Main Group Chemistry 14 (2015) 105–114
DOI 10.3233/MGC-140156
IOS Press

Syntheses, structures and properties of a new compound of the type [Zn(4,4′-dmo-2,2′-bpy)$_2$(CH$_3$COO)]$_2$[Zn(SCN)$_4$]·H$_2$O with zinc in two cationic and one anionic complexes

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Abstract.
A new compound of zinc(II) with the ligand 4,4′-dimethoxy-2,2′-bipyridine(4,4′-dmo-2,2′-bpy), [Zn(4,4′-dmo-2,2′-bpy)$_2$(CH$_3$COO)]$_2$[Zn(SCN)$_4$]·H$_2$O, has been obtained as white single crystals by the branched tube method and characterized by elemental analysis, IR and ^{1}H NMR spectroscopy and by X-ray crystallography. Thermal and electrochemical properties were also studied. The crystal structure consits of two discrete [Zn(4,4′-dmo-2,2′-bpy)$_2$(CH$_3$COO)]$^+$ cations and a [Zn(SCN)$_4$]$^{2-}$ anion. Zinc(II) cations in the [Zn(4,4′-dmo-2,2′-bpy)$_2$(CH$_3$COO)]$^+$ units have a distorted octahedral surrounding by ZnN$_4$O$_2$ coordinated through four N atoms of 4,4′-dmo-2,2′-bpy and two O atoms of acetate. Zinc(II) in [Zn(SCN)$_4$]$^{2-}$ has a distorted tetrahedral coordination environment with an ZnN$_4$ ligated by four N atoms of the terminal thiocyanates. In the solid state, [Zn(4,4′-dmo-2,2′-bpy)(CH$_3$COO)]$^+$ cations are interconnected by tetrahedral [Zn(NCS)$_4$]$^{2-}$ units by cooperative C–H···O, C–H···S, C–H···N and π-π stacking interactions resulting in a 2D network structure. Establishment of such networks seems to be aiding the crystallization.

Keywords: Zinc(II), cation complexes, anion complexes, weak interactions

1. Introduction

The design and construction of inorganic–organic hybrid materials has attracted considerable attention in recent years for their special functional properties such as optics, magnetism, separation and catalysis as well as the variety of architectures and topologies [1, 2]. Among them, the synthesis of hybrid materials using anion complexes as counter ions is a strategy allowing us to probe systematically their effect on the cation backbone. Thus, we are attempting to control the topology of the crystal structure [3].

Recently, the synthesis and structural characterization of multidimensional homo- and heterometallic coordination polymers based on the pseudo-halides SCN$^-$ [4] has been in the focus of many research

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groups worldwide. This interest is based not only on the high versatility of their binding modes which allow a rich architectonical diversity in corresponding structures, but also on their exceptional potential applications. The thiocyanate ligand with its marked ambidentate character and all the versatile coordination modes described above is expected to afford a number of homo-and heterometallic discrete one-, two-and three dimensional structural assemblies with specific structural features and optical and magnetic properties [5]. Simultaneous presence of two different metal centers can potentially give rise to interesting physico-chemical properties and lead to attractive novel topologies and intriguing frameworks. However, despite the various coordination modes of the SCN^- group to the metalions, it is not widely used in the design and synthesis of inorganic compounds and the heterometallic thiocyanato bridged species are comparatively less numerous [6].

Some zinc thiocyanate systems have been reported in literature. However, the synthesis of inorganic–organic hybrid materials using zinc thiocyanate anionic systems and cation complexes as counter ions is still rare or lacking [7]. Our current interest is the combination of zinc thiocyanate anions with cationic zinc complexes as counter ions resulting in fascinating hybrid materials and significant use in bioinorganic chemistry, too [8].

This strategy is anticipated to result in appealing structural, electrochemical, and thermal properties which should lead to interesting new functional materials. As a part of continuing investigations on inorganic–organic hybrid compounds based on zinc cation and anion complexes, we report the synthesis and crystal structure determination of the new hybrid compound $[Zn(4,4'\text{-dmo-}2,2'\text{-bpy})_2(CH_3COO)]_2[Zn(SCN)_4]\cdot H_2O$ displaying two different positions of Zn ions in the cyclic voltammograms.

2. Experimental

2.1. Materials and measurements

4,4′-dimethoxy-2,2′-bipyridine, is commercially available from Aldrich (97%) and is used as received. All chemicals were of reagent grade and used without further purification.

IR spectra were recorded as KBr disc using Perkin-Elmer 597 and Nicolet 510P spectrometers. Microanalyses were carried out using a Heraeus CHN-O- Rapid analyzer. ^{1}H NMR spectra were measured with a BRUKER DRX-500 AVANCE spectrometer at 500 MHz. Thermal analyses were carried out on a Perkin-Elmer instrument. Electrochemical measurements were performed with Potentiostat/ Galvanostat Autolab30 in a conventional three-electrode glass cell containing glassy carbon (GCE) as working electrode, a Pt plate as auxiliary electrode, and Ag/Ag^+ as pseudo-reference electrode standardized by the redox couple ferrocenium/ferrocene (Fc^+/Fc). GCE was polished to a mirror-like surface with alumina and water slurry on polishing cloth and rinsed with doubly distilled water. Then, it was subsequently cleaned ultrasonically in acetone, absolute ethanol and distilled water. Prior to the electrochemical experiments, the electrode was dried with an argon gas stream, and the solutions were purged with pure argon gas for at least 10 min; additionally, an argon atmosphere was maintained over the solution during the experiments. Cyclic voltammetry was carried out in blank solution [DMSO + 0.1 M tetra-n-butyl ammonium perchlorate (TBAP)] containing each of the compounds with a scan rate of 50 mV s^{-1} at 25 °C.

2.2. Preparation and crystal growth of $[Zn(4,4'\text{-dmo-}2,2'\text{-bpy})_2(CH_3COO)]_2[Zn(SCN)_4]\cdot H_2O$

4,4′-Dimethoxy-2,2′-bipyridine (0.108 g, 0.5 mmol) was placed in one of the arms of a branched tube (diagram 1) [9], zinc(II) acetate trihydrate (0.14 g, 0.5 mmol) and potassium thiocyanate (0.097 g, 1 mmol) was placed in the other arm. Methanol and water in a ratio of 1:1 were carefully added to fill both arms. The tube was then sealed and the ligand-containing arm was immersed in a thermostat bath at 60°C while the other arm was maintained at ambient temperature. After 1 day, crystals in the cooler arm were filtered off, washed with mother liquid and dried in air, yield:69 %. Elemental Analysis Calculated for $C_{56}H_{54}N_{12}O_{12}S_4Zn_3$: C 46.91, H 3.77, N 11.73. Found: C 46.75, H 3.80, N 11.54. IR (cm^{-1}) selected bands: 746(w), 765(s), 829 (vs, C-H), 1037(vs), 1242(vs) 1384, 1473, 1558(s, aromatic ring), 2085(vs, thiocyanate), 2965(w, C-H aliphatic), 3053(w, C-H aromatic).^{1}H NMR (DMSO, δ): 8.50 (s, 8H, a), 8.18 (d, 8H, d), 7.30 (d, 8H, c), 3.40 (s, 12H, b), 2.10 (s, 6H,) ppm.

2.3. Crystal structure determination

Data collection for X-ray crystal structure determination was performed on a Agilent Super Nova providing Mo-K_α radiation ($\lambda = 0.71073$ Å) at 123 K. The data were corrected for Lorentz and polarization effects. Absorption was corrected by multi-scans [10]. The crystal structure was solved using SIR2004 [11] and refined with SHELX-97 [12]. All non-hydrogen atoms were refined using anisotropic displacement parameters. The hydrogen atoms were located in idealized positions and refined isotropically according to the riding model. The disordered H_2O molecules in **1** could not be refined to any reasonable molecule from difference Fourier peaks. In the void midpoint, size and number of electrons were refined and the contribution to the calculated structure factors of the disordered water is taken into account with the program SQUEEZE [13]. The void is detected around (0.171 0.384 0.236), with the size of 122 Å^3, and 11 electrons. This corresponds to one water molecule. The Flack-x-parameter is equal to zero (0.002(5)), indicating that no inversion twin is present. Checks for higher symmetry were carried out and did not suggest any missed symmetry element. The crystal data and structure refinement of compound **1** is summarized in Table 1.

3. Result and discussion

3.1. Spectroscopic and thermal studies

Architectures of this kind of supramolecular compounds constructed with zinc(II) and the ligand 5,5′-dmo-2,2′-bpy have not been reported so far. Herein, we report the synthesis and crystal structure of $[Zn(4,4'\text{-dmo-}2,2'\text{-bpy})_2(CH_3COO)]_2[Zn(SCN)_4]\cdot H_2O$, a new ionic compound consisting of two zinc centred cations and an anionic zinc(II) complex. Single crystals of **1** were grown by the branched tube method (diagram 1). The reaction between the ligand 4,4′-dmo-2,2′-bpy, $Zn(CH_3COO)_2\cdot 3H_2O$ and KSCN by diffusion along a thermal gradient in water/methanol solution yields **1** as white crystals. It is an air-stable and high-melting solid which is soluble in DMSO.

The IR spectrum of **1** shows absorption bands resulting from the skeletal vibrations of the aromatic rings in the range of 1400–1600 cm^{-1}. The relatively weak absorption bands at around 2965 cm^{-1} are due to the C–H modes involving the –CH_3 group of the ligand in **1**, and the relatively weak absorption bands at around 3053 cm^{-1} are due to the C–H modes of the aromatic rings. A single νas(CN) band at 2085 cm^{-1} indicates the presence of terminal thiocyanate [7]. The weak absorption band at 765 cm^{-1} is assigned to a blue shifted CS stretching mode as compared to the corresponding ν(CS) for KSCN at 746 cm^{-1} [14]. The bands in the region 565–1060 cm^{-1} originate from the in plane or out of plane bending vibrations of the aromatic C–H groups [15]. The ^{1}H-NMR spectrum of the DMSO solution of **1** displays three signals assigned to the CH protons of the pyridine groups of the 4,4′-dmo-2,2′-bpy ligands in the

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

Identification code	$[Zn(4,4'\text{-dmo-}2,2'\text{-bpy})_2(CH_3COO)]_2[Zn(NCS)_4]\ H_2O$
Empirical formula	$C_{56}H_{54}N_{12}O_{12}S_4Zn_3$
Formula weight	1411.65
Crystal system	Monoclinic
Space group	*Cc*
Unit cell dimensions	$a = 15.8926$ (3) Å
	$b = 24.1386$ (3) Å
	$c = 17.7336$ (4) Å
	$\beta = 108.012$ (2)°
Volume	6469.7 (2) $Å^3$
Z	4
Density (calculated)	1.449 Mg m^{-3}
Absorption coefficient	1.30 mm^{-1}
F(000)	2896
θ range for data collection	3.09 to 32.43
Index ranges	$-20 \leq h \leq 23$
	$-31 \leq k \leq 36$
	$-26 \leq l \leq 21$
Reflections collected	29847
Independent reflections	16930[$R_{(int)} = 0.049$]
Completeness to theta	91.80%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	16930/0/794
Goodness-of-fit on F^2	1.033
Final R. [$I_0 > 2\sigma(I_0)$]	$R1 = 0.0454$, $wR2 = 0.0970$
R indices (all data)	$R1 = 0.0641$, $wR2 = 0.1041$
Largest diff. Peak, hole	1.14, -1-34 e. Å
Flack parameter	0.002(5)
Temperature	123 K

region 7–9 ppm. Protons of the methoxy groups of the 4,4′-dmo-2,2′-bpy ligand and of the acetate anions are observed at 3.4 and 2.1 ppm, respectively.

In order to examine the thermal stability of **1**, thermal gravimetric (TG) and differential thermal analyses (DTA) were carried out between 30 and 900°C (Fig. 1). **1** does not melt and is stable up to 210°C where it begins to decompose. The TG curve indicates the release of 4,4′-dmo-2,2′-bpy and the decomposition of acetate and thiocyanate anions in two steps at 220–300 °C and 550-750°C with endothermic effects (Fig. 1). The solid residue formed at around 900°C is supposed to be ZnS (obs: 55.80, calc: 57.90%).

3.2. Electrochemical studies

The voltammogram of **1** shows two metal-centered reduction peaks at −1.3 and −1.6 V (Fig. 2). In the case of free Zn^{2+} ions there was only one reduction peak at about −1.4 V related to the reduction of Zn^{II} to Zn^0 [16]. In order to evaluate the origin of the two reduction peaks of **1**, the ratio of currents of the metal-centered and ligand-centered peaks were measured as about 1:1 and 1:2 for the first and second

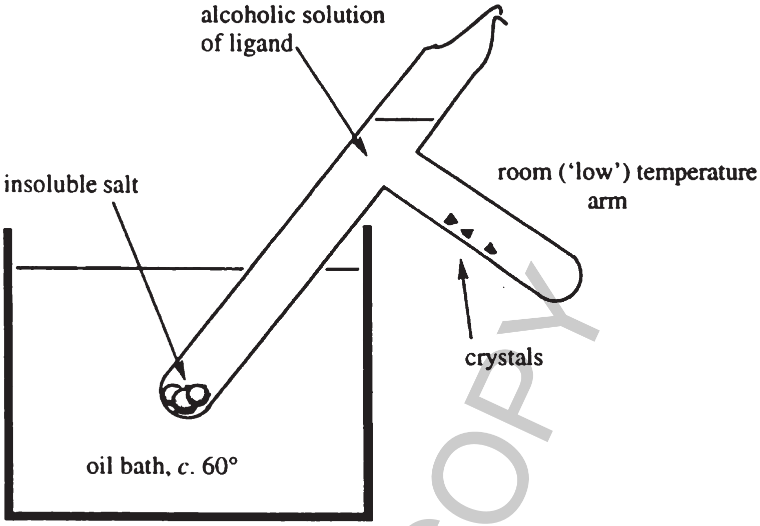

Diagram 1. The "branched tube" method used for obtaining crystalline of **1**.

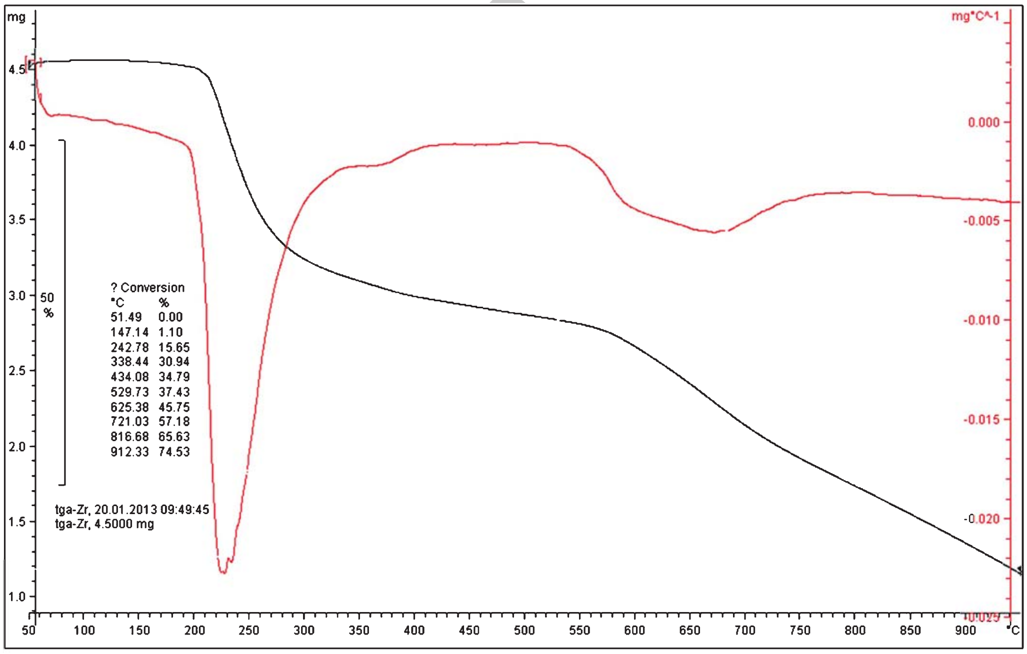

Fig. 1. Thermogravimetric (TG, left scale) and differential thermal analysis (DTA, right scale) of **1**.

peak (R_{Zna} and R_{Znb}), respectively. Therefore, the two reduction peaks may be attributed to the presence of two different positions for Zn ions in complexed form. The position with a less negative reduction potential (less stable) are two times of the other position (more stable). In the reverse scan a weak broad oxidation peak about -0.5 V was observed which can be attributed to the oxidation of Zn^0.

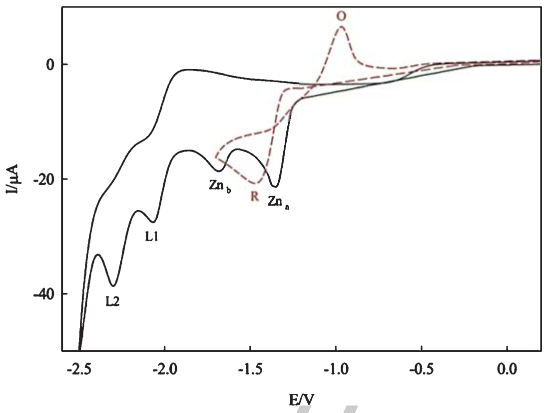

Fig. 2. Cyclic voltammograms of **1** at glassy carbon electrode in the presence of 0.1 M TBAP (scan rate, 50 mVs^{-1}).

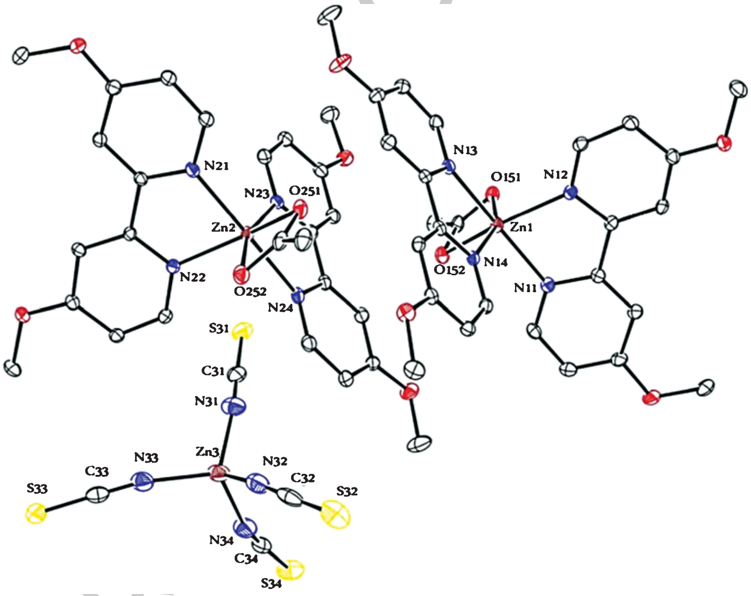

Fig. 3. ORTEP diagram of the asymmetric unit of $[Zn(4,4'\text{-dmo-}2,2'\text{-bpy})_2(CH_3COO)]_2[Zn(SCN)_4]\cdot H_2O$ **1** showing three complexes of Zn(II); disordered water is omitted for clarity.

3.3. Description of the crystal structures

The crystal structure of **1** as determined by single-crystal X-ray diffraction is composed of three molecular parts: anion complexes, cation complexes, and disordered water molecules. A perspective view of **1** together with the atom labeling scheme is presented in Fig. 3.

The crystal structure of **1** consists of two $[Zn(4,4'\text{-dmo-}2,2'\text{-bpy})_2(CH_3COO)]^+$ complex cations, $[Zn(NCS)_4]^{2-}$ complex anions and water molecules disordered by symmetry. Relevant bond parameters are given in Table 2.

The Zn atoms in the complex cations are ligated by the four N donor atoms of two chelating 4,4′-dmo-2,2′-bpy molecules and two O donor atoms of acetate anion to form a distorted octahedral geometry. The

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

Zn1—N11	2.111(3)	Zn3—N34	1.937(7)
Zn1—N13	2.113(3)	Zn3—N31	1.953(6)
Zn1—N14	2.130(3)	Zn3—N33	1.968 (5)
Zn1—N12	2.130(3)	Zn3—N32	1.973(7)
Zn1—O152	2.182(3)		
Zn1—O151	2.184(3)	N31—Zn3—N32	113.1(2)
Zn2—O251	2.088(3)	N31—Zn3—N33	109.9(2)
Zn2—N22	2.095(3)	N31—Zn3—N34	109.3(3)
Zn2—N23	2.119(3)	N32—Zn3—N33	110.9(2)
Zn2—N21	2.117(3)	N32—Zn3—N34	103.2(3)
Zn2—N24	2.127(3)	N33—Zn3—N34	110.3(2)
Zn2—O252	2.323(3)		
N11—Zn1—N12	77.6(1)	N21—Zn2—N22	77.3(1)
N11—Zn1—N13	169.5(1)	N21—Zn2—N24	170.2(1)
N11—Zn1—N14	93.4(1)	N21—Zn2—N23	94.7(1)
N11—Zn1—O151	97.6(1)	N21—Zn2—O252	96.4(1)
N11—Zn1—O152	90.8(1)	N21—Zn2—O251	92.1(1)
N12—Zn1—N13	98.7(1)	N22—Zn2—N24	98.8(1)
N12—Zn1—N14	102.3(1)	N22—Zn2—N23	103.9 (1)
N12—Zn1—O151	96.4(1)	N22—Zn2—O252	91.7(1)
N12—Zn1—O152	152.8(1)	N22—Zn2—O251	148.2 (1)
N13—Zn1—N14	77.7(1)	N23—Zn2—N24	77.5(1)
N13—Zn1—O151	92.5(1)	N24—Zn2—O252	92.6(1)
N13—Zn1—O152	96.6(1)	N24—Zn2—O251	95.7(1)
N14—Zn1—O151	160.0(1)	N23—Zn2—O252	162.6(1)
N14—Zn1—O152	102.9(1)	N23—Zn2—O251	106.8(1)
O151—Zn1—O152	60.4(1)	O251—Zn2—O252	59.4(1)

Zn-N bond distances in these cations are in the range from 2.095(3) to 2.130(4) Å, and Zn-O bond distances for Zn1 and Zn2 are 2.182(3), 2.184(3) Å, and 2.088(3), 2.323(4) Å, respectively. The Zn–N and Zn–O bond lengths [average values 2.118(4) and 2.193(4) Å] are in agreement with those reported for similar compounds [7, 17]. The four terminal N-coordinated isothiocyanato groups in the $[Zn(NCS)_4]^{2-}$ complex anion form a distorted coordination tetrahedron around Zn3, with bond parameters in the following ranges: Zn3-N: 1.937(7)-1.973(7) Å; N-Zn3-N: 103.2(3)-113.1(2)°; Zn-N-C: 157.2(5)-169.2(5)°.The thiocyanate groups are almost linear with N–C–S angles range of 172.7(6)–179.1(5)°. The S–C average distance of 1.595(2) Å and C–N average distance of 1.165(3) Å are in accordance with the values observed in other thiocyanato-containing metal complexes [18, 19]. The shortest Zn···Zn separation is 6.372(2) Å.

Intermolecular, intramolecular, and π-π stacking interactions are observed in **1**, and are responsible for the packing of the complex cations in the crystalline compound. An inspection of the data of **1** for weak directional intermolecular interactions by the programs Platon and Mercury, which were used for calculating the supramolecular interactions, reveals C–H···O [20], C–H···N [21], and C–H···S [13] interactions, and π-π stacking [22] (Table 3).

The packing diagram of **1** exhibits a 2D self-assembled structure through π-π stacking (slipped face-to-face), with 3.440 and 3.387 Å between the aromatic rings, which is remarkably shorter than for normal

Table 3
Intermolecular interactions for **1**

D-H···A	H···A/Å	D···A/Å	D-H···A/°
C144-H144···O251$^{\#1}$	2.349	3.128	139
C234-H234···O152$^{\#1}$	2.377	3.207	145.6
C224-H224···O151$^{\#2}$	2.41	3.266	149.7
C124-H124···O252$^{\#3}$	2.483	3.361	153.7
C114-H114···O252$^{\#3}$	2.493	3.348	149.8
C244-H244···O152$^{\#1}$	2.511	3.385	153.1
C116-H11A···O252$^{\#3}$	2.58	3.361	136.9
C214-H214···O151$^{\#2}$	2.625	3.48	149.8
C134-H134···O251$^{\#1}$	2.631	3.49	150.6
C152-H15C···O221$^{\#3}$	2.631	3.423	137.9
C126-H12C···O241$^{\#4}$	2.708	3.514	139.9
C221-H221···N31$^{\#1}$	2.636	3.414	139.4
C116-H11B···N32$^{\#3}$	2.74	3.509	135.7
C216-H21A···S34$^{\#5}$	2.866	3.739	148.7
C134-H134···S34$^{\#6}$	2.911	3.673	138
C211-H211···S34$^{\#7}$	2.991	3.883	157.2
O251···S34$^{\#6}$		3.191	
π-π stacking (slipped face-to-face)		3.44	
π-π stacking (slipped face-to-face)		3.387	

symmetrycodes: #1 *x*, *y*, *z*;#2 1/2+*x*, -1/2+*y*, *z*; #3 -1/2+*x*, 1/2+*y*, *z*; #4 *x*, 2-*y*, -1/2+*z*;#5 1+*x*, *y*, *z*;#6 1/2+*x*, 3/2-*y*, -1/2+*z*;#7 1/2+*x*, 3/2-*y*, 1/2+*z*.

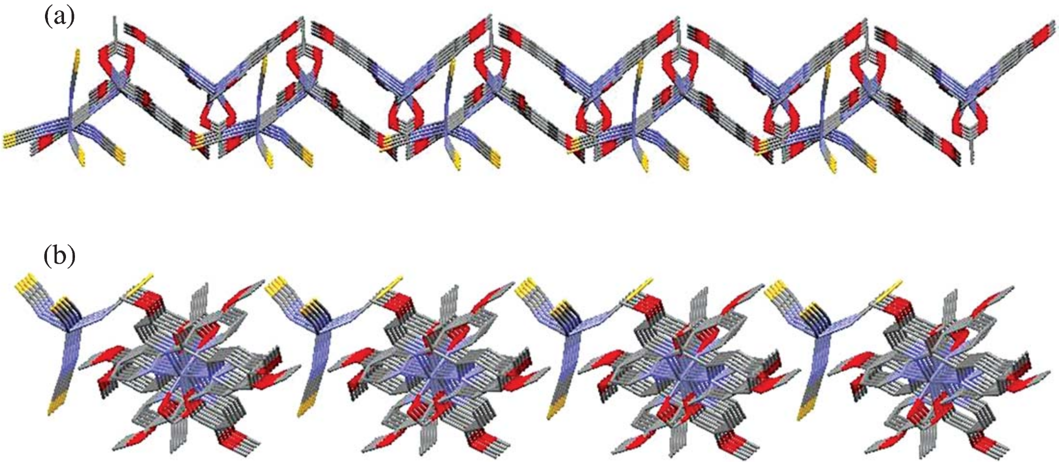

Fig. 4. (a) $\pi\cdots\pi$ stacking interactions in **1**. Formation of 2D supramolecular layers along [100] *via* $\pi\cdots\pi$ interactions; (b) packing of 2D layers of **1** to form 3D supramolecular layers *via* intermolecular interactions along [001].

π-π stacking [23]. In addition to π-π stacking 3D supramolecular networks by C–H···O, C–H···N and C–H···S interactions are found in **1**. These are substantially shorter than the van der Waals distances of 2.72 Å for the H···O, 2.75 Å for the H···N and 3.00 Å for the H···S distance (Table 3, Fig. 4) [24].

In summary, the crystal structure of **1** is surprising because it represents a new two-dimensional framework with three Zn(II) complexes incorporated in three different functions, two cationic, and one anionic.

Acknowledgments

This investigation supported by Payame Noor University and Islamic Azad University are gratefully acknowledged by FM and HS.

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Appendix A. Supplementary data

CCDC number of 1005052 contains the supplementary crystallographic data for **1**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.htmlor from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk