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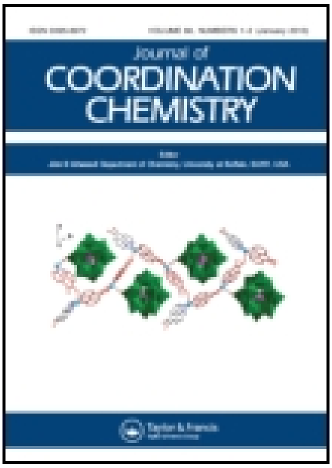

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Solid and solution study of tetranuclear zinc citrates with N-donor chelates

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Solid and solution study of tetranuclear zinc citrates with N-donor chelates

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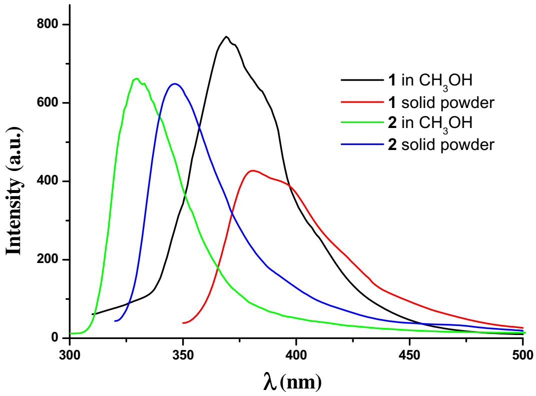

Two tetranuclear zinc(II) citrates with N-heterocycle ligand, $[Zn_4(Hcit)_2(phen)_4(H_2O)_4]\cdot 2NO_3\cdot 10H_2O$ (**1**) and $[Zn_4(Hcit)_2(bpy)_4(H_2O)_6]\cdot 2NO_3\cdot 12H_2O$ (**2**) (H_4cit = citric acid, phen = 1,10-phenanthroline, bpy = 2,2′-bipyridine), were synthesized from aqueous solution and characterized by Infrared, Powder X-ray diffraction, fluorescence spectra and X-ray structural analyses. **1** and **2** show strong fluorescent emission in dilute solution and solid state.

Tetranuclear zinc(II) citrates with N-heterocycle ligand, $[Zn_4(Hcit)_2(phen)_4(H_2O)_4]\cdot 2NO_3\cdot 10H_2O$ (**1**) and $[Zn_4(Hcit)_2(bpy)_4(H_2O)_6]\cdot 2NO_3\cdot 12H_2O$ (**2**) (H_4cit = citric acid, phen = 1,10-phenanthroline, bpy = 2,2′-bipyridine), were synthesized from aqueous solution and characterized by Infrared, Powder X-ray diffraction, fluorescence spectra, and X-ray structural analyses. Complexes **1** and **2** are centrosymmetric tetranuclear species with two crystallographically independent Zn(II) ions, which display different coordination geometries, while the citrate ligand shows similar coordination modes and bridges three different Zn ions. In **1**, the Zn1 is five-coordinate by three oxygens from two citrates and two nitrogens from phen. There exist weak interactions between Zn1 and O4a atom of β-carboxy group of citrate (Zn1⋯O4a = 2.895 Å). Zn2 is six-coordinate by two oxygens from one citrate, two nitrogens from phen, and two water molecules. Zn1 and Zn2 are bridged by one citrate to form a dinuclear unit, which is further extended to a tetranuclear unit. In **2**, two citrates bridge two pairs of symmetry-related Zn(II) ions into a tetranuclear unit. The structural analyses of **1** and **2** indicate that different tetranuclear species are caused by arrangement of citrates with different steric

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hindrance of N-chelates. ^{1}H and ^{13}C NMR spectra indicate that **2** remains coordinated in D_2O. Moreover, both **1** and **2** show strong fluorescent emission in dilute solution and solid state.

Keywords: Zinc; Citric acid; Bipyridine; Phenanthroline; Fluorescence; ^{13}C NMR; Crystal structure

1. Introduction

Zinc is an important trace metal ion in all living organisms, influencing nutrition [1], gene expression and cell division [2, 3], and even in plant metabolic processes [4]. It has a wide range of applications, including batteries [5], alloys [6], dye-casting [7], dental materials [8], Zn-doped ferrites [9, 10], etc. Zn(II) can coordinate with various ligands, producing complexes with unusual structural features and remarkable physical and chemical properties. Zinc compounds with carboxylate ligands are of great interest owing to their role in biochemical systems, catalysis, and materials chemistry [11]. Carboxylate ligands play an important role in coordination chemistry owing to their diverse coordination modes and high structural stability. Carboxylate-rich polydentate ligands have been used as precursors to assemble Zn(II) ions into aggregates with relevance in bioinorganic chemistry [12]. Citric acid, an α-hydroxytricarboxylic acid, is abundant in physiological fluids and has versatility toward transition metal ions [13, 14]. This molecule can give mononuclear, dinuclear, and polynuclear compounds of quite different natures through its binding to metal ions via hydroxy, α-carboxy, and/or one or two β-carboxy groups [15–24]. N-donor ligands such as imidazole, 1,10-phenanthroline, 2,2-bipyridine and their derivatives have also attracted attention in construction of metal–organic frameworks (MOFs) [25]. Many efforts have been devoted to use of N- and O-donor organic ligands to bridge metal ions to construct MOFs [26]. As part of our ongoing efforts in extension of MOFs with metal salts and α-hydroxycarboxylic acids as well as N-donor ligands, we report here the syntheses, spectroscopic properties, and crystal structures of two new tetranuclear zinc complexes, $[Zn_4(Hcit)_2(phen)_4(H_2O)_4]\cdot 2NO_3\cdot 10H_2O$ (**1**) and $[Zn_4(Hcit)_2(bpy)_4(H_2O)_6]\cdot 2NO_3\cdot 12H_2O$ (**2**) (H_4cit = citric acid, phen = 1,10-phenanthroline, bpy = 2,2-bipyridine).

2. Experimental

2.1. *Materials and general methods*

The pH was measured with the potentiometric method with a digital PHB-8 pH meter. Infrared (IR) spectra were recorded as Nujol mulls between KBr plates using a Nicolet 360 FT-IR spectrometer or a Thermo Electron NEXUS FT-IR spectrometer (Thermo Electron Corporation). Powder X-ray diffraction (PXRD) analyses were recorded on a Rigaku Ultima IV diffractometer (Cu Kα radiation, $\lambda = 1.5406$ Å) (Rigaku Corporation). ^{1}H and ^{13}C NMR spectra of **2** were recorded on a Bruker NMR instrument (Swiss Bruker company) using D_2O as solvent. Chemical shifts are reported in parts per million with CD_3OD as reference. Fluorescence spectra of **1** and **2** were measured with a Hitachi F-4500 fluorescence spectrophotometer (Hitachi company) at room temperature.

2.2. *Preparation of [$Zn_4(Hcit)_2(phen)_4(H_2O)_4$]·$2NO_3$·$10H_2O$ (1)*

Citric acid (0.21 g, 1.0 mM) and 1,10-phenanthroline (0.40 g, 2.0 mM) were added to a stirred solution of $Zn(NO_3)_2·6H_2O$ (0.59 g, 2.0 mM) in water (50 mL). The pH of the solution was adjusted to 4.8 with dilute ammonium hydroxide. The mixture was heated in a water bath at 60 °C for one week, then the mixture was cooled to room temperature and left standing for several days to give colorless crystalline **1**. The product was isolated by filtration and dried in air. Yield: 0.79 g (91%). IR (KBr, cm^{-1}): $3413_{s,br}$, 1655_{vw}, 1609_{s}, 1585_{s}, 1519_{m}, 1430_{s}, 1400_{s}, 1385_{s}, 1312_{m}, 1106_{w}, 1039_{w}, 851_{m}, 728_{s}, 681_{w}, 552_{w}.

2.3. *Preparation of [$Zn_4(Hcit)_2(bpy)_4(H_2O)_6$]·$2NO_3$·$12H_2O$ (2)*

Citric acid (0.21 g, 1.0 mM) and 2,2-bipyridine (0.31 g, 2.0 mM) were added to a stirred solution of $Zn(NO_3)_2·6H_2O$ (0.59 g, 2.0 mM) in water (20 mL). The pH of the solution was adjusted to 4.8 with dilute ammonium hydroxide. The mixture was heated in a water bath at 60 °C for five days, then the mixture was cooled to room temperature and left standing for several days to give colorless crystalline product **2**. The product was isolated by filtration and dried in air. Yield: 0.76 g (89%). IR (KBr, cm^{-1}): $3433_{s,br}$, 1606_{s}, 1598_{s}, 1475_{w}, 1444_{s}, 1384_{vs}, 1317_{w}, 1024_{w}, 773_{m}, 736_{w}, 653_{w}. ^1H NMR (400 MHz, D_2O): δ 8.56 (s, 1H), 8.32 (s, 1H), 8.15 (t, $J = 7.4$ Hz, 1H), 7.62 (t, $J = 6.2$ Hz, 1H), 2.79 (d, $J = 16.8$ Hz, 2H), 2.55 (d, $J = 17.2$ Hz, 2H) ppm; ^{13}C NMR (100 MHz, D_2O): δ 183.50, 180.38, 150.25, 150.00, 143.32, 128.73, 124.09, 76.99, 45.92 ppm.

Table 1. Crystallographic data for **1** and **2**.

	1	**2**
Empirical formula	$C_{60}H_{70}N_{10}O_{34}Zn_4$	$C_{52}H_{78}N_{10}O_{38}Zn_4$
Formula weight	1736.74	1712.72
Crystal color	Colorless	Colorless
Crystal system	Triclinic	Triclinic
Cell constants		
a (Å)	11.7731(6)	12.160(7)
b (Å)	12.5481(5)	12.510(7)
c (Å)	13.6855(5)	14.338(8)
α (°)	76.264(3)	93.130(1)
β (°)	65.510(4)	110.666(7)
γ (°)	69.527(4)	116.098(7)
V ($Å^3$)	1713.5(1)	1774.6(2)
Space group	$P\bar{1}$	$P\bar{1}$
Z	1	1
D_{Calcd} ($g\ cm^{-3}$)	1.683	1.603
F (0 0 0)	892	884
Reflections collected/unique/R_{int}	16350/6739/0.0242	18986/8109/0.0524
Data/restraints/parameters	6739/18/526	8109/26/523
θ Range (°)	2.17–26.00	1.57–27.49
Goodness-of-fit on F^2	1.065	1.101
R_1[a], wR_2 [$I > 2\sigma(I)$][b]	0.0319, 0.0771	0.0402, 0.1120
R_1[a], wR_2[b] (all data)	0.0431, 0.0789	0.0479, 0.1206
Largest diff. peak and hole ($e\ Å^{-3}$)	1.155, −1.039	0.519, −0.872

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma(|F_o|)$.

[b] $wR_2 = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$.

2.4. *X-ray crystallography*

Data collection of **1** was performed on an Oxford Gemini S Ultra system (Oxford Diffraction Co., Ltd) with Mo Kα radiation (λ = 0.71073 Å) at 173 K. Absorption corrections were applied by using the program CrysAlis (multi-scan). Data collection of **2** was performed on a Rigaku XtaLAB mini diffractometer (Rigaku Corporation) equipped with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 293 K. Semi-empirical absorption corrections were applied using SADABS [27]. The structures were solved by WinGX package [28] and refined by full-matrix least-squares procedures with anisotropic thermal parameters for all the non-hydrogen atoms using SHELXL-97 [29]. Hydrogens, except the disordered

Table 2. Selected bond distances (Å) and angles (°) for **1**.

Zn(1)–O(5a)	1.955(2)	O(2)–Zn(1)–N(1)	162.52(7)
Zn(1)–O(2)	2.050(2)	O(1)–Zn(1)–N(1)	86.21(7)
Zn(1)–O(1)	2.067(2)	N(2)–Zn(1)–N(1)	78.87(8)
Zn(1)–N(2)	2.080(2)	O(2w)–Zn(2)–O(1w)	94.41(8)
Zn(1)–N(1)	2.136(2)	O(2w)–Zn(2)–O(6)	91.15(7)
Zn(2)–O(2w)	2.012(2)	O(1w)–Zn(2)–O(6)	93.20(8)
Zn(2)–O(1w)	2.102(2)	O(2w)–Zn(2)–N(3)	102.87(8)
Zn(2)–O(6)	2.112(2)	O(1w)–Zn(2)–N(3)	92.29(8)
Zn(2)–N(3)	2.115(2)	O(6)–Zn(2)–N(3)	164.51(7)
Zn(2)–N(4)	2.117(2)	O(2w)–Zn(2)–N(4)	104.40(8)
Zn(2)–O(7)	2.404(2)	O(1w)–Zn(2)–N(4)	160.52(8)
O(5a)–Zn(1)–O(2)	100.98(7)	O(6)–Zn(2)–N(4)	91.48(8)
O(5a)–Zn(1)–O(1)	115.55(7)	N(3)–Zn(2)–N(4)	78.77(8)
O(2)–Zn(1)–O(1)	78.16(6)	O(2w)–Zn(2)–O(7)	148.00(7)
O(5a)–Zn(1)–N(2)	133.46(7)	O(1w)–Zn(2)–O(7)	81.19(7)
O(2)–Zn(1)–N(2)	98.89(7)	O(6)–Zn(2)–O(7)	57.76(6)
O(1)–Zn(1)–N(2)	109.51(7)	N(3)–Zn(2)–O(7)	108.95(7)
O(5a)–Zn(1)–N(1)	92.75(8)	N(4)–Zn(2)–O(7)	85.38(7)

Note: Symmetric transformation: *a*: $2 - x$, $-y$, $1 - z$.

Table 3. Selected bond distances (Å) and angles (°) for **2**.

Zn(1)–O(2)	2.048(2)	O(2)–Zn(1)–O(1)	75.31(7)
Zn(1)–O(2w)	2.097(2)	O(2w)–Zn(1)–O(1)	82.69(8)
Zn(1)–O(1w)	2.110(2)	O(1w)–Zn(1)–O(1)	165.02(7)
Zn(1)–N(2)	2.132(2)	N(2)–Zn(1)–O(1)	95.76(7)
Zn(1)–N(1)	2.144(2)	N(1)–Zn(1)–O(1)	95.53(9)
Zn(1)–O(1)	2.189(2)	O(6a)–Zn(2)–O(3w)	91.79(9)
Zn(2)–O(6a)	2.059(2)	O(6a)–Zn(2)–O(4)	87.20(8)
Zn(2)–O(3w)	2.061(2)	O(3w)–Zn(2)–O(4)	153.10(8)
Zn(2)–O(4)	2.110(2)	O(6a)–Zn(2)–N(3)	94.00(8)
Zn(2)–N(3)	2.113(2)	O(3w)–Zn(2)–N(3)	103.03(8)
Zn(2)–N(4)	2.118(2)	O(4)–Zn(2)–N(3)	103.86(8)
Zn(2)–O(5)	2.378(2)	O(6a)–Zn(2)–N(4)	171.67(8)
O(2)–Zn(1)–O(2w)	95.31(8)	O(3w)–Zn(2)–N(4)	89.48(9)
O(2)–Zn(1)–O(1w)	92.70(8)	O(4)–Zn(2)–N(4)	95.37(9)
O(2w)–Zn(1)–O(1w)	89.66(9)	N(3)–Zn(2)–N(4)	77.69(8)
O(2)–Zn(1)–N(2)	168.46(8)	O(6a)–Zn(2)–O(5)	95.69(8)
O(2w)–Zn(1)–N(2)	90.70(8)	O(3w)–Zn(2)–O(5)	95.45(7)
O(1w)–Zn(1)–N(2)	97.19(8)	O(4)–Zn(2)–O(5)	57.99(7)
O(2)–Zn(1)–N(1)	97.03(8)	N(3)–Zn(2)–O(5)	158.82(8)
O(2w)–Zn(1)–N(1)	166.66(8)	N(4)–Zn(2)–O(5)	92.38(7)
O(1w)–Zn(1)–N(1)	94.8(1)	O(6a)–Zn(2)–C(4)	90.14(8)
N(2)–Zn(1)–N(1)	76.29(8)	O(3w)–Zn(2)–C(4)	123.99(8)

Note: Symmetric transformation: *a*: $-x - 1$, $-y - 1$, $-z + 1$.

water molecules (O1w and O7w of **1**, O7w of **2**), were included and located from a difference Fourier map but not refined anistropically. Crystallographic data and structural refinements for **1** and **2** are given in table 1. Selected bond lengths and angles of **1** and **2** are listed in tables 2 and 3. CCDC deposition numbers are 933447 and 959262.

3. Results and discussion

3.1. *Synthesis*

Complexes **1** and **2** were prepared from the one-pot reaction of Zn(II) nitrate, citric acid, and phen/bpy with a molar ratio of 2 : 1 : 2. The optimal pH value was 4.8 through the addition of dilute ammonium hydroxide. Both complexes were stable in air at room temperature for long periods of time. **1** is insoluble in common solvents, while 2,2′-bipyridine product **2** is soluble in water, which is suitable for solution NMR measurement. FT-IR spectra of **1** and **2** display characteristic features of coordinated citrate (figure S1, see online supplementary material at http://dx.doi.org/10.1080/00958972.2014.944174). The absence of IR absorption bands around 1700 cm^{-1} was attributed to full deprotonation of carboxy groups in the citrate ligands of **1** and **2**, as revealed by structural analysis. The strong peaks at 1609, 1585 and 1430, 1385 cm^{-1} for **1**; 1606, 1598 and 1444, 1384 cm^{-1} for **2** correspond to ν_{asym} and ν_{sym} of the carboxy groups, respectively. IR spectra of **1** and **2** also show $\nu_{O\text{–}H}$ of water centered at 3413 and 3433 cm^{-1}, respectively.

3.2. *Structure description*

Single crystal X-ray structure analysis shows that **1** crystallizes in the triclinic space group $P\bar{1}$. It consists of a tetrameric cationic unit $[Zn_4(Hcit)_2(phen)_4(H_2O)_4]^{2+}$, nitrates, and lattice waters. As shown in figure 1, there are two independent zinc ions, which display different coordination geometries. In this centrosymmetric tetramer, Zn1 is surrounded by two

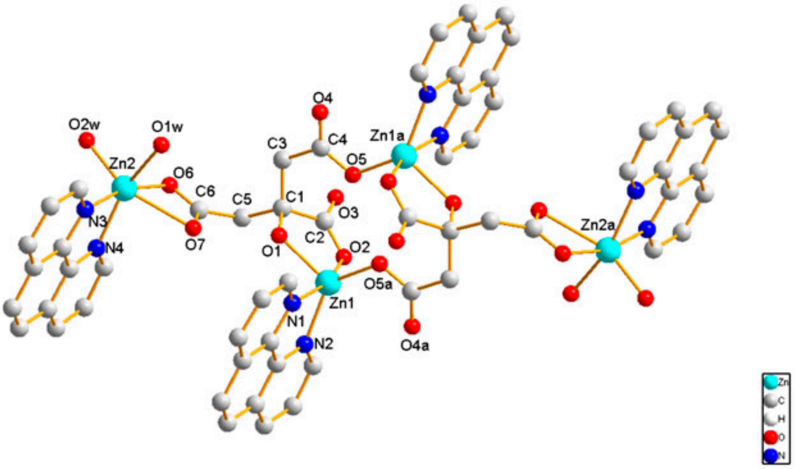

Figure 1. Tetrameric cationic unit $[Zn_4(Hcit)_2(phen)_4(H_2O)_4]^{2+}$ in $[Zn_4(Hcit)_2(phen)_4(H_2O)_4]\cdot 2NO_3\cdot 10H_2O$ (**1**).

nitrogens from phenanthroline and three oxygens (O1, O2, and O5a) belonging to α-hydroxy, α-carboxy, and β-carboxy groups of two different citrate ligands. The Zn–O distances range from 1.955(2) to 2.067(2) Å and the Zn–N distances are 2.080(2), 2.136(2) Å. Weak interactions exist between Zn1 and O4a of β-carboxy with a distance of 2.895 Å. Zn2 is surrounded by two nitrogens (N3, N4) from phenanthroline, two coordinated waters (O1w, O2w), and two oxygens (O6, O7) from one β-carboxy group of citrate, containing a weakly coordinated Zn2–O7 bond [2.404(2) Å]. The other Zn–O distances range from 2.012(2) to 2.112(2) Å and the Zn–N distances are 2.115(2), 2.117(2) Å. Zn1 and Zn2 are bridged by one citrate ligand to form dinuclear $[Zn_2(Hcit)(phen)_2(H_2O)_2]^+$. Zn1 is further doubly connected to symmetry-related Zn1a via two citrate ligands, generating a centrosymmetric tetranuclear $[Zn_4(Hcit)_2(phen)_4(H_2O)_4]^{2+}$.

Complex **2** crystallizes in the triclinic space group $P\bar{1}$ and consists of four zinc ions, two citrate ligands, four bpy molecules, six coordinated waters, and two nitrates as counter anions. A total of twelve lattice waters cocrystallized with the complex. A structural view of the tetranuclear zinc cluster **2** is depicted in figure 2. The centrosymmetric tetrameric cationic unit $[Zn_4(Hcit)_2(bpy)_4(H_2O)_6]^{2+}$ consists of two crystallographically independent Zn(II) ions. Zn1 shows ZnO_4N_2 coordination from two oxygens (O1, O2) belonging to α-hydroxy and α-carboxy groups of one citrate, two coordinated waters (O1w, O2w), and two nitrogens (N1, N2) from bpy. The Zn–O distances range from 2.048(2) to 2.189(2) Å and the Zn–N distances are 2.144(2), 2.132(2) Å. The Zn2 center adopts ZnO_4N_2 coordination provided by three oxygens (O4, O5, and O6a) from two bridging β-carboxy groups of two different citrates [Zn–O = 2.059(2)–2.378(2) Å], two N from bpy [Zn–N = 2.113(2), 2.118(2) Å] and one coordinated water [Zn–O3w = 2.061(2) Å]. Zn1 and Zn2 are bridged by one citrate to form dinuclear $[Zn_2(Hcit)(bpy)_2(H_2O)_3]^+$. Furthermore, two pairs of symmetry-related Zn(II) ions are connected by β-carboxylic O to form tetranuclear $[Zn_4(Hcit)_2(bpy)_4(H_2O)_6]^{2+}$.

In **1** and **2**, each citrate coordinates to three Zn ions. The citrate shows similar coordination styles, but displays distinct spatial connection modes. In **1**, the Zn1 and symmetry-related Zn1a are doubly bridged via two citrates to form a dinuclear unit, which is further

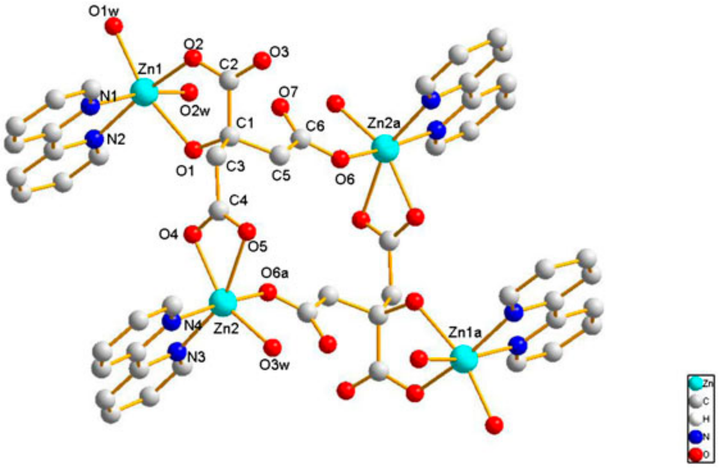

Figure 2. Tetrameric cationic unit $[Zn_4(Hcit)_2(bpy)_4(H_2O)_6]^{2+}$ in $[Zn_4(Hcit)_2(bpy)_4(H_2O)_6]\cdot 2NO_3\cdot 12H_2O$ (**2**).

extended to a tetranuclear unit through bridging Zn2 and Zn2a by the remaining β-carboxy group of citrate. In **2**, three Zn ions, Zn1, Zn2, and symmetry-related Zn2a, are connected by the same citrate. The two citrate ligands bridge the symmetry-related Zn(II) ions into a tetranuclear unit. The secondary ligands are 1,10-phenanthroline and 2,2-bipyridine in **1** and **2**, respectively. In **2**, two waters coordinate Zn1 to accomplish the six-coordination, while the bulky chelate phen in **1** hindered coordination of water with Zn1, forming weak interactions between Zn1 and β-carboxylic O4a of the citrate ligand (Zn1···O4a = 2.895 Å). Obviously, the spatial connection modes of citrate exert considerable influence on the molecular structures of **1** and **2**, and auxiliary N-donor ligands are also responsible for the formation of two tetranuclear zinc clusters. Strong hydrogen bonds are formed among hydroxy and carboxy oxygens, coordinated and lattice waters (table S1). Through these strong hydrogen bonds as well as π–π stacking interactions among phen/bpy planes, the distinct tetrameric zinc clusters in **1** and **2** are extended to build up a 3-D supramolecular architecture (figures S2 and S3). The purities of **1** and **2** have been proved by PXRD of the bulk products (figures S4 and S5), in which the experimental values are in agreement with that of theoretical simulation based on the single-crystal data.

3.3. *NMR spectroscopy*

Compound **1** is insoluble in common solvents and could not be studied by solution NMR measurement, while **2** is soluble in water, allowing solution NMR measurement. ^{1}H and ^{13}C NMR spectra of **2** are shown in figures S6 and 3. The ^{13}C NMR spectrum of **2** showed only one set of resonances. This is an indication that **2** remains as coordinated species in solution. In comparison with the corresponding carbons in K_3Hcit under comparable conditions [^{13}C NMR δ_C (D_2O) ppm: 180.0 $(CO_2)_\alpha$, 176.3 $(CO_2)_\beta$, 76.1 (≡CO), 46.0 (=CH_2)], the obvious downfield shifts at 183.50, 180.38, 76.99, and 45.92 ppm of **2** are assigned to the resonances of α-carboxy, β-carboxy, alcoholic, and methylene carbons of citrate, respectively. Moreover, peaks at 150.25, 150.00, 143.32, 128.73, and 124.09 ppm are assigned for the resonances of coordinated 2,2′-bipyridine. ^{1}H NMR spectrum of **2** also shows only one set of resonances. The peaks at 8.56–7.60 ppm belong to the resonances of 2,2′-bipyridine, while the peaks at 2.82–2.53 ppm are assigned for the methylene groups of citrate.

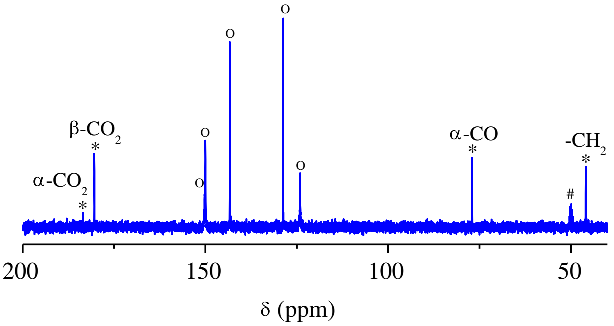

Figure 3. ^{13}C NMR spectrum of $[Zn_4(Hcit)_2(bpy)_4(H_2O)_6]\cdot 2NO_3\cdot 12H_2O$ (**2**). Labels: citrate (*); bpy (o); CD_3OD (#).

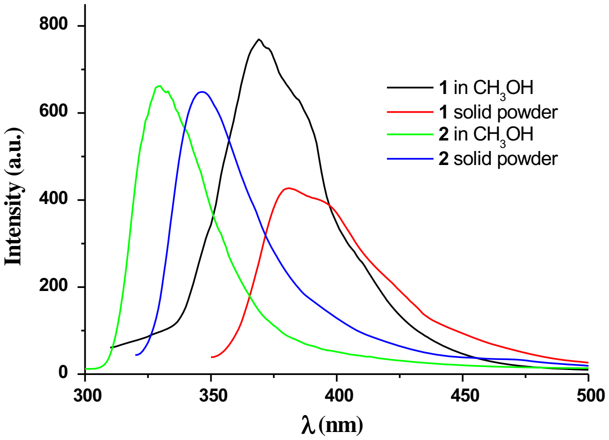

Figure 4. Fluorescent properties of **1** and **2** in dilute solution and in solid state at room temperature.

3.4. *Fluorescent property*

Fluorescent properties of **1** and **2** were investigated both in dilute solution and in solid state at room temperature (figure 4). Upon excitation at 336 nm, solid **1** displays a strong fluorescent emission band at 381 nm. The emission of **1** in methanol is at 369 nm ($\lambda_{ex} = 290$ nm) with a shoulder. There is significant luminescence in the solid state, and a 12 nm red-shift was observed compared to that in solution. Similar phenomenon was observed for **2**. After complexation of both bpy and citrate with Zn(II), solid **2** exhibits an intense emission band at 346 nm ($\lambda_{ex} = 300$ nm). The emission of **2** in methanol shows a peak at 329 nm ($\lambda_{ex} = 260$ nm), and a 17 nm blue-shift was observed compared to that in solid. Since the Zn^{II} ions are difficult to oxidize or reduce due to their d^{10} configuration, the emission peaks for **1** and **2** are neither metal-to-ligand nor ligand-to-metal charge transfer in nature, but may be assigned to intraligand (π–π*) fluorescent emission [30–32].

4. Conclusion

Two tetranuclear Zn(II) citrates with different N donor chelates are obtained in aqueous solution. Although both tetranuclear zinc clusters **1** and **2** are generated by two bridging citrate ligands in similar coordination modes, the final structures are different. Through comparison of their structures, we conclude that spatial connection modes of the citrate have a crucial effect on the structures of **1** and **2**, while auxiliary ligands are responsible for the constructions of frameworks. Both compounds exhibit strong solid-state fluorescent emission, which may arise from intraligand (π–π*) fluorescent emission. When **2** was dissolved in water, it seems the tetranuclear skeleton remains in solution, based on NMR measurement.

Supplementary material

Electronic supplementary information (ESI) available: X-ray crystallographic data in CIF format; IR spectra; views of 3-D network structures; simulated and measured XRD patterns of two compounds; hydrogen bonds. CCDC reference numbers 933447 for **1**, 959262 for **2**.

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