Scientific paper

Cd(II) and Zn(II) Coordination Polymers Assembled from Benzoyltrifluoroacetone and 1,2-Bis(4-Pyridyl)Ethane Ancillary ligands

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Abstract

Two novel cadmium(II) and zinc(II) metal-organic coordination polymers with a *β*-diketone and N-donor ancillary ligands, $[Cd(bpe)(btfa)_2]_n$ (**1**) and $[Zn(bpe)(btfa)_2]_n$ (**2**), (Hbtfa = benzoyltrifluoroacetone and bpe = 1,2-bis(4-pyridyl)ethane), have been prepared and characterized by elemental analysis, IR and ^{1}H NMR spectroscopy, and studied by thermal gravimetric analysis as well as single crystal X-ray diffraction. The crystal and molecular structures of **1** and **2** have been solved by X-ray diffraction and they turned out to be one-dimensional polymers with zigzag (**1**) and linear (**2**) dispositions of the metal atoms. These one-dimensional polymers are further connected to form a 3D supramolecular network by C–H···O and C–H···F interactions. Thermal stabilities of these polymeric complexes have also been investigated.

Keywords: Coordination polymers; *β*-Diketone; 1,2-Bis(4-pyridyl)ethane

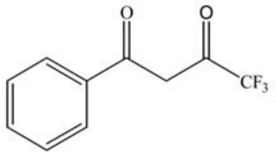
1. Introduction

The designed construction of metal–organic complexes from various molecular building blocks connected by coordination bond, supramolecular contacts (hydrogen bond, π–π stacking, etc.), or their combination, is an interesting research area not only because of their tremendous potential properties as functional solid materials in the areas of catalysis,[1] gas adsorption,[2] luminescence,[3] non-linear optics,[4] magnetism[5] and ion exchange,[6] but also for their intriguing structural diversities and new topologies.

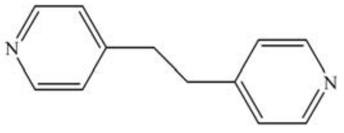
The combination of organic ligand 'spacers' and metal ion 'nodes' has been regarded as the most common synthetic approach to produce such coordination polymers. As d^{10} metal ions, Cd^{2+} and $Zn^{2+}$are particularly suited for the construction of coordination polymers and networks, since their spherical d^{10} configuration is associated with a flexible coordination environment so that tetrahedral, five-coordinated or octahedral geometries are possible and severe distortions of the ideal polyhedrons can easily occur. A successful approach to build these metal coordinated networks is to select suitable multi-dentate ligands as spacers and, among these, flexible bipyridyl-based ligand with pyridine rings linked by aliphatic chain, such as 1,2-bis(4-pyridyl)ethane (bpe), can freely rotate to meet the requirement of coordination geometries of metal ions in the assembly process. This ligand is good candidate to produce unique structural motifs with beautiful aesthetics and useful functional properties.[7] In contrast, unsaturated metal complexes of β-diketonates are of interest as building blocks of supramolecular structures. Several crystalline products have been synthesized using $[M(\beta\text{-diketonato})_2]$ complexes (M = Pb, Cd, Ag) and different bridging and chelating ligands.[8]

However, we must not forget that a variety of weak interactions and subtle factors can play a decisive role in orienting the outcome of the crystallization processes, so that a 'true' engineering of polymeric networks, both from a structural and a functional point of view, still remains a quite difficult challenge.

In the present work, 1,2-bis(4-pyridyl)ethane ligands was employed to react with Cd(II) and Zn(II) to produce one-dimensional coordination polymers in the presence of benzoyltrifluoroacetonate anion (Scheme 1). The structures reported here differ from others in that other bipyridyl analogous ligands have used (4,4'-bipyridyl) that do not act as spacers resulting in H-bond superstructures being built instead.[8c,d and 9]



Hbtfa or Htfpb: 4,4,4-trifluoro-1-phenyl-1,3-butanedione



bpe: 1,2-bis(4-pyridyl)ethane

Scheme 1: The ligands Hbtfa and bpe

2. Experimental

2. 1. Material and Measurements

All chemicals were reagent grade and used without further purification. FT-IR spectra were collected on a Mattson 1000 spectrophotometer using KBr pellets in the range of 450–4000 cm^{-1}. Elemental analyses (CHN) were performed using a Carlo ERBA model EA 1108 analyzer whereas ^{1}H NMR spectra were obtained using a Bruker spectrometer at 250 MHz in [D6]DMSO. Thermogravimetrical analyses (TGA) were performed in N_2 atmosphere with a flow rate of 20 ml/min on a Seiko Instruments thermal analyzer from 20 to 800 °C, with a heating rate of 10 °C/min in the ceramic crucibles.

2. 2. Crystallography

Diffraction data for **1** and **2** were collected at room temperature and 100 K (with an Oxford Cyrosystem Cobra low-temperature attachment), respectively. The data were collected using a Bruker SMART APEXII CCD diffractometer with graphite monochromatic MoK$_{á}$ radiation (λ = 0.71073 Å) at a detector distance of 5 cm and an AsPEXII software.[10] The collected data were reduced using SAINT program,[10] and the empirical absorption corrections were performed using SADABS program.[10] Structures were solved using direct methods and were refined using the least-squares method from SHELXTL software package.[11] All non-hydrogen atoms were refined anisotropically unless otherwise noted. Hydrogen atoms were located and included at their calculated positions. Materials for publication were prepared using SHELXTL[11] and ORTEP III.[12] All fluorine atoms in trifluoromethyl group in **1** are rotationally disordered about the three C–F bonds and the ratio of occupancies for three components are fixed to 0.40 : 0.30 : 0.30; both minor components of fluorine atoms were refined isotropically. Full crystallographic data, in CIF format, may be obtained from the Cambridge Crystallographic Data Centre (CCDC-915370 for **1** and CCDC-915371 for **2**) *via* . The crystal data and structure refinement of compounds **1** and **2** are summarized in Table 1. Selected bond lengths and angles of **1** and **2** are listed in Table 2.

2. 3. Synthesis of [Cd(bpe)(btfa)$_2$]$_n$ (1)

1,2-bis(4-pyridyl)ethane (0.184 g, 1.0 mmol) was placed in one of the arms of a branched tube[13] whereas cadmium(II) acetate (0.115 g, 0.50 mmol) and benzoyltrifluoroacetone (0.216 g, 1.0 mmol) were placed in the other arm. Methanol and water in a ratio of 2:1 were carefully added to fill both arms. The tube was then sealed and the ligand-containing arm was immersed in a bath at 60 °C whereas the other was maintained at ambient temperature. After 2 days, crystals that were deposited in the cooler arm were filtered, washed with acetone and ether, and dried in air. Yield: 0.25 g (70%). Analysis: Found: C 52.49%, H 3.10%, N 3.55%, Calculated for $C_{32}H_{24}CdF_6N_2O_4$: C 52.82%, H 3.30%, N 3.85%. IR (cm^{-1}) selected bands: 3059(w), 2938(w), 2857(w), 1618(s), 1585(s), 1517(s), 1473(s), 1348(m), 1316(m), 1248(m), 1187(m), 1015 (m), 767(m), 649(w), 512(w). ^{1}H NMR (DMSO, δ): 8.42(d, 4H, pyridyl of bpe), 7.82(d, 4H, pyridyl of bpe), 7.2–7.6(m, 10H, phenyl of btfa$^-$), 6.19 (s, 2H, =CH– of btfa$^-$) and 2.91 (d, –CH$_2$– of bpe).

2. 4. Synthesis of [Zn(bpe)(btfa)$_2$]$_n$ (2)

Complex **2** was synthesized in the same way as complex **1** using zinc(II) acetate instead of cadmium(II) acetate. Yield: 0.19 g (56%). Analysis: Found: C 56.49%, H 3.80%, N 4.45%, Calculated for $C_{32}H_{24}F_6N_2O_4Zn$: C 56.47%, H 3.53%, N 4.12%. IR (cm^{-1}) selected bands: 3055(w), 2927(w), 2864(w), 1625(s), 1582(s), 1522(s), 1491(s), 1352(m), 1256(m), 1194(m), 1014(m), 785(m), 666(w). ^{1}H NMR (DMSO, δ): 8.43(d, 4H, pyridyl of bpe), 7.84(d, 4H, pyridyl of bpe), 7.25–7.60(m, 10H, phenyl of btfa$^-$), 6.22 (s, 2H, =CH– of btfa$^-$) and 2.92 (d, 4H, –CH$_2$– of bpe).

3. Results and Discussion

3. 1. Spectroscopic and Thermal Analysis

IR spectra confirm the presence of organic ligands used in the syntheses (through the typical vibrations of pyridine aromatic rings, and diketonate groups). The presence of the bpe ligand is provided by the signals $\nu_{as}(CH_2)$

Table 1. Crystal data and structure refinement for **1** and **2**

	2	**1**
Identification code	$[Cd(bpe)(btfa)_2]_n$	$[Zn(bpe)(btfa)_2]_n$
Empirical formula	$C_{32}H_{24}CdF_6N_2O_4$	$C_{32}H_{24}F_6N_2O_4Zn$
Formula weight	726.93	679.90
Crystal system	Orthorhombic	Monoclinic
Space group	*P ccn*	$P\,2_1/c$
Unit cell dimensions	a = 17.9986(10) Å	a = 14.9131(2) Å
	b = 11.2127(6) Å	b = 17.6978(3) Å
	c = 15.6293(9) Å	c = 11.61820(10) Å
		β = 99.069(1)°
Volume	3154.2(3) Å^3	3028.05(7) Å^3
Temperature (K)	293(2)	100(2)
Z	4	4
Density (calculated)	1.531 g cm^{-3}	1.491 g cm^{-3}
Absorption coefficient	0.766 mm^{-1}	0.888 mm^{-1}
F(000)	1456	1384
θ range for data collection	3.18–35.89	1.80–31.07
Index ranges	$-29 \le h \le 29$	$-21 \le h \le 21$
	$-11 \le k \le 18$	$-18 \le k \le 25$
	$-25 \le l \le 23$	$-16 \le l \le 16$
Reflections collected	45332	37566
Independent reflections	7387 [$R_{(int)}$ = 0.0322]	9680 [$R_{(int)}$ = 0.0419]
Completeness to theta	99.5 %	99.7 %
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	7387/0/231	9680/0/409
Goodness-of-fit on F^2	1.033	1.042
R_1, wR_2 [$I_0 > 2\sigma(I_0)$]	0.0386, 0.1127	0.0420, 0.0898
R_1, wR_2 (all data)	0.0719, 0.1439	0.0757, 0.1035
Largest dF peak, hole	0.80, –0.54 e. Å^{-3}	0.44, –0.45 e. Å^{-3}

at 2938 (**1**) and 2927 (**2**) cm^{-1}; $\nu_s(CH_2)$ at 2857 (**1**) and 2864 cm^{-1} (**2**). The bpe ligand is characterized by $\nu_{as}(CC)$ at 1585 (**1**) and 1582 cm^{-1} (**2**); $\nu_s(CC)$ at 1515 (**1**), 1491 cm^{-1} (**2**) vibrations, and the combined effect of the $\nu(CC)$ and $\delta(CCH)$ stretchings at 1015 (**1**) and 1014 cm^{-1} (**2**). The relatively weak absorption bands at around 3059 and 3055 cm^{-1} are due to the C–H modes involving the aromatic ring hydrogen atoms. The IR spectra of compounds showed strong bands at 1618, 1625 cm^{-1} and at 1517, 1522 cm^{-1}, assigned to the ν(C=O) and ν(C=C) stretching of btfa$^-$ anions. These bands are at significantly lower energies than those found for free Hbtfa (1655 cm^{-1}) and are indicative of β-diketonate chelation to Cd(II) and Zn(II). The absorption bands in the frequency range 1260–1130 cm^{-1} correspond with the C–F modes of the β-diketonates.[14] The ^{1}H NMR spectra of the DMSO solu-

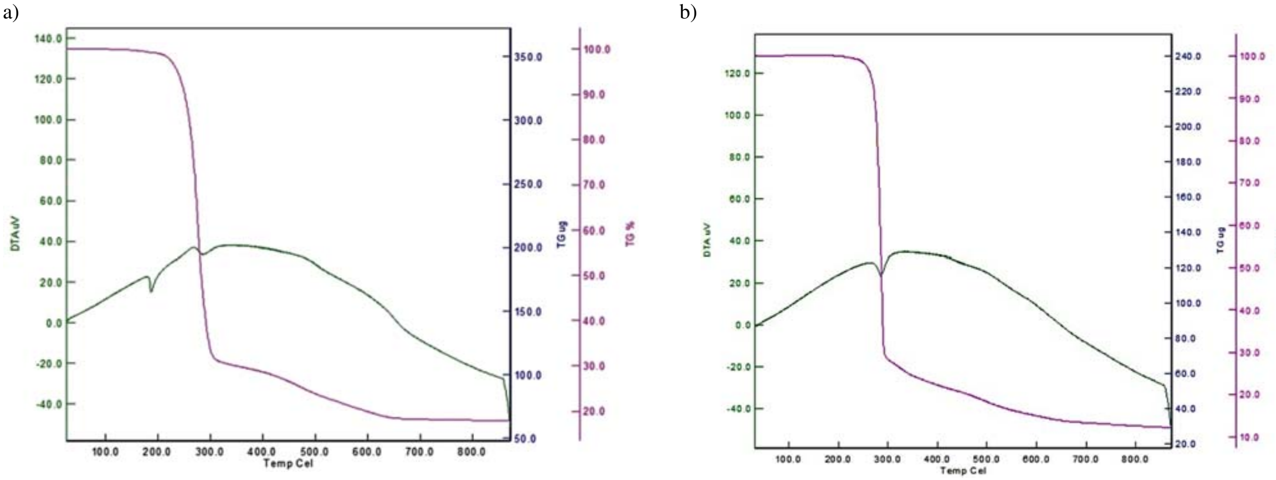


Figure 1. The TGA curves of a) **1** and b) **2**.

tions of **1** and **2** display three different protons of the bpe ligand at 8.4, 7.8 (aromatic protons) and 2.9 (aliphatic protons) ppm and the singlets at 6.19 (**1**) and 6.22 (**2**) ppm of =CH– protons of btfa$^-$ anions. In **1** and **2**, distinct peaks at 7.25–7.60 ppm were assigned to the five protons of the phenyl ring of the btfa$^-$ anions.

In order to investigate the thermal stability of both complexes, TGA was performed in a N_2 atmosphere. The TGA curves show that complexes **1** and **2** exhibit similar decomposition pathways. The TGA curves illustrate no weight loss up to 265 °C for **1** and up to 275°C for **2**, demonstrating that **1** and **2** are retained up to these temperatures. The thermal decomposition of the compounds occurs in two steps: the first step (sharp endothermic decomposition) in the temperature range 265–300 °C (almost 70% weight) for **1** and 280–300 °C (almost 70% weight) for **2**, the second step in the temperature range 300–650 °C almost 12% and 16% weight for **1** and **2**, respectively, corresponds to the decomposition of the compounds (Fig. 1). The mass loss calculations as well as the microanalyses of the solid residues suggest that the residue left as a final decomposition product of the complexes is CdO and ZnO, and the total mass loss of 18.12% for **1** (calc. 18.93%) and 13.25% for **2** (calc. 11.98%), respectively, agrees well with the proposed structures. These results indicate that **1** and **2** have medium thermal stability and in accord with the conclusion reported that a fluorinated substituent of a ligand leads to an improved thermal and oxidative stability.[15]

3. 3 Description of the Crystal Structures of 1 and 2

Single crystal structure determinations of **1** and **2** indicate the formation of one-dimensional coordination polymers (Figs. 2(a) and 3). Utilizing the bridging *N*,*N*'-donor ligand bpe, two 1D complexes of **1** and **2** are obtained. Polymer **1** crystallizes in space group *P ccn* and the asymmetric unit of compound **1** is constrained with two crystallographic symmetry elements. The asymmetric fragment of 1D polymer has crystallographic symmetry that is imposed with two-fold axes going through the cadmium atom and as well imposed inversion centre between C16 and its symmetry related carbon atom. As shown in Figure 2, Cd1 is coordinated by four oxygen atoms of two btfa anions and two *cis* bpe nitrogen atoms to give a Cd-O_4N_2 distorted octahedral environment (Φ = 69.42, θ = 54.59, ρ = 172.98; Φ is the twist angle between the enhanced triangles around the C_3 axis; θ is angle between the mean plane of the two triangles and the chelate planes defined by the metal and each pair of near eclipsed vertices; ρ is angle between the metal and trans O-donor sites),[16] in which O1–O2–N1–O1^i constitutes the equatorial plane and the apical positions are occupied by O2^i and N^i. The Cd–O bond lengths vary from 2.274(2) to 2.280(2) Å, while the Cd–N bond length is 2.341(2) Å (Table 2), which are in the normal range.[17] The overall structure of **1** can be described as a 1D framework consisting of Cd-bpe zigzag layers. The bpe ligand adopts an anti-conformation with the C–CH_2–CH_2–C torsion angle of 180° and a parallel arrangement of the pyridyl rings.[18] The Cd···Cd separation across the bpe molecule equals to 13.906 Å.

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

1			
Cd1–O1	2.275(2)	Cd1–N1	2.341(2)
Cd1–O2	2.281(2)	N1–Cd1–N1^i	90.94(10)
O1–Cd1–O1^i	173.40(10)	O1–Cd1–O2^i	105.52(7)
O1–Cd1–O2	79.29(6)	O2^i–Cd1–O2	89.35(12)
O1–Cd1–N1	85.67(6)	O1^i–Cd1–N1	89.70(7)
O2^i–Cd1–N1	91.89(7)	O2–Cd1–N1	164.68(7)
i: 0.5–*x*, 1.5–*y*, *z*			
2			
Zn1–O2	2.0906(13)	Zn2–O4	2.0642(13)
Zn1–O1	2.1175(12)	Zn2–O3	2.0991(12)
Zn1–N1	2.1190(14)	Zn2–N2	2.1462(15)
O2–Zn1–O1	87.24(5)	O4–Zn2–O3	88.68(5)
O2–Zn1–N1	90.25(5)	O4–Zn2–N2	90.55(5)
O1–Zn1–N1	88.40(5)	O3–Zn2–N2	89.32(5)

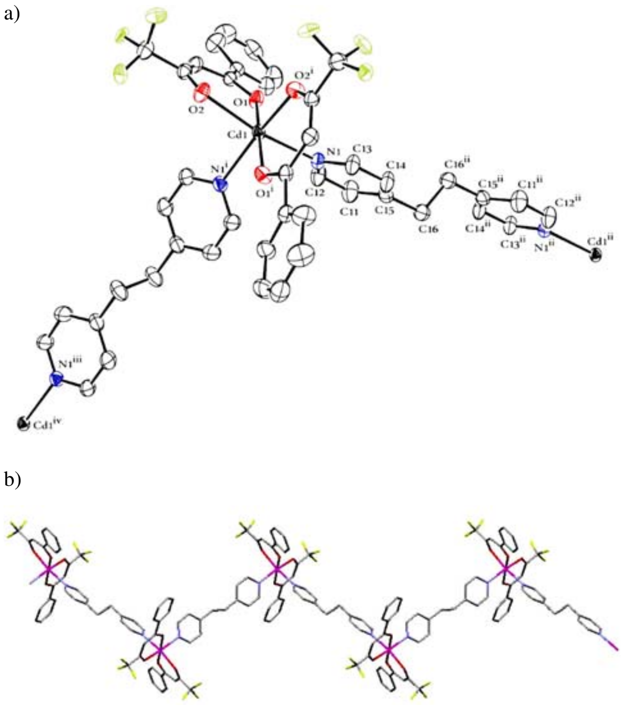


Figure 2. (a) ORTEP view of **1**, displacement ellipsoids are shown at the 30% probability level; disordered fluorine and hydrogen atoms are omitted for clarity; symmetry codes: i: 0.5 – *x*, 1.5 – *y*, *z*; ii: 1 – *x*, 2 – *y*, 1 – *z*; iii: –0.5 + *x*, –0.5 + *y*, 1 – *z*; iv: –*x*, 1 – *y*, 1 – *z*; (b) Fragment of the 1D zigzag coordination polymer of **1**.

Single-crystal X–ray diffraction reveals that complex **2** crystallizes in space group *P* $2_1/c$ with two crystallographically independent Zn ions. The Zn atom are six-coordinated by two nitrogen atoms of bpe in a trans fashion locating at the axial sites as well as four oxygen atoms of two btfa anions at the equatorial plane to give ZnO_4N_2 distorted octahedral environment (for Zn1: Φ = 62.34, θ = 55.01, ρ = 180.00 and Zn2: Φ = 61.25, θ = 54.84, ρ = 180.00),[16] (see Figure 3). The average Zn1–O bond length (2.104 Å) is larger than the average Zn2–O bond length (2.081 Å) and the Zn2–N bond length (2.147 Å) is also larger than the Zn1–N bond length (2.118 Å).[19] The overall structure of **2** can be described as an infinite 1D linear coordination polymer chains (Fig. 3). The bipyridine spacer adopts an anti conformation with the corresponding C–CH_2–CH_2–C torsion angle of 176.94°, and the two pyridyl (aromatic) rings are not coplanar with each other (the twist angle between the rings is 5.02°).

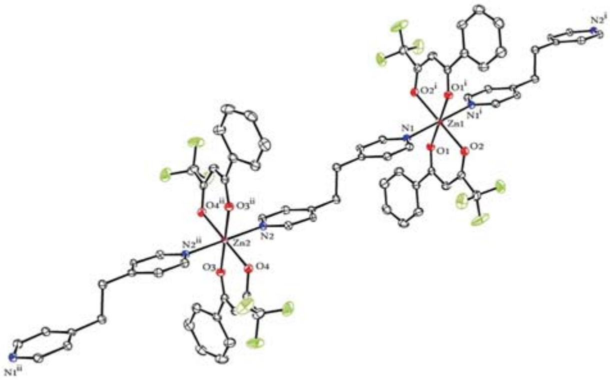


Figure 3. Fragment of the 1D linear coordination polymer of **2**, displacement ellipsoids are shown at the 30% probability level, hydrogen atoms are omitted for clarity; symmetry codes: i: 1 – *x*, –*y*, –*z*; ii: –*x*, 1 – *y*, 1 – *z*.

An inspection of **1** and **2** for weak directional intermolecular interactions by the programs PLATON and MERCURY, which were used for calculating the supramolecular interactions, shows that there are C–H···O and C–H···F interactions (hydrogen bond parameters are listed in Table 3).[20,21] The H···O and H···F separations range from 2.325 to 2.654 Å, which are indicative of moderate-to-strong intermolecular interactions.[22] These chains are parallel in the crystal packing of **2**, forming a layer packing structure.[23] In addition, weak C–H···π intermolecular interactions using hydrogen H25A and aromatic ring [N2/C18–C22 (*Cg*) (*x*, *y*, 1 + *z*)] with distance of 3.029 Å along with isotropic van der Waals involving aromatic phenyl rings with a stacking distance of 3.295 Å form molecular chains along the crystallographic *c* axis (Figure 4).[24] There are short F···F interactions[25] with the distance of 2.909(3) Å (F3··· F5(1 – *x*, 1 – *y*, 1 – *z*)) which are less than the sum of van der Waals radii for fluorine (2.94 Å).[26] The chains of **1** and **2** are further connected to form 3D supramolecular frameworks by the mentioned intermolecular interactions (Figure 4).

A useful comparison of the result of the present study with those of another are provided by a recent structural study of the phenyl containing fluorine β-diketones complex of Cd(II) with 4,4'-bipyridine.[27] The average Cd–O bond length of **1** is 2.277Å and is larger than in the previously published complex.[27] It seems reasonable to assume that these differences in bond lengths result from the flexibility of bpe ligand compared to 4,4'-bpy ligand and the different intermolecular interactions detected in the reported structures.

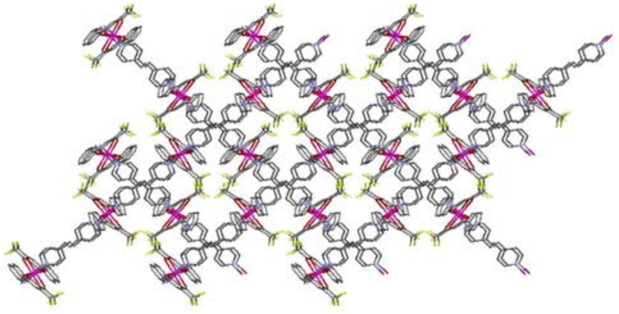


Figure 4. A part of three-dimensional network of **2** along the crystallographic *ab* plane, with rotated 90 degrees, generated from the intermolecular interactions.

4. Conclusion

Two Cd^{II} and Zn^{II} coordination polymers based on fluorined β-diketone (Hbtfa) and 1,2-bis(4-pyridyl)ethane have been prepared and characterized, showing diverse one-dimensional polymer chains with zigzag (**1**) or linear

Table 3. Hydrogen bonding for **1** and **2**

D–H···A	H···A/Å	D···A/Å	D–H···A/°
1			
C12–H12A··· F2 (0.5 – *x*, *y*, 0.5 + *z*)	2.330	3.234(8)	163.62
C5–H5A··· F1 (0.5 – *x*, 0.5 – *y*, *z*)	2.597	3.504(7)	165.70
C3–H3A··· O1 (1 – *x*, –0.5 + *y*, 0.5 – *z*)	2.669	3.527(4)	153.77
2			
C2–H2A··· F3 (1 – *x*, –0.5 + *y*, 0.5 – *z*)	2.530	3.232(2)	130.84
C1–H1A··· F4 (*x*, 0.5 – *y*, –0.5 + *z*)	2.604	3.445(2)	147.74
C2–H2A··· F5 (*x*, 0.5 – *y*, –0.5 + *z*)	2.652	3.302(3)	126.13

(**2**) disposition of the metal atoms. The ability of weak interactions to control packing of molecular moieties to generate different patterns suggests their importance in crystal engineering. It is clear that such weak interactions are prolific in molecular assemblies providing both directionality and flexibility in the crystal structures. Further studies on the mapping of the charge density distributions followed by a topological analysis of the regions in C–F···π, C–H···π, C–F···H–C, C–H···O, F···F, π···π interactions are currently in progress.

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Povzetek

Sintetizirali smo dva nova Cd(II) in Zn(II) metalo-organska koordinacijska polimera z β-diketonom in N-donorskim ligandom, $[Cd(bpe)(btfa)_2]_n$ (**1**) in $[Zn(bpe)(btfa)_2]_n$ (**2**), (Hbtfa = benzoiltrifluoroaceton in bpe = 1,2-bis(4-piridil)etan). Karakterizirana sta bila s pomočjo elementne analize, IR in ^{1}H NMR spectroskopije ter z uporabo termogravimetrične analize. Kristalni in molekulski strukturi **1** in **2** sta bili določeni z rentgensko difrakcijo. Spojini kristalizirata v obliki eno-dimenzionalnih polimerov s cik-cak (**1**) in linearno (**2**) razporeditvijo kovinskih centrov. Eno-dimenzionalni polimeri tvorijo 3D supramolekularno mrežo preko C–H···O in C–H···F interakcij. Določena je bila tudi termična stabilnost obeh spojin.