Complex 4					
Cd1–O1 ^{#3}	2.335(3)	Cd1–N4 ^{#3}	2.326(3)	Cd1–O6 ^{#3}	2.296(2)
O6 ^{#3} –Cd1–O6 ^{#3}	180.00(12)	O6 ^{#3} –Cd1–N4	85.39(10)	O6 ^{#3} –Cd1–N4 ^{#3}	94.61(10)
O6 ^{#3} –Cd1–O1	81.80(9)	O6 ^{#3} –Cd1–O1 ^{#3}	98.20(9)	N4 ^{#3} –Cd1–O1 ^{#3}	95.61(10)
N4 ^{#3} –Cd1–O1	84.39(10)	N4–Cd1–N4 ^{#3}	180.00(11)		
Complex 5					
Cu1–O3 ^{#1}	1.970(3)	Cu1–N4 ^{#1}	2.023(3)		
O3 ^{#1} –Cu1–O3	180.00(4)	O3 ^{#1} –Cu1–N4	86.49(12)	O3 ^{#1} –Cu1–N4 ^{#1}	93.51(12)
N4–Cu1–N4 ^{#1}	180.0(3)				

Symmetry codes: ^{#1} $-x + 1, -y, -z$; ^{#2} $-x, -y + 2, -z + 1$; ^{#3} $-x + 1, -y + 1, -z$.

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