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Coordination Polymers Built with Transition Metal Sulphates and Angular 2,5-bis(imidazol-1-yl)thiphene (thim$_2$): Synthesis, Structure and Photoluminescent Properties

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Abstract

The reactions of angular tritopic ligand 2,5-bis(imidazol-1-yl)thiophene (thim$_2$) with different metal sulphates afforded six new CPs $\{[M(thim_2)(SO_4)(H_2O)_2]_2\cdot(thim_2)\cdot(H_2O)\}_n$ [M= Zn (**1**); Mn (**2**)], $\{[Cd(thim_2)(SO_4)(H_2O)]\cdot(H_2O)\}_n$ (**3**) and $\{[M(thim_2)_2(SO_4)]\cdot(H_2O)_x\}_n$ [M = Co, x = 7, (**4**); Ni, x=7 (**5**); Cu, x= 6.5 (**6**)]. CPs **1** and **2** are an isostructural 1D double chain propagating in wave like fashion. Whereas, CP **3** exhibits a layered 2D network and in the case of **4-6** an isostructural 3D framework containing of 1D rhombic channel was obtained. In all the CPs there is an interesting sulphate ion binding mode to the metal centers, such as four membered M_2O_4 rings (**1** and **2**), six membered (Cd_2SO_3) 1-D chain (**3**) and MSO_4 (**4-6**) 1-D chain, which is further linked by thim$_2$ to form an inorganic organic hybrid type systems. The stability of CPs (**1-6**) was monitored by TGA and solid state photoluminescence study was carried out for **1** and **3** at room temperature.

Introduction

The design and construction of coordination polymers (CPs) have received great attention because of their intriguing topology and structural diversity as well as potential applications in the areas of material science and catalysis.[1] The coordination nature of metal ions and ligands are the key tools to regulate the framework structure. Earlier, much efforts have been devoted using linear rod like ligands (linkers) such as, 4,4'bipyridine/pyrazine or 1,4-benzene dicarboxylic acid (BDC) or its analogs for the construction of diverse CPs ranging from 1D to 3D networks.[2] Some of these CPs show excellent sorption and catalytic properties. However less efforts have been given towards the flexible or semi rigid angular linkers for the preparation of CPs.

The flexible or semi rigid angular linkers with potential functional information may provide greater structural diversity with additional properties.[3] In this regard, CPs containing linkers with amido, metalloligands or chiral groups serve as a source of catalysts besides having novel helical, linear or chiral structures.[4] Also, CPs with selective transition metal or lanthanide ions shows good luminescent or magnetic properties.[5] Besides the metal based luminescence, there has been an interest to study the luminescent properties of CPs containing luminescent organic linkers with different transition or lanthanide metal ions. Organothiopenes, including, polythiophenes, or oligothiophenes are known for its luminescence and conducting properties.[6] Recently the CPs or MOFs based on organothiophene ligands have been synthesized and their luminescence properties have been evaluated.[7] Among them, the coordination properties of angular ligand based on thiophene moiety have been explored.[7a, 7e, 8]

Recently, we are engaged in understanding the conformational effects of angular ligands made up of five and six-membered heterocyclic ring combinations, for example 2,6-bis(imidazol-1yl-)-pyridine (pyim$_2$), in the synthesis of CPs.[9] In continuation, we have been also interested to study these same effects using three, five membered heterocyclic ring systems in the preparation of CPs and their applications. Here we have chosen an angular ligand, 2,5-bis(imidazol-1-yl)thiophene (thim$_2$), which exhibits three coordination sites including two terminal imidazolyl nitrogens and one thiophene sulphur atom.[10] This angular ligand is expected to form a convergent or divergent product on reacting with various metal centers. Also, thim$_2$ can adopt various conformations, like *cis-cis*, *cis-trans* and *trans-trans*, with respect to thiophene (Scheme 1). Further the dihedral angle between thiophene ring and two imidazolyl rings as well as between two imidazolyl rings within the thim$_2$ can also change as per the structure requirement. Taking all these features into account, we have carried out the reactions of thim$_2$ with different transition metal salts.

In this paper we have used divalent transition metal sulphates as precursors. Like silicates and phosphates, the sulphate anions can also participate in binding to the metal ions and impart structural diversity.[11] In recent years, the focus is given to the synthesis of metal sulphate containing CPs/framework in which M-O-S bonds forms interesting inorganic structures. In these examples, sulphate ions display different coordination modes to metal ions such as monodentate, chelate and bridging.[12] Further, a recent survey reveals that the sulphate ions can adopt 18 different ways of coordination to metal ions.[13] Thus the reactions of metal sulphates and thim$_2$ was carried out. Herein, we have discussed the synthesis and structural characterizations of six new CPs $\{[M(thim_2)(SO_4)(H_2O)_2]_2\cdot(thim_2)\cdot(H_2O)\}_n$ [M= Zn (**1**); Mn (**2**)], $\{[Cd(thim_2)(SO_4)(H_2O)]\cdot(H_2O)\}_n$ (**3**), $\{[M(thim_2)_2(SO_4)]\cdot(H_2O)_x\}_n$ M = Co, x = 7, (**4**); Ni, x=7 (**5**); Cu, x= 6.5 (**6**)]. Thermal stability (**1-6**) and photoluminescence properties of CPs (**1** and **3**) were also investigated.

Experimental Section

Materials and physical measurements. 2,5 dibromo thiophene and CuI (Sigma Aldrich) as well as other chemicals such as anhyd. K_2CO_3, imidazole, and metal sulphates (s d fine-cHEM. Ltd.) were procured and used as received. Solvents were procured, from s d fine-cHEM. Ltd. and purified by standard procedures prior to use.[14] Thim$_2$ was prepared according to the modified literature procedure.[15] Infrared spectra (IR) were recorded using KBr pellet in the range of 4000-400 cm^{-1} on Bruker vector-22 (CPs. **1** and **3**) and Perkin–Elmer model 1320 spectrometer (CPs **2**, and **4-6**). Thermogravimetric analysis (TGA) was performed on Mettler Toledo star system under nitrogen atmosphere (heating rate of 5 ^{o}C/min). Microanalyses for all the compounds were recorded using Perkin Elmer Series-II 2400 Elemental Analyzer. Solid state emission spectra were recorded using a ZSX primus series, Rigaku corporation spectrometer, at room temperature. Powder X-ray diffraction spectra (CuK$_\alpha$ radiation, scan rate 3^{o}/min, 293 K) were recorded on a Bruker D8 advance series 2 powder X-ray diffractometer (**1**-**5**) and PANalytical X'Pert Pro X-ray diffractometer (**6**).

Single-Crystal X-ray Studies. Single crystal X-ray data were collected at 100 K on a Bruker SMART APEX CCD diffractometer using graphite-monochromated MoK$_\alpha$ radiation (λ= 0.71073 Å). SAINT software was employed for data integration and reduction.[16] Absorption correction was performed with SADABS. All the structures were solved by the direct method using SHELXS-97 and refined on F^2 by full-matrix least squares technique using the SHELXL-97.[17] All hydrogen atoms were included in idealized position using a riding model. Non hydrogen atoms were refined anisotropically. The hydrogen atoms of water molecules were located from difference Fourier maps and the O-H bond distances constrained to ~0.80-0.90 Å with the DFIX command. In complexes **4-6**, the disordered solvent molecules present in the channel were treated by squeeze refinement using PLATON.[18] All the squeezed solvent molecules have been incorporated in the empirical formula as well as formula weight of the respective CP.

Synthesis of 2,5-bis(imidazol-1-yl)thiophene(thim$_2$). Thim$_2$ was synthesised with little modification from the reported procedure.[15] In a schlenk flask CuI (0.76 g, 4.0 mmol) and dry DMF (20 mL) was added under nitrogen atmosphere. To this imidazole (2.32 g, 34.1 mmol), 2,5-dibromo thiophene (1.8 mL, 16.5 mmol) and anhyd. K_2CO_3 (4.28 g, 31.0 mmol) was added and the reaction mixture was heated to 120 °C for 4 days under nitrogen atmosphere. The reaction mixture was cooled to the room temperature and diluted with DCM (20 mL) and filtered. The solution was washed with water (4x100 mL) and dried over anhyd. $MgSO_4$. Removal of DCM under reduced pressure gave a dark brown oil which when further purified by column chromatography using silica gel (1% methanol in chloroform) afforded the pure colorless product. The colorless crystals of thim$_2$ were obtained from DCM/Hexane (1:2) solution. Yield: 0.85 g (23.1 % based on imidazole). The NMR, IR and CHN values match with the already reported values.[19]

Synthesis of $[Zn(thim_2)(SO_4)(H_2O)_2]_2\cdot(thim_2)\cdot(H_2O)\}_n$ (1). To the solution of $ZnSO_4\cdot7H_2O$ (0.029 g, 0.1 mmol) in MeOH/H_2O (20 mL/2 mL) was added slowly a solution of thim$_2$ (0.022 g, 0.1 mmol) in CH_3OH /$CHCl_3$ (10 mL/5 mL) and stirred for 30 min. The solution was filtered and kept for crystallization by slow evaporation at room temperature. Colorless crystals of **1** were obtained after 4 days. Yield: 0.030 g (91 %, based on $ZnSO_4\cdot7H_2O$). Anal. calcd. for $C_{20}H_{22}N_8O_7S_3Zn$: C, 37.06; H, 3.42; N, 17.29 %. Found: C, 36.91; H, 3.56; N, 17.56%. IR (cm^{-1}) 3431(m), 3272(m), 3152(m), 3125(s), 3090(s), 1629(w), 1578(vs), 1535(s), 1512(s), 1484(s), 1347(w), 1316(m), 1304(s), 1268(m), 1243(m), 1209(m), 1158(vs), 1115(vs), 1071(s), 1044(s), 1029(vs), 944(vs), 924(s), 875(w), 843(w), 812(s), 796(s), 733(m), 649(s), 622(s), 595(m), 521(w), 499(w).

Synthesis of [Mn(thim$_2$)(SO$_4$)(H$_2$O)$_2$]$_2$·(thim$_2$)·(H$_2$O)}$_n$ (2). A methanolic solution (20 mL) of thim$_2$ (0.022 g, 0.1 mmol) was added to an aq. solution (7 mL of water) of $MnSO_4 \cdot H_2O$ (0.017 g, 0.1 mmol) and stirred for 1 h. The solution was filtered and kept for crystallization by slow evaporation at room temperature. Pale yellow colored crystals of **2** were obtained after 15 days. Yield: 0.023 g (92 %, based on $MnSO_4 \cdot H_2O$). Anal. calcd for $C_{20}H_{22}N_8O_7S_3Mn$: C, 37.67; H, 3.47; N, 17.57 %. Found: C, 37.48; H, 3.26; N, 16.92 %. IR (cm^{-1}) 3433(m), 3289(m), 3152(m), 3121(s), 3085(s), 1625(m), 1579(vs), 1530(s), 1512(s), 1484(s), 1364(w), 1347(w), 1314(s), 1304(s), 1287(m), 1253(m), 1243(m),1220(m), 1210(m), 1165(vs), 1141(vs), 1113(vs), 1086(m), 1072(m), 1045(s), 1027(vs), 937(vs), 837(m), 810(s), 797(s), 758(m), 649(s), 621(m), 598(m), 520(w), 495(w).

Synthesis of {[Cd(thim$_2$)(SO$_4$)(H$_2$O)]·(H$_2$O)}$_n$ (3). A methanolic solution (12 mL) of thim$_2$ (0.022 g, 0.1 mmol) was layered on an aq. solution (7 mL) of $CdSO_4 \cdot 8/3H_2O$ (0.026 g, 0.1 mmol). Colorless single crystals were obtained after two weeks. Yield: 0.020 g, (43%, based on $CdSO_4 \cdot 8/3H_2O$). Anal. calcd. for $C_{10}H_{12}N_4O_6S_2Cd$: C, 26.06; H, 2.62; N, 12.15 %. Found: C, 26.30; H, 2.38; N, 12.09 %. IR (cm^{-1}) 3399(m), 3109(m), 1584(s), 1524(m), 1502(m), 1351(w), 1314(m), 1274(w), 1259(m), 1222(w), 1116(vs), 1037(vs), 961(s), 942(s), 924(m), 836(w), 789(m), 744(m), 643(m), 618(m), 595(m), 516(w), 494(w).

Synthesis of {[Co(thim$_2$)$_2$(SO$_4$)]·(H$_2$O)$_7$}$_n$ (4). A methanolic solution (12 mL) of thim$_2$ (0.043 g, 0.2 mmol) was layered on an aq. solution (7 mL) of $CoSO_4 \cdot 7H_2O$ (0.028 g, 0.1 mmol). Pink colored single crystals were obtained after two weeks. Yield: 0.025 g, (42%, based on $CoSO_4 \cdot 7H_2O$). Anal. calcd for $C_{20}H_{30}N_8O_{11}S_3Co$: C, 33.66; H, 4.23 N, 15.70 %. Found: C, 33.61; H, 4.42; N, 15.08 %. IR (cm^{-1}) 3410 (br), 3092(m), 1626(w), 1580(s), 1526(s), 1487(m), 1366(w), 1345(w), 1313(m), 1263(m), 1241(m), 1217(m), 1164(s), 1113(vs), 1047(vs), 972(m), 935(m), 905(w), 873(w), 829(m),722(w), 663(m), 652(m), 603(m), 547(w), 521(w), 495(w), 414(w).

Synthesis of $\{[Ni(thim_2)_2(SO_4)]\cdot(H_2O)_7\}_n$ (5). The same reaction procedure was used as for **4** except that $CoSO_4\cdot7H_2O$ was replaced by $NiSO_4\cdot6H_2O$ (0.026 g, 0.1 mmol). Green colored single crystals of **5** were obtained after two weeks. Yield: 0.0178 g (30 %, based on $NiSO_4\cdot6H_2O$). Anal. calcd for $C_{20}H_{30}N_8O_{11}S_3Ni$: C, 33.67; H, 4.23; N, 15.70 %. Found: C, 33.55; H, 4.64; N, 15.05 %. IR (cm^{-1}) 3413(w), 3118(m), 3059(m), 1573(vs), 1525(s), 1487(vs), 1369(w), 1306(s), 1254(m), 1197(w), 1156(vs), 1111(vs), 1067(vs), 1043(vs), 995(w), 930(s), 820(m), 786(m), 729(s), 652(s), 616(m), 593(m), 538(m), 493(w).

Synthesis of $\{[Cu(thim_2)_2(SO_4)]\cdot(H_2O)_{6.5}\}_n$ (6). A methanolic solution (12 mL) of $thim_2$ (0.022 g, 0.1 mmol) was layered on an aq. solution (7 mL) of $CuSO_4\cdot5H_2O$ (0.0249 g, 0.1 mmol). After two weeks blue colored single crystals were obtained. Yield: 0.006 g (16.7 %, based on $CuSO_4\cdot5H_2O$. Anal. calcd for $C_{20}H_{29}N_8O_{10.5}S_3Cu$: C, 33.86 %; H, 4.12% N, 15.79%. Found: C, 33.13; H, 4.03; N, 16.07 %. IR (cm^{-1}) 3444(br), 3098(m), 1639(w), 1579(s), 1531(vs), 1495(m), 1345(w), 1313(m), 1277(m), 1218(w),1150(vs), 1112(vs), 1091(vs), 1056(vs), 1035(s), 971(w), 945(m), 904(w), 832(m), 749(w), 724(w), 665(m), 603(m), 548(w), 521(w), 498(w).

Results and Discussion.

All the six CPs (**1-6**) were synthesised by the reactions of metal sulphates with $thim_2$ in the molar ratios of 1:1 and/or 1:2. For **1** and **2**, the reactions were carried out by stirring, whereas for rest of the complexes layering methodology was employed. However, except in CP (**3**), in all other cases the 1:2 complexes were formed irrespective of the difference in the starting material stoichiometric ratios. All the six CPs (**1**-**6**) were analyzed based on IR, elemental analysis and single crystal X-ray diffraction methods besides the TGA (**1-6**) and luminescence studies (**1** and **3**). The IR spectra of **1**-**6** show a broad peak around 3400 cm^{-1} for O-H streching frequency corresponding to the presence of water molecules (Figure S1-S6). Further, IR spectra reveal multiple absorption peaks for different binding modes of sulphates ions (υ_1- υ_4) with the metal centres (Table1).[20] For instance, IR spectra of **1** and **2** show characteristics single absorption peaks for υ_1 [944(vs) cm^{-1} (**1**); 937(vs) cm^{-1} (**2**)] and υ_2 [499(w) cm^{-1} (**1**); 495(w) cm^{-1} (**2**)] besides three absorption peaks for the υ_3 [1158(vs), 1115(vs), and 1071(s) (**1**); 1165(vs), 1141(vs), and 1072(m) cm^{-1} (**2**)] and υ_4 [649(s), 622(m), and 595(m) cm^{-1} (**1**); 649(s), 621(m), and 598(m) cm^{-1} (**2**)]. In contrast, for **3** υ_1 is split into two peaks (961(s) and 942(s) cm^{-1}), leaving one peak for υ_2 494(w) cm^{-1}), but for υ_3 and υ_4 a single (1116(vs) cm^{-1}) and three absorption peaks (643(m), 618(m), and 595(m) cm^{-1}) were obtained. However, for **4-6**, the IR spectra show one characteristic absorption peak (υ_1 and υ_2) as well as three absorption peaks for υ_3 and υ_4. The above values for **4-6**, suggests C_{2v} symmetry (bidentate bridging mode) of $[SO_4]^{2-}$ whereas in rest of the CPs it was very difficult to predict the binding modes of sulphate ions to the metal centers.

Single-crystal X-ray structure of CPs 1-6

Structural analysis of $[M(thim_2)(SO_4)(H_2O)_2]_2\cdot(thim_2)\cdot(H_2O)\}_n$ [M= Zn(1) and Mn (2)]

CPs **1** and **2** crystallize in orthorhombic, *Pbcn* space group and they are isostructural (Table 2). Hence, the structure of **1** will be discussed here. The selected bond lengths and angles of **1** and **2** are depicted in Table 3. The structure of **1** consists of a 1D double chain CP with lattice water and uncoordinated thim$_2$ molecules. The zinc ions in these chains adopt distorted octahedral geometry, containing two imidazolyl nitrogen atoms from two distinct thim$_2$ ligands, two oxygen atoms from two sulphate ions and remaining two oxygen atoms from two coordinated water molecules [Figure1(a)]. Each of these zinc ions in a chain are bridged by two oxygen atoms of different sulphate ions, 2.2000 connecting mode (based on Harris notation[21]; $\mu_2:\eta^1$), to form a four membered Zn_2O_2 ring. The remaining coordination numbers of the zinc ions in the plane of an octahedron were saturated by two terminal water molecules. Further, each zinc ion in Zn_2O_2 ring is axially coordinated to two distinct imidazolyl nitrogen atoms of $thim_2$, in *trans* binding mode to form a 1D double chain in which the two chains propagate in paralleled wave form [Figure 1(b)].

The bond distances of M–N in **1** and **2** [Zn, 2.081 (3) Å; Mn, 2.217 (3) Å] are similar to that of the reported M–N bond distances [Zn, av. 1.98(6) Å; Mn, av. 2.256(4) Å] found in metal-imidazole CPs.[22] Whereas the M–O bond distances of oxygen atoms bridging between two metal atoms show two different bond distances [Zn, 2.187(2) Å and 2.250(2) Å (**1**); Mn, 2.227(2) Å and 2.256(2) Å (**2**)] which are unusually longer, even more than water bound M–O(W) distances [Zn–O, av. 2.099(2) Å (**1**); Mn–O, 2.174(3) Å (**2**)], and the M–O of the reported monodentate [Zn–O, 2.050(2) Å; Mn–O, 2.135(4) Å] or bridged bidentate $[SO_4]^{2-}$ ion [Zn–O, 2.041(3) Å; Zn–O, 2.102(4) Å; Mn–O, 2.150(6) Å; Mn–O, 2.205(6) Å] of zinc and manganese CPs.[12j, 23] Such four membered ring binding modes of sulphate ions in **1** and **2** are not observed so far in zinc and manganese containing sulphate complexes or CPs. In **1** and **2,** imidazole rings are in *cis*-*cis* mode with respect to thiophene group and they are twisted away from the central thiophene ring (Table 4). The M····M distances in M_2O_4 rings and intra chain are 3.486(6) Å (**1**); and 3.504(3) (**2**) and 11.067(3) Å (**1**) and 11.141(8) Å (**2**) respectively.

Interestingly, the uncoordinated $thim_2$ molecules lies between the two different 1D double chain CP [Figure 1(c)] and forms a supramolecular 3D structure along the *a* axis through the short O–H····N interactions which exists between the nitrogen atoms of uncoordinated thim$_2$ and coordinated water molecules as shown in Figure 1(d) (Table 5).

Structural analysis of {[Cd(thim$_2$)(SO$_4$)(H$_2$O)]·(H$_2$O)}$_n$ (3).

Single crystal X-ray analysis reveals that **3** crystallizes in orthorhombic system, space group *Pbca* (Table 2). The important bond parameters are given in the Table 3. Unlike in **1** and **2**, the CP **3** is made of 1:1 complexation of thim$_2$ and cadmium sulphate which is same as that of the starting material ratios. **3** is a layered 2D CP, in which the asymmetric unit is composed of one cadmium ion, one thim$_2$ ligand, one sulphate anion, one coordinated and lattice water molecules. The cadmium ion is hexacoordinated and consists of two nitrogen atoms of imidazole rings from two different thim$_2$ ligand and three oxygen atoms from three different sulphate ions as well as one oxygen atom of coordinated water molecule, displaying a distorted octahedral geometry [(Figure 2(a)]. The sulphate ion ligates to the metal centers in 3.2100 (μ_3:η^1: η^2)coordination mode to form a puckered six member [Cd$_2$SO$_3$] ring, which extends along *a* direction to form a 1D chain [(Figure 2(b)]. Further each of these 1D chains are connected by the two imidazolyl nitrogen atoms of thim$_2$ through axially, *trans* to each other, to form 2D CP [Figure 2(c)]. Within 2D layers, the adjacent chains of [Cd$_2$SO$_3$] rings are tilted (Figure S7) [dihedral angle between two chains is 63.16(6)º], whereas, the alternate chains of these rings are present in the parallel planes forming a ···*ABAB*··· type layered structure. Between the *ABA* units the thim$_2$ are present in wave like pattern [Figure 2(d)] and this continues uniformly in *c* direction. Interestingly, these 2D layers are linked through C–H····O supramolecular interactions in *ABAB* fashion to form a 3D network [Figure 2(e, f), Table (6)].

The Cd–N bond distances (Cd–N, av. 2.236(5)Å) in **3** show similarity with the known cadmium imidazolyl CP.[22] As expected the bond distances of single bridged oxygen atom Cd–O

[Cd(1) –O(4), 2.360(5) Å] is shorter than the doubly bridged oxygen atoms [Cd(1)–O(1), 2.414 (4) Å and 2.474 (5) Å) and these distances are longer than bridged bidentate sulphate oxygen atoms between two cadmium units (Harris notation, 2.1100, Cd–O, av. 2.235(4)Å).[23a] The Cd····Cd distances within the six membered rings and alternate cadmium atoms in the layers are 4.040(6) Å and 21.667(0) Å respectively. Also the two imidazole rings (*cis*-*cis*) within each thim$_2$ are twisted (more as compared to **1** and **2**) from the central thiophene ring by dihedral angle of 20.32(4)º and 12.75(7)º respectively. However it is 18.82(1)º between two imidazolyl rings, which is smaller than **1** and **2** (Table 4).

Structural analysis of {[M(thim$_2$)$_2$(SO$_4$)]·(H$_2$O)$_x$}$_n$ M = Co, x = 7, (4), Ni, x=7 (5), and Cu, x= 6.5 (6)]

The X-ray structural analysis reveals that CPs **4-6** possess isostructural framework with 1:2 stoichiometric ratio of metal sulphates (Co, Ni and Cu) and thim$_2$, irrespective of different molar ratios in the case of thim$_2$ and copper sulphate precursor (1:1). Therefore, only the structure of **4** is discussed here. CP **4** crystallizes in the monoclinic system, *C*2/*c* space group. The overall structure is a 3D neutral framework with 1D rhombic channel occupied by guest water molecules. The asymmetric unit of **4** is composed of one cobalt ion (half occupancy), one thim$_2$, and half of sulphate ion. The cobalt ion exhibits an octahedral geometry with *trans* coordination modes containing four nitrogen atoms, from four different units of thim$_2$ in plane, and two oxygen atoms of two sulphate ions present in the axial position [Figure 3(a)]. The coordinated oxygen atoms of sulphate ions adopt 2.1100 (μ_2: η^1: η^1) connecting mode and binds to different cobalt ions to form a 1D chain along *c* axis [Figure 3(b)]. The nitrogen atoms of thim$_2$, present in octahedral planes, connect adjacent cobalt ions through its planes resulting in a 2D rhombic grid along crystallographic *ab* plane [Figure 3(c)]. A closer analysis of these binding modes reveals that 1D cobalt sulphate chains and the 2D rhombic grids form the 3D framework [Figure 3(d)], in which 1D channels are present along *c* directions [Figure 3(e)]. Within this 3D network, there is a presence of flexible cube made of metal sulphate and thim$_2$ units [Figure S8-S9].

The M–N [Co, av. 2.134(3)Å, Ni, av. 2.085(4)Å; Cu, av. 2.154(3)Å], except Co–N, and M–O [Co, 2.113(2)Å, Ni, 2.101(3)Å; Cu, 2.304(2)Å], except Co–O and Ni–O, bond distances are found to be longer than the already reported similar M–N [Co, av. 2.132(9)Å, Ni, av. 2.050(5)Å; Cu, av. 1.999(8)Å] and M–O distances [Co, av. 2.095(9)Å, Ni, av. 2.159(4)Å; Cu, av. 2.552(7)Å] given in metal imidazole CPs and in metal sulphate 1D chains.[24] The framework consisting of 1D rhombic channel along *c* direction with the window dimension between the metal centers are 13.43(7) Å × 21.36(9) Å(**4**), 13.49(8) Å × 21.26(1) Å(**5**), and 12.93(8) Å × 21.31(5) Å(**6**). Within each thim$_2$ ligand, the imidazole rings are twisted and coordinated to the metal ion in *cis – trans* modes and these rings are not in the same plane as the thiophene moiety, which is indicated by the dihedral angle between two imidazolyl rings and central thiophene ring in thim$_2$ as well as the dihedral angle between two imidazolyl rings. Compared to **1-3**, the dihedral angles between the imidazole rings are larger in **4-6**. Unlike the former CPs, the flexible -M-O-S-O-M- zig-zag wire-like chain in the latter gives greater conformational freedom between the five-membered rings leading to larger values of twists between the imidazoles as well as imidazole and thiophene moiety (Table 4).

TGA and PXRD analysis

The thermal stability of **1-6** was monitored using TGA under nitrogen atmosphere and except CP **6**, all the TGA spectra show well defined decomposition. For **1** and **2**, TGA shows a gradual weight loss [calculated 8.3 % (**1**) and 8.5 % (**2**); observed, 7.9 % (**1**) and 8.9 % (**2**)] corresponding to one lattice and two coordinated water molecules. This resultant structure is stable upto ~260 °C (264 °C, **1**; 272 °C, **2**) (Figure S10-S11). In case of **3** the loss of lattice and coordinated water molecule (calculated 7.8 %; observed 7.3 %) was observed between 84 °C – 177 °C and the resultant structure is stable upto 306 °C (Figure S12). Compared to **1-3**, CPs **4** and **5** shows loss of guest water molecules (calculated ~17.7 %, **4** and **5** observed, 16.0 %, **4** and **5**) and the corresponding framework is stable upto 350 °C [355 °C, (**4**); 360 °C (**5**)] (Figure S13-S14). However, in **6** there is continuous loss of guest water molecules upto 181 °C and later a sudden fall of TGA curve from 210 °C onwards suggesting the collapse of intermediate structure (Figure S15). To confirm the sample purity powder X-ray analysis was performed for all the CPs. For **1-6** the simulated spectra correlates with the experimental spectra which confirm the phase purity of these CPs at room temperature (Figure S16-S21).

Luminescent properties:

Luminescent CPs are attracting current research interest because of their potential applications in photo chemistry, electrochemical display, chemical sensors among others.[25] CPs composed of d^{10} metal centers and organic ligand are promising candidates as luminating material due to their higher stability and ability to tune the emission wavelength of organic ligand.[26] Luminescent properties of free ligand, **1** and **3** were investigated in the solid state at room temperature. The emission spectra of ligand, **1** and **3** is depicted collectively in Figure 4. The ligand emission spectra show a broad band at 400 nm (λ_{ex} = 260 nm). In case of **1** and **3,** an enhanced strong emission broad band was obtained at 405 nm (λ_{ex} = 266 nm) and 395 nm (λ_{ex} = 293nm) respectively. These emission spectra indicate the similarity with ligand spectra thus, the luminating behavior of **1** and **3** could be attributed to the intra ligand charge transfer transitions. In addition it is noteworthy that **1** and **3** exhibit intense luminescence compared to the ligand which may be caused by increased rigidity of the ligand due to its coordination to the metal center which effectively reduces the loss of energy by radiation-less decay.[27]

Conclusion

In summary, six new CPs based on thim$_2$ ligand and different transition metal sulphates have been synthesized under room temperature conditions. CPs **1-6** display structural variations from 1D chain to 3D network structures. In these structures the metal ion adopts the octahedral geometry along with different sulphate connectivity modes and ligand conformation which imparts the structural diversity. In CPs **1** and **2** coordination mode of sulphate $\mu_2{:}\eta^1$ forms a four membered M_2O_4 ring and connectivity of ligands leads to the formation of 1D double chain. Whereas CP **3** display $\mu_3{:}\eta^1{:}\eta^2$ sulphate binding mode which generates the 1D inorganic chain made-up of six member Cd_2SO_3 units and ligand coordination extends the network as 2D. For CP **4-6**, metal ions with ligands form 2D rhombic grid and axial coordination through sulphate in μ_2: η^1: η^1 bridging mode leading to 3D framework structure. The thim$_2$ ligand adopts the conformation *cis-cis* in CPs **1-3** and *cis-trans* in CPs **4-6**. Also, the connecting modes of sulphate ion which form M_2O_2 four membered ring (**1**-**2**) and Cd_2SO_3 six membered ring (**3**), to the best of our knowledge, were not observed so far in the respective metal sulphates complexes or in CPs.[12-13] Taking the overall structural formation, CPs (**1**-**6**) can be inferred as inorganic organic hybrid system. The photoluminescence study of **1** and **3** showed an enhancement of intensity, compared to the thim$_2$. Further research for the construction of new coordination polymers using thim$_2$ with different transition metal salts and in the presence or absence of co-ligands as well as involvement of thiophene binding to the metal centers is under progress.

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Supporting information

Additional figures, TGA, Powder X-ray diffraction patterns. X-ray crystallographic data in CIF format have been deposited with the Cambridge Structural Database (CCDC 980514, CCDC 980513, CCDC 909607, CCDC 911463, CCDC 908158, CCDC 911465).

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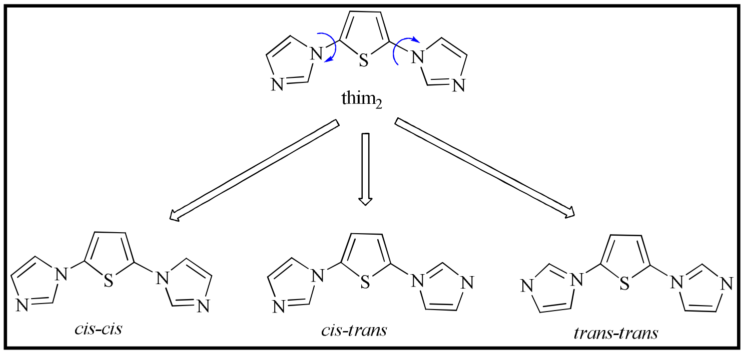


Scheme 1. Conformations of thim$_2$

Table 1. Representation of the IR streching frequencies of sulphate in **1-6**

Compound no.	**IR stretching frequencies (υ_1- υ_4) cm^{-1}**			
	υ_1	**υ_2**	**υ_3**	**υ_4**
1	944(vs)	499(w)	1158(vs), 1115(vs), 1071(s)	649(s), 622(s), 595(m)
2	937(vs)	495(w)	1165(vs), 1141(vs), 1072(m)	649(s), 621(m), 598(m)
3	961(s), 942(s)	494(w)	1116(vs)	643(m), 618(m), 595(m)
4	972(m)	495(w)	1164(s), 1113(vs)	663(m), 603(m), 547(w)
5	995(w)	493(w)	1156(vs), 1111(vs), 1067(vs)	652(s), 616(m), 593(m)
6	971(w)	498(w)	1150(vs), 1112(vs), 1056(vs)	665(m), 603(m), 548(m)

Table 2. Crystal data and structure refinement parameters for **1-6**

Compound	**1**	**2**	**3**	**4**	**5**	**6**
Formula	$C_{20}H_{22}N_8O_7S_3Zn$	$C_{20}H_{22}N_8O_7S_3Mn$	$C_{10}H_{12}N_4O_6S_2Cd$	$C_{20}H_{30}N_8O_{11}S_3Co$	$C_{20}H_{30}N_8O_{11}S_3Ni$	$C_{20}H_{29}N_8O_{10.5}S_3Cu$
Formula wt.	648.01	637.58	460.76	713.63	713.39	709.23
Space group	*Pbcn*	*Pbcn*	*Pbca*	*C*2/*c*	*C*2/*c*	*C*2/*c*
a (Å)	24.646(4)	24.729(5)	6.9658(7)	17.867(4)	17.711(4)	17.537(4)
b (Å)	9.2484(1)	9.3762(1)	18.5806(1)	13.437(3)	13.498(3)	12.938(3)
c (Å)	22.124(3)	22.271(5)	21.667(2)	12.678(3)	12.670(3)	13.328(3)
α, deg	90.000	90.000	90.000	90.000	90.000	90.000
β, deg	90.000	90.000	90.000	92.95(3)	92.83(3)	93.78(3)
γ, deg	90.000	90.000	90.000	90.000	90.000	90.000
V/Å^3	5042.8(13)	5163.99(18)	2804.4(5)	3039.8(11)	3025.3(10)	3017.4(11)
Z	8	8	8	4	4	4
D_{calcd} g/cm^3	1.707	1.640	2.163	1.284	1.289	1.303
F(000)	2656	2616	1792	1196	1200	1204
GOF	1.088	1.053	1.122	1.162	1.127	1.128
R_1/ wR_2 [$I > 2\sigma(I)$]	0.0441, 0.1137	0.0508, 0.1148	0.0503, 0.1170	0.0493, 0.1352	0.0522, 0.1496	0.0548, 0.1456
R_1/ wR_2 (all data)	0.0565, 0.1418	0.0900, 0.1453	0.0651, 0.1426	0.0602, 0.1659	0.0691, 0.1668	0.0750, 0.1760

Table 3. Selected bond distances (Å) and angles(°) for CPs **1-6**

1		
Zn(1)-N(4) 2.080(2) Zn(1)-N(1) 2.082(2)	Zn(1)-O(5W) 2.092(8) Zn(1)-O(6W) 2.106(2)	Zn(1)-O(1)#1 2.187(2) Zn(1)-O(1) 2.250(1)
N(4)-Zn(1)-N(1) 178.81(9) N(4)-Zn(1)-O(5W) 88.92(8) N(1)-Zn(1)-O(5W) 91.02(8) N(4)-Zn(1)-O(6W) 87.53(9) N(1)-Zn(1)-O(6W) 91.29(9) #1 -x+1,-y+1,-z+2	O(5W)-Zn(1)-O(6W) 95.75(8) N(4)-Zn(1)-O(1)#1 89.91(8) N(1)-Zn(1)-O(1)#1 90.36(8) O(5W)-Zn(1)-O(1)#1 169.39(8) O(6W)-Zn(1)-O(1)#1 94.73(8)	N(4)-Zn(1)-O(1) 89.80(8) N(1)-Zn(1)-O(1) 91.39(8) O(5W)-Zn(1)-O(1) 93.02(7) O(6W)-Zn(1)-O(1) 170.78(8) O(1)#1-Zn(1)-O(1) 76.43(7)
2		
Mn(1)-N(1) 2.216(3) Mn(1)-N(4) 2.220(3)	Mn(1)-O(5W) 2.163(3) Mn(1)-O(6W) 2.186(3)	Mn(1)-O(1)#1 2.227(2) Mn(1)-O(1) 2.256(2)
N(1)-Mn(1)-N(4) 176.77(11) O(5W)-Mn(1)-O(1)#1 171.67(9) O(6W)-Mn(1)-O(1) 170.59(10) N(1)-Mn(1)-O(1) 92.72(10) N(4)-Mn(1)-O(1) 90.51(10) #1 -x+1,-y+2,-z+2	O(6W)-Mn(1)-O(1)#1 93.74(10) N(1)-Mn(1)-O(1)#1 90.65(10) N(4)-Mn(1)-O(1)#1 90.16(10) O(5W)-Mn(1)-O(1) 94.55(9) O(1)#1-Mn(1)-O(1) 77.16(9)	O(5W)-Mn(1)-O(6W) 94.51(10) O(5W)-Mn(1)-N(1) 90.55(11) O(6W)-Mn(1)-N(1) 89.75(10) O(5W)-Mn(1)-N(4) 89.10(10) O(6W)-Mn(1)-N(4) 87.08(10)
3		
Cd(1)-N(1) 2.228(5) Cd(1)-N(4)#1 2.245(5	Cd(1)-O(1) 2.414(4) Cd(1)-O(1)#3 2.474(5)	Cd(1)-O(5W) 2.358(5) Cd(1)-O(4)#2 2.360(5)

N(1)-Cd(1)-N(4)#1 167.9(2) N(1)-Cd(1)-O(5W) 88.27(18) N(4)#1-Cd(1)-O(5W) 99.55(18) N(1)-Cd(1)-O(4)#2 91.0(2) N(4)#1-Cd(1)-O(4)#2 99.3(2) #1 x,-y+1/2,z-1/2	O(5W)-Cd(1)-O(4)#2 80.22(18) N(1)-Cd(1)-O(1) 84.57(17) N(4)#1-Cd(1)-O(1) 90.85(17) O(5W)-Cd(1)-O(1) 159.87(16) O(4)#2-Cd(1)-O(1) 81.12(18) #2 x-1/2,-y+1/2,-z+1	N(1)-Cd(1)-O(1)#3 87.88(18) N(4)#1-Cd(1)-O(1)#3 84.48(17) O(5W)-Cd(1)-O(1)#3 80.04(15) O(4)#2-Cd(1)-O(1)#3 160.25(17) O(1)-Cd(1)-O(1)#3 118.36(13) #3 x+1/2,-y+1/2,-z+1
4		
Co(1)-N(4) 2.111(3)	Co(1)-O(1) 2.113(2)	Co(1)-N(1) 2.158(3)
N(4)-Co(1)-N(4) 180.0 N(1)-Co(1)-N(1) 180.00(8)	O(1)-Co(1)-O(1) 180.0 O(1)-Co(1)-N(1) 93.00(10)	N(4)-Co(1)-O(1) 92.31(10) N(4)-Co(1)-N(1) 95.06(10)
5		
Ni(1)-N(4) 2.068(4)	Ni(1)-O(1) 2.101(3)	Ni(1)-N(1) 2.103(4)
N(4)-Ni(1)-N(4) 180.0 N(1)-Ni(1)-N(1) 180.0	O(1)-Ni(1)-O(1) 180.0 N(4)-Ni(1)-N(1) 94.60(18)	O(1)-Ni(1)-N(1) 92.68(16) N(4)-Ni(1)-O(1) 92.40(15)
6		
Cu(1)-N(3) 2.005(3)	Cu(1)-N(1) 2.047(3)	Cu(1)-O(1) 2.304(2)
N(3)-Cu(1)-N(3) 180.0 O(1)-Cu(1)-O(1) 180.0	N(1)-Cu(1)-N(1) 180.00(9) N(1)-Cu(1)-O(1) 87.33(11)	N(3)-Cu(1)-N(1) 93.52(12) N(3)-Cu(1)-O(1) 89.23(11)

Table 4. Representation of the dihedral angle in **1-6**

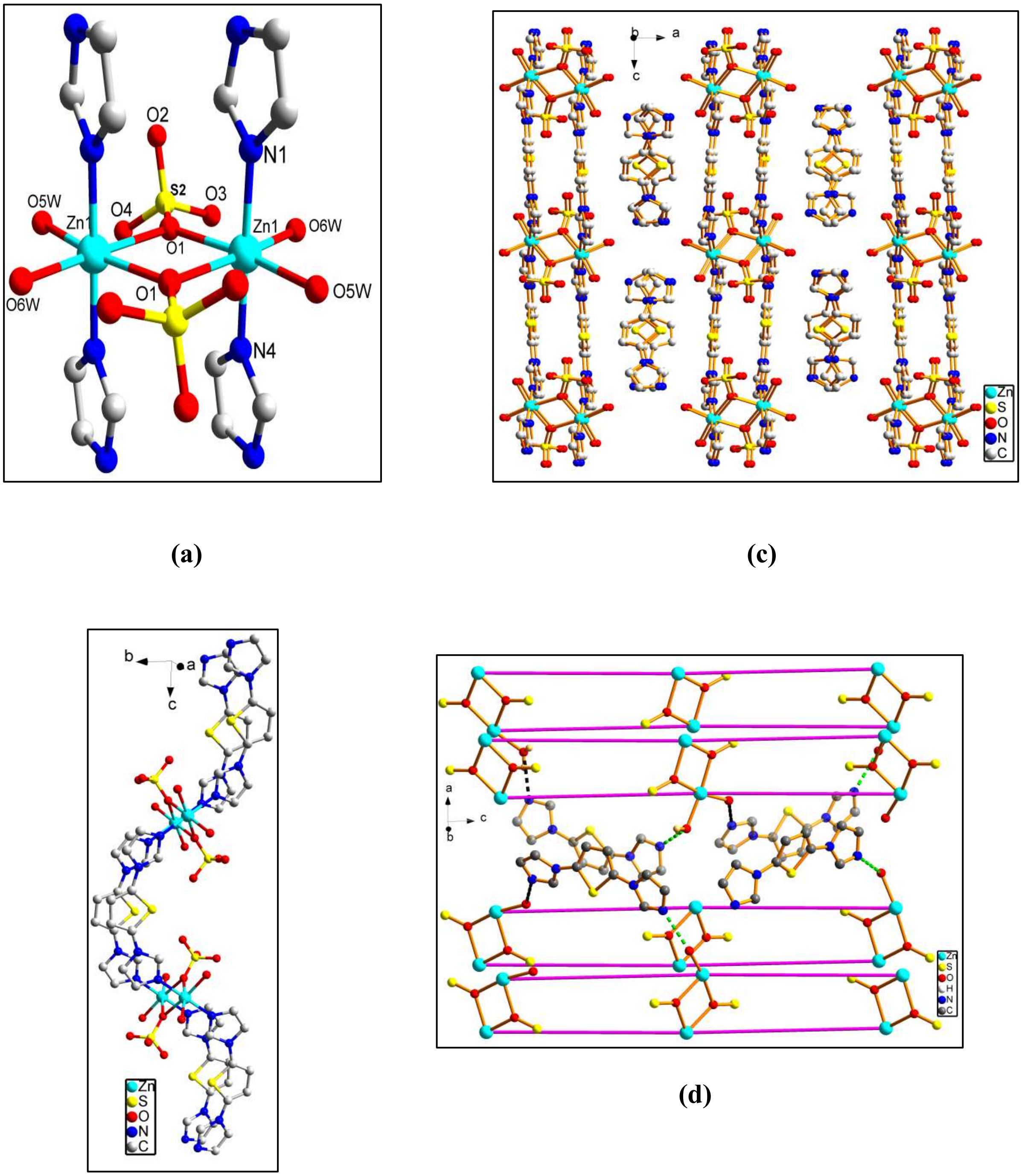
CP	**Dihedral angle between thiophene and imidazole unit (°)**	**Dihedral angle between two imidazole units (°)**
1	14.98(1)/9.27(2)	22.18(2)
2	14.81(2)/9.86(7)	22.84(1)
3	20.32(4)/12.75(7)	18.82(1)
4	47.56(4)/21.28(6)	65.89(1)
5	49.68(7)/20.27(6)	66.82(4)
6	56.91(1)/12.02(2)	64.36(2)

Table 5. O–H····N interactions present in **1-2**

Compound No.	***D*–H····*A***	H····***A*** (Å)	***D*····*A*** (Å)	***D*-H····*A*** (°)
1	O5W–H5W1····N8	1.870(7)	2.716(8)	169.98(7)
	O6W–H6W····N5	1.954(2)	2.768(5)	163.07(9)
2	O6W–H6W····N5	1.969(1)	2.764(4)	162.90(1)
	O5W–H5W1····N8	1.865(1)	2.716(6)	172.08(1)

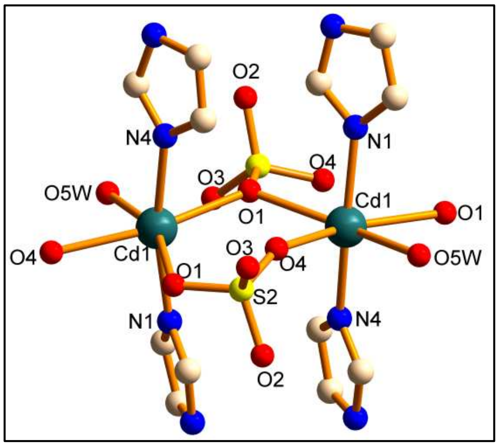
Table 6. C–H····O interactions present in **3**

Compound no.	***D*–H····*A***	H····***A*** Å	***D*····*A*** Å	***D*–H····*A*** (°)
3	C5–H5····O5W	2.762(1)	3.394(7)	133.24(4)
	C3–H3····O3	2.438(1)	3.291(2)	149.64(9)

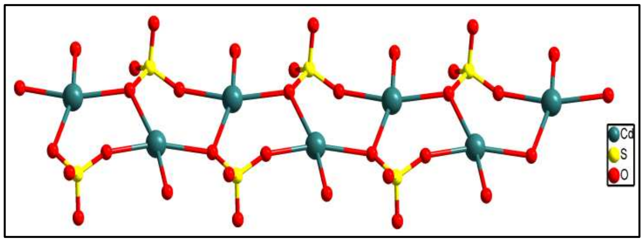


(a) (c) (b) (d)

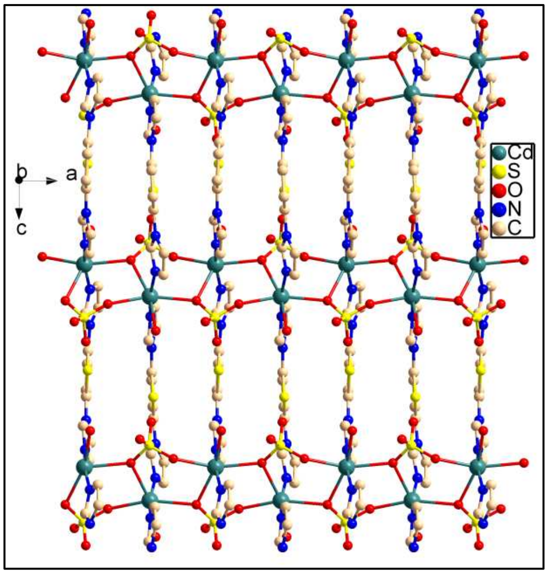
Figure 1


O2
N4
N1
O4
O3
O5W
O1
Cd1
O1
O4
Cd1
O3
O4
O5W
O1
S2
N1
N4
O2

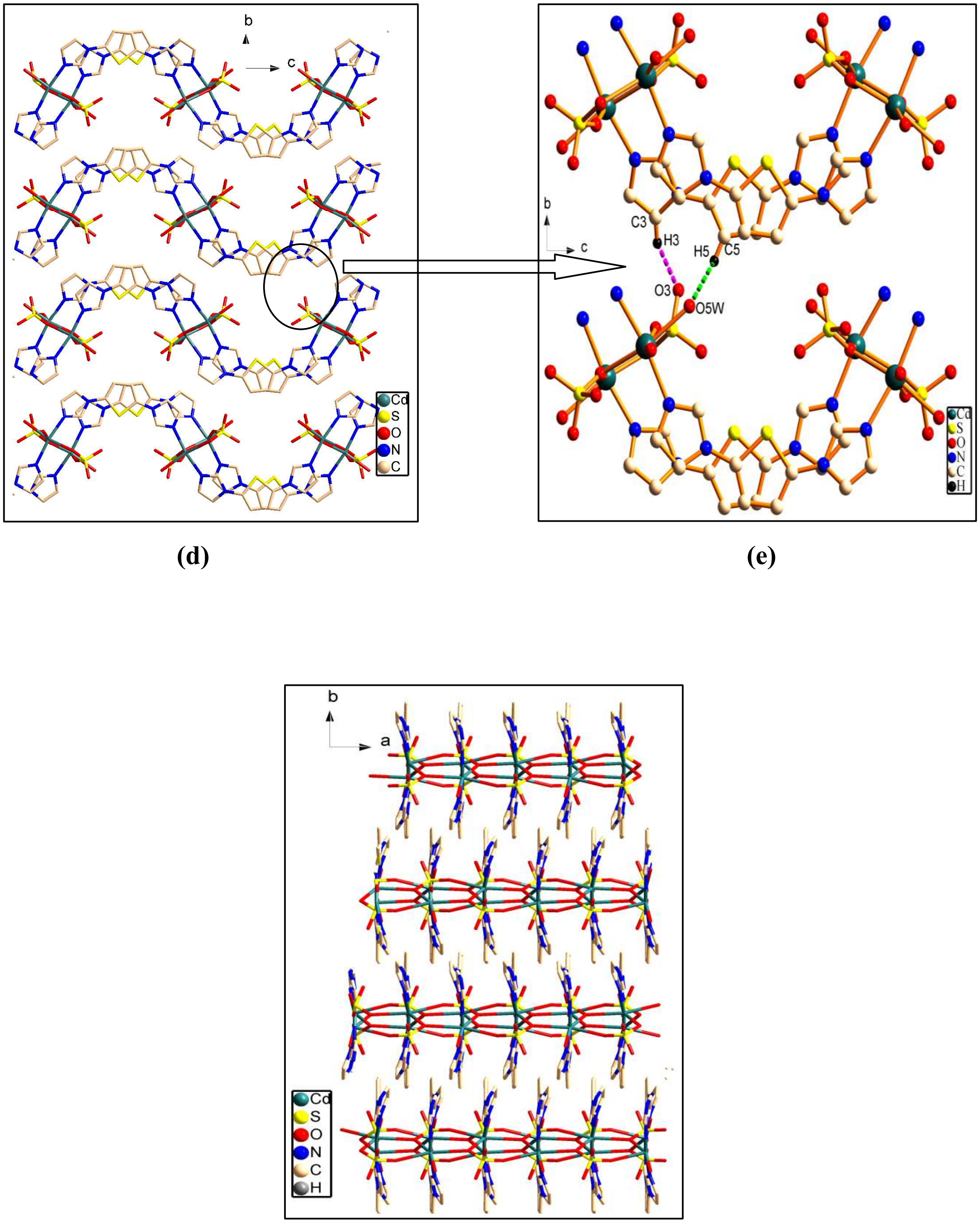
(a)


Cd
S
O

(b)


b
a
c
Cd
S
O
N
C

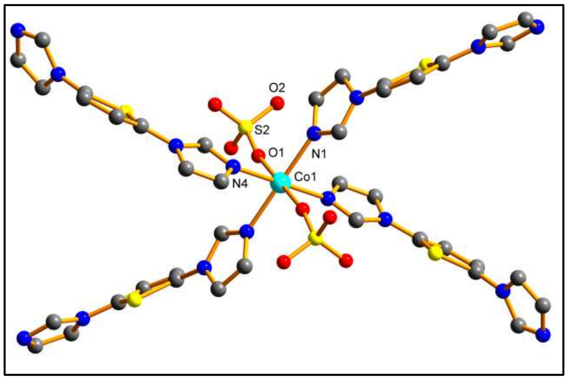
(c)



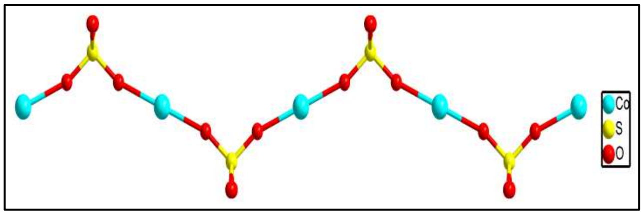
(d) (e)

(f)

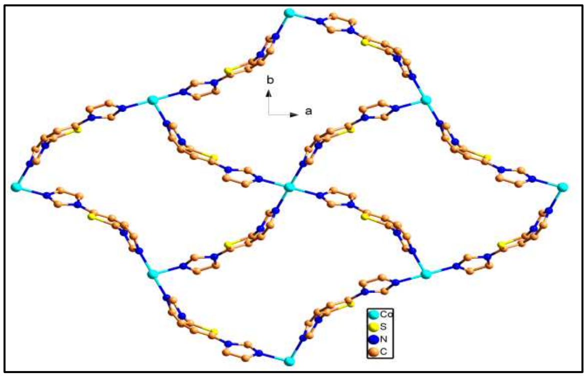
Figure 2



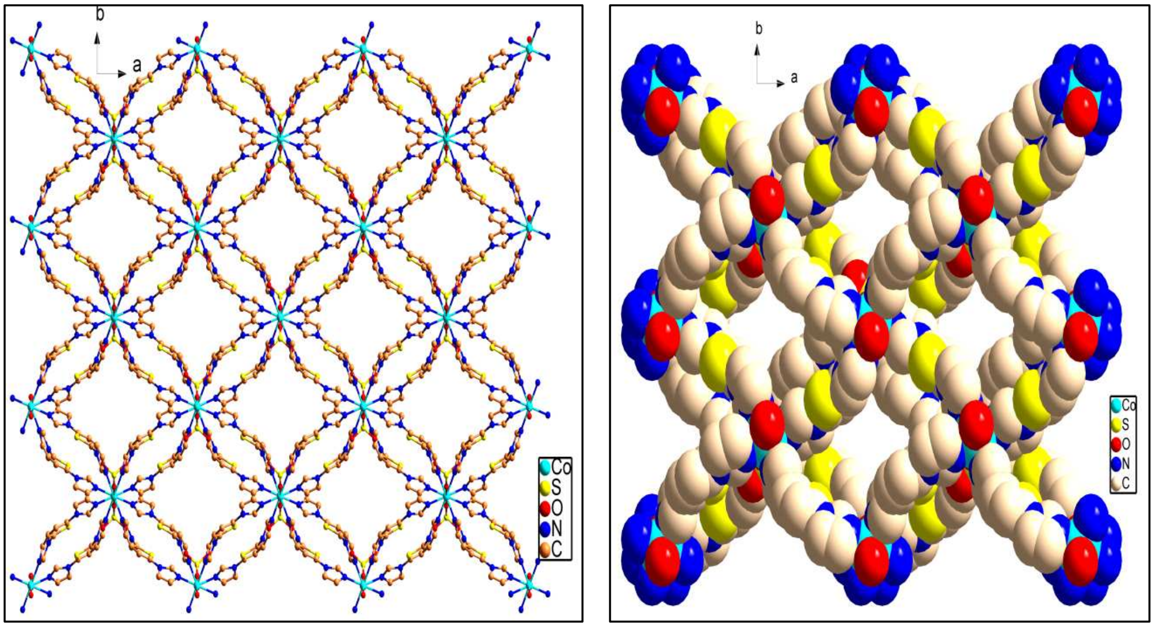
(a)



(b)



(c)



(d) (e)

Figure 3

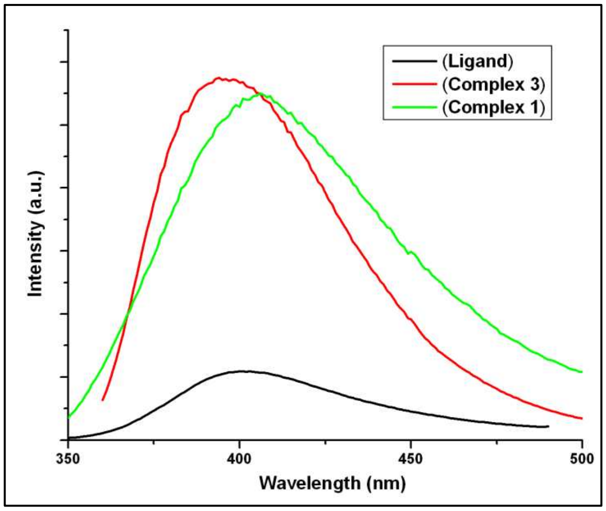


Figure 4

Captions for the Figures

Figure 1	(a) Coordination environment surrounding zinc ion in **1** (b) 1D double chain structure of **1** (c) 3D supramolecular structure (d) Supramolecular interactions between chains and unncordinated ligand molecules are shown (Coordinated ligand, some H_2O molecules, O atoms of sulphte units and H atoms are removed for clarity)
Figure 2	(a) Coordination environment surrounding cadmium ion in **3** (b) 1D chain made of puckered six membered [Cd_2SO_3] ring (c) The 2D sheet along *b* direction. (d) Depicting a wave like pattern along the *a* axis (e) Representation of the CH····O interaction (f) View of *ABAB* pattern of 2D layers, formed through supramolecular interactions.
Figure 3	(a) Coordination environment around Co(II) ion (b) Sulphate ion connecting pattern to the metal center (c) View of the 2D rhombic grid along *c* axis (d) 3D view of **4** along the *c* direction (e) View of the 1D channel along the *c* axis.
Figure 4	Solid state emission spectra of **1** and **3** at room temperature

For the Table of Contents only

Coordination Polymers Built with Transition Metal Sulphates and Angular 2,5-bis(imidazol-1-yl)thiphene (thim$_2$): Synthesis, Structure and Photoluminescent Properties

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Six new CPs, based on thim$_2$ and metal sulphates have been synthesised. Photoluminescence property for CP **1** and **3** has been investigated.