Influence of the counter anion and steric hindrance of pyrazolyl and imidazolyl flexible ligands on the structure of zinc-based coordination polymers.

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Abstract

Treatments of flexible 1,4-bis(3,5-dimethylpyrazolyl)butane (bbd), 1,4-bis(imidazolyl)butane (bib) and 1,4-bis(2-methylimidazolyl)butane (bmib) ligands with zinc salts at room temperature, resulted in the formation of four novel metal-organic coordination architectures: $[ZnI_2(\mu\text{-bbd})]_n$ (**1**), $[Zn(NCS)_2(\mu\text{-bbd})]_n$ (**2**), $\{[Zn(\mu\text{-bib})_2](ClO_4)_2\cdot(Et_2O)_{0.5}\cdot(H_2O)_{0.25}\}_n$ (**3**) and $\{[Zn(\mu\text{-bmib})_2](ClO_4)_2\cdot(H_2O)_4\}_n$ (**4**). X-ray crystallographic analyses show different 1D and 3D polymeric structures for compounds **1-4** due to the variation of the counter anions, solvent, steric hindrance and position of donating atoms in the structure of flexible ligands. In **1** and **2**, one-dimensional (1D) zig-zag polymeric chains are formed via metal centers and μ-bbd ligands.Complex **3** shows a 3-fold interpenetrated 3D architecture with 10^3-**ths** network topology. In contrast to **3**, in the structure of **4** neighboring Zn(II) ions are interconnected by a double-bridging μ-bmib ligands to form an infinite 1D polymeric double chain. The conformations of the flexible ligands were analyzed in detail.

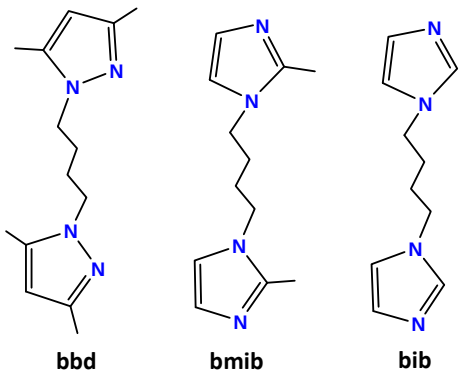
Keywords: Zinc, Coordination polymer, Flexible ligand, Counter anion effect, Pyrazolyl and imidazolyl ligand

1. Introduction

The past decade has seen an explosive growth in preparation, characterization, and study of materials known as coordination polymers or metal-organic frameworks (MOFs). These materials are constructed by self-assembly of transition metal ions or metal-containing clusters, known as secondary building units (SBUs), and organic bridging ligands through strong coordination bonds obtaining 1D to 3D networks. By varying the SBUs and organic linkers thousands of MOFs with fascinating structures and interesting properties have been prepared and studied [1]. The construction of MOFs remains a popular area due to their potential applications in various fields such as separation[2], gas storage[3], ion exchange[4], magnetism[5], luminescence[6], sensing[7], drug delivery[8] and catalysis[9].Generally, the chemical structures of these materials are influenced by many factors, such as crystallization solvent, the nature of the counter anion, the preferred coordination environment of the metal center and the location and orientation of donor atoms in a polydentate ligand. The ability of such ligands to participate in non-covalent bonds, such as hydrogen-bonding and π···π stacking interactions have also a significant structure-directing influence. Factors such as steric hindrance, flexibility and spacer length of the ligands and the metal/ligand ratio also play important roles in the generation of novel coordination polymers [10]. The sp^3 hybridization of -CH_2- spacers allow flexible ligands to bend and rotate freely when coordinate to metal centers, generating different conformations and making possible the formation of a variety of architectures and topologies. In recent years, there is an increasing interest in coordination architectures built by flexible bis(imidazolyl)[11] and bis(pyrazolyl)-based [10a-c,12] bridging ligands due to the fact that the five-membered aromatic N-heterocycles, including imidazole- and pyrazole-derivatives, are known to function as ligands in compounds which are widely used in medicine, agriculture, industry and coordination chemistry. Imidazolate is also an important ligand in many metalloenzymes, such as copper/zinc superoxide dismutases [13].

In order to extend our work on the synthesis and structural characterizations of novel topological frameworks and investigate the influence of the reaction condition and solvent system, as well as the effect of steric hindrance of the imidazole and pyrazole ring substituents of the flexible ligands on the structure of complexes, the syntheses, crystal structures and thermal stabilities of four new zinc-based coordination polymers containing

flexible bidentate nitrogen donor ligands (scheme 1) are reported here.



Scheme 1: Structures of the ligands used in this work.

2. Experimental Section

2. 1. Materials and Physical Measurements

All experiments were carried out in air. The starting materials were purchased from commercial sources and used without further purification; bbd [12a], bib [11f] and bmib [14] were prepared from them by published methods. The infrared spectra (4000-400 cm^{-1}) were recorded from KBr discs with a BOMEN MB102 FT-IR spectrometer. The elemental analyses for C, H and N were performed on a Costech-ECS 4010 CHNSO analyzer. Thermal analysis was performed on a Bahr-STA 503 TG/DTA or on a Perkin-Elmer Diamond TG/DTA thermal analyzers under dynamic nitrogen. A ramp rate of 10 ˚C.min^{-1} in the range of 50-800°C was used.

2.2. Preparation of the coordination polymers

2. 2. 1. Synthesis of $[ZnI_2(\mu\text{-bbd})]_n$ (1).

bbd (0.13 g, 0.53 mmol) was added to a solution of ZnI_2 (0.17 g, 0.53 mmol) in CH_3OH (40 mL) and the reaction mixture was stirred at room temperature overnight. The resulting colorless solution was filtered and the clear filtrate was concentrated under reduced pressure to ca. 20 mL. Colorless air-stable single crystals of **1** were obtained by leaving the saturated solution of **1** to stand in a refrigerator for 3-4 days. The crystals were washed with diethyl ether and dried in vacuum. (0.21g, 68% yield based on Zn). Anal. Calcd for $C_{14}H_{22}I_2N_4Zn$: C 29.7, H 3.9, N 9.9; Found: C 30.1, H 3.8, N 9.7. FT-IR (cm^{-1}): 491(w), 701(w), 738(w), 797(s), 808(s), 920(w), 1009(m), 1046(s), 1112(m), 1230(w), 1272(m), 1324(m), 1376(s), 1421(s), 1466(s), 1551(vs), 2866(w), 2934(m) 3121(w).

2. 2. 2. Synthesis of $[Zn(NCS)_2(\mu\text{-bbd})]_n$ (2).

$ZnCl_2$ (0.2 g, 1.46 mmol) was added to a solution of KSCN (0.28 g, 2.9 mmol) in CH_3CN or CH_3OH (40 mL) and the reaction mixture was stirred for 0.5 h at room temperature. bbd (0.36 g, 1.46 mmol) was added to the resulting solution and the reaction mixture was stirred at room temperature overnight. The colorless mixture was then filtered to remove small amount of white precipitate. Colorless air-stable single crystals of **2** were obtained using the same method as for crystallization of compound **1**. The crystals were washed with diethyl ether and dried in vacuum. (0.35g, 56% yield based on Zn). Anal. Calcd for $C_{16}H_{22}N_6S_2Zn$: C 44.9, H 5.2, N 19.6; Found: C 44.2, H 5.1, N 19.1. FT-IR (cm^{-1}): 481(w), 690(w), 751(w), 811(m), 917(w), 1052(s), 1117(m), 1230(w), 1208(w) 1271(w), 1389(m), 1454(m), 1471(m), 1551(vs), 2049(vs; NCS), 2072(vs; NCS), 2932(w), 2956(w), 3126(w).

2. 2. 3. Synthesis of $\{[Zn(\mu\text{-bib})_2](ClO_4)_2\cdot(Et_2O)_{0.5}\cdot(H_2O)_{0.25}\}_n$ (3).

The bib (0.085 g, 0.45 mmol) was added to a solution of $Zn(ClO_4)_2.6H_2O$ (0.083 g, 0.22 mmol) in DMF (15 mL) and the reaction mixture was stirred at room temperature for 2h and then filtered. Colorless needle-shaped single crystals of **3** were obtained by slow evaporation of the solvent at room temperature in a Petri dish after 2-3 days. The crystals were washed with EtOH and diethyl ether and dried in vacuum. (0.07g, 51% yield based on Zn). Anal. Calcd for $C_{22}H_{33.5}Cl_2N_8O_{8.8}Zn$: C 38.5, H 4.9, N 16.3; Found: C 38.4, H 4.6, N 16.5. FT-IR (cm^{-1}): 623(s; ClO_4), 658(s), 766(m), 842(m), 956(s), 1095(vs; ClO_4), 1245(s), 1295(w), 1360(w), 1385(w), 1454(m), 1526(s), 1538(s), 1675(s), 2959(w), 3054(w), 3130(s).

2. 2. 4. Synthesis of $\{[Zn(\mu\text{-bmib})_2](ClO_4)_2\cdot(H_2O)_4\}_n$ (4).

A solution of 24 mg (0.11 mmol) bmib in 3 mL acetone was carefully layered over a solution of 20 mg (0.054 mmol) of $Zn(ClO_4)_2.6H_2O$ in 3 mL H_2O at room temperature. After five days, colorless block-like crystals of **4** were obtained. The supernatant solvent was removed; the crystals were washed with EtOH and diethyl ether and dried in vacuum (22 mg, 59% yield based on Zn). Anal. Calcd for $C_{24}H_{40}Cl_2N_8O_{10}Zn$: C 39.1, H 5.4, N 15.2; Found: C 38.8, H 5.2, N 15.1. FT-IR (cm^{-1}): 623(s; ClO_4), 658(s), 767(m), 843(m), 955(s), 1094(vs; ClO_4), 1245(s), 1294(w), 1358(w), 1385(w), 1454(m), 1526(s), 1538(s), 1675(s), 2961(m), 3054(w), 3130(s).

Caution: Perchlorate compounds are potentially explosive and should be handled with care.

2. 3. X-ray crystallographic study

X-ray data were collected on an Oxford Diffraction Gemini for **1** and **3** and on a BrukerApexII for **2** and **4** using MoKα radiation. The structures were solved using direct methods and refined using a full-matrix least squares procedure based on F^2 using all data [15]. Hydrogen atoms were placed at geometrically estimated positions. Details relating to the crystals and the structural refinements are presented in Table 1. In compound **3** the guest molecules of diethylether and water have been refined with isotropic thermal parameters and without the hydrogen atoms. One ligand has a N(2)-C(4)-C(5a,b)-C(6a,b)-C(7)-N(4) chain with a disorder modelled with 50%-50% for C5a/C5b, C6a/C6b and isotropic thermal parameter. To avoid short contact the hydrogens have been removed for the whole carbon chain. To avoid unreasonable C-C distances, restrains have been imposed. In compound **4** the clathrate water molecule is disorder 50% over two position and has been refined without hydrogens and with isotropic thermal parameters. Full details of crystal data and the structure refinements, in CIF format, are available as supporting information. CCDC reference numbers 930745-930748 for **1**-**4**.

3. Results and Discussion

3. 1. Synthesis and Spectroscopic Characterization

Compounds **1**-**4** were obtained by one pot reactions at room temperature. Treatment of bbd with ZnI_2 (molar ratio = 1:1) in CH_3OH gave rise to 1D polymeric chain $[ZnI_2(\mu\text{-bbd})]_n$ (**1**) (68% yield). Analogous reactions of bbd with $ZnCl_2$ and KSCN in CH_3CN or CH_3OH with a molar ratio of 1:2:2, produced the 1D polymeric chain $[Zn(NCS)_2(\mu\text{-bbd})]_n$ (**2**) (56% yield). One-pot reaction of $Zn(ClO_4)_2.6H_2O$ and imizadolyl-based ligand (bib) (molar ratio = 1:2) in DMF with stirring at room temperature for 2h, afforded the coordination network $\{[Zn(\mu\text{-bib})_2](ClO_4)_2\cdot(Et_2O)_{0.5}\cdot(H_2O)_{0.25}\}_n$ (**3**) (51% yield). The related $\{[Zn(\mu\text{-bib})_2](ClO_4)_2\}_n$ complex [11d] was synthesized by using the same starting material as used for **3**, in H_2O/C_2H_5OH solvent under hydrothermal condition. By comparison, the $\{[Zn(bib)_2](ClO_4)_2\}_n$ coordination polymer has 1D double chain structure, while complex **3** possesses a 3D 3-fold interpenetrating framework with 10^3-**ths** topology. Thus, parameters such as the reaction temperature and solvent system have crucial effects on the structure and topology of these complexes. Compound $\{[Zn(\mu\text{-bmib})_2](ClO_4)_2\cdot(H_2O)_4\}_n$ (**4**) was obtained from slow diffusion method by layering an acetone solution of bmib over a solution of $Zn(ClO_4)_2.6H_2O$ in H_2O in a molar ratio of 2:1 at room temperature (59% yield). **4** shows a

1D double chain structure which extends to a 3D supramolecular framework by C-H···O hydrogen bonds to the perchlorate anions. All our attempts to synthesize the analogous complexes of **3** and **4** with the bbd ligand failed. Large steric hindrance due to the presence of two methyl substituents on the pyrazole rings prevent simultaneous coordination of four bulky 3,5-dimethyl pyrazole groups to a metal center. All the colorless complexes are stable at room temperature. Powders of **1** and **2** are soluble in MeCN, DMF and DMSO. Compound **3** is insoluble in common organic solvents such as $CHCl_3$, MeCN, DMF and DMSO whereas the powder of **4** is moderately soluble in DMF and DMSO. The elemental analyses results for C, H, N, match well with the composition of crystal structure determinations.

The infrared spectra of the complexes **1** and **2** exhibit characteristic bands of the coordinated μ-bbd ligands at 2934(m), 1551(vs), 1466 (s), 1421 (s) and 1376 (s) cm^{-1} for **1** and 2932(m), 1551(vs), 1471 (m), 1454 (m) and 1389 (m) cm^{-1} for **2**. The 1551 cm^{-1} band correspond to the stretching vibration of C=N bonds typical of the pyrazole rings of μ-bbd ligands. This band is shifted to lower frequencies with respect to the spectrum of the free 3,5-dimethylpyrazole (1595 cm^{-1}) [10b,16]. The infrared spectrum of **2** also shows two adjacent intense bands at 2049 and 2072 cm^{-1} assigned to CN stretching vibration of two different N-coordinated terminal thiocyanate groups. This observation could be rationalized by the existence of two different bond lengths for the CN bonds of the SCN-groups in the crystal structure of complex **2** (Table 2).The infrared spectra of **3** and **4** show characteristic bands of the coordinated bib and bmib ligands in the range of 600-1550 cm^{-1}, dominated by imidazole ring stretching, bending and deformation vibrations. The bands in the range of 2860-2960 cm^{-1} may be attributed to the C-H stretching vibrations of $-(CH_2)_4-$ spacer group in the linker ligands. The infrared spectra of the complexes **3** and **4** also display two sharp bands at 622 and 1095 cm^{-1} for **3** and at 623 and 1104 cm^{-1} for **4** due to the vibration bands of ClO_4^- counter anion. The bands at 3130 cm^{-1} for **3** and 3140 cm^{-1} for **4** and also weak broad peaks appear in the range of 3520-3630 cm^{-1}, attributed to the vibration bands of water guest molecules, present in the structure of **3** and **4**. The FT-IR results are consistent with the crystallographic study.

3. 2. Description of crystal structures

3. 2. 1. Crystal structure of $[ZnI_2(\mu\text{-bbd})]_n$ (1)

Single crystal X-ray structural analysis reveals that **1** crystallizes in the monoclinic space group *C*2/*c*. The asymmetric unit of **1** contains half Zn(II) ion, half centro-symmetric μ-bbd

ligand and one iodo ligand (Fig. 1a). The Zn(II) ion reside on a 2-fold axis and is coordinated by two symmetry-related iodide anions with Zn-I distance of 2.5908(4) Å and two N atoms of two crystallographic equivalent μ-bbd ligands with Zn-N distance of 2.053(2) Å in a distorted tetrahedral ZnN_2I_2 coordination geometry. These distances are comparable with the corresponding values reported for the dimer $[Zn_2I_4(tr_2eth)_2]$ [17] [tr_2eth= 1,2-bis(1,2,4-triazol-4-yl)ethane], monomer $[ZnI_2(BpsMe_2)]$ [18] [BpsMe= Bis(3,5-dimethylpyrazol-1-yl)silane] and other N-donor adducts of ZnI_2 with an N_2I_2 donor set. A structural comparison between **1** and $[Zn_2I_4(tr_2eth)_2]$ and $[ZnI_2(BpsMe_2)]$ complexes shows that the variation of the linker ligand has decisive influence on the structural topology of the complexes.

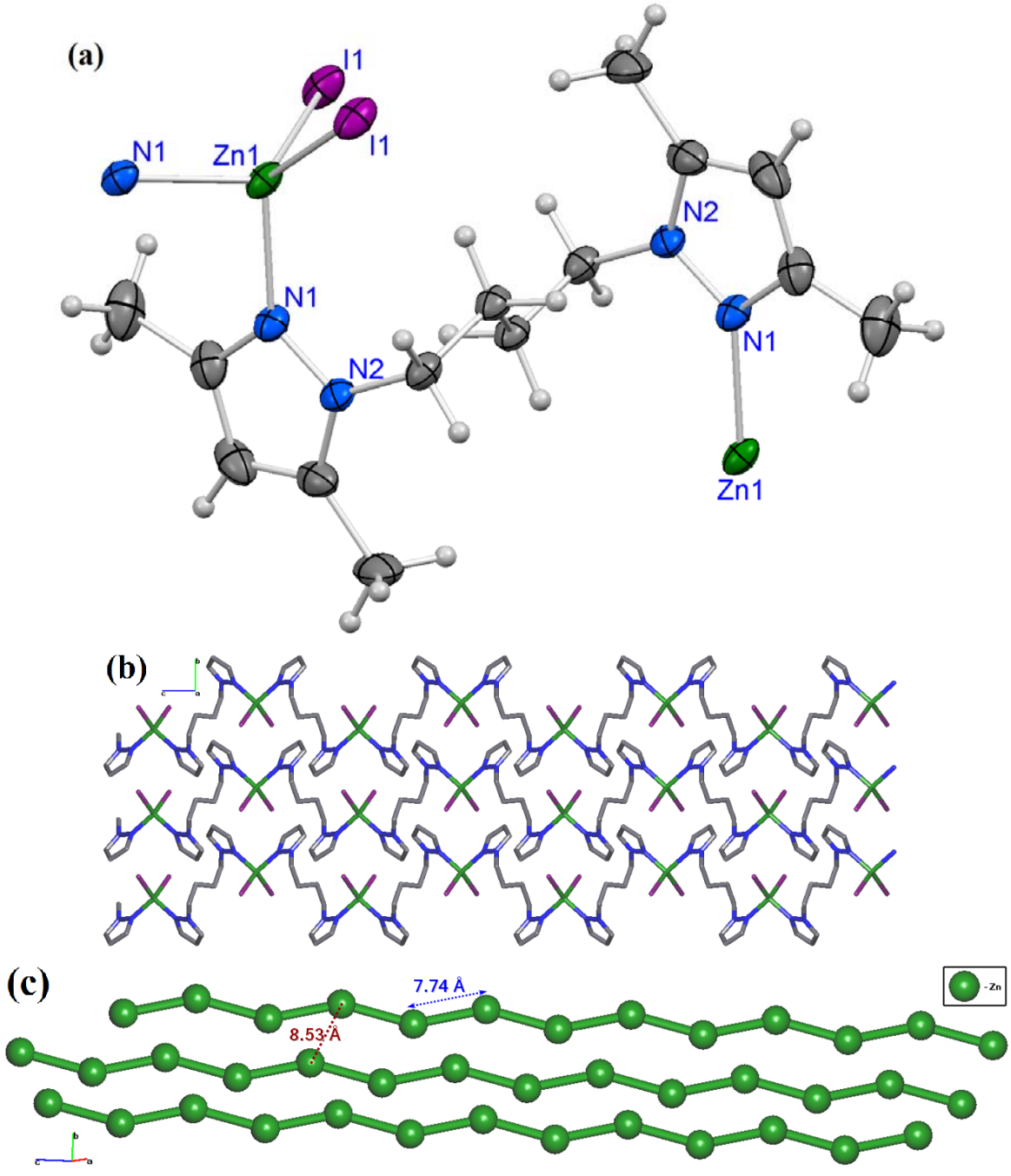


Fig. 1. The structure of $[ZnI_2(\mu\text{-bbd})]_n$ (**1**). (a) View of the $[ZnI_2(\mu\text{-bbd})]$ unit in **1** with a labeling scheme for non-H and C atoms. (b) View of three parallel adjacent 1D chains along *a* axis; the chains run along the *c* axis. H atoms and methyl substituents were omitted for clarity (c) Schematic view of three neighboring zig-zag chains; Zn···Zn distance within each polymeric chain is 7.74 Å, while the shortest inter-chain Zn···Zn distance is 8.53 Å.

The bond angles around the metal center range from 98.3° to 121.7° (Table 2). The remarkable deviations from the ideal tetrahedral angle can be explained with the need of accommodating the organic ligand and the halogen atoms around the metal center. The bbd molecule acts as a bidentate bridging ligand coordinating metal centers through its nitrogen atoms to form a polymeric one-dimensional zig-zag chain structure along the crystallographic *c* axis (Fig. 1b), with Zn···Zn separation of 7.74Å.The shortest Zn···Zn separation of 8.53Å between adjacent neutral chains is governed by the steric hindrance of the pyrazolyl rings (Fig. 1c). All the μ-bbd ligands are crystallographically equivalent and exhibit a *gauche-anti-gauche'* conformation with a (Zn)N-to-N(Zn) distance of 6.33 Å. The dihedral angle between the mean planes of the pyrazole rings of the centro-symmetric bbd ligand is 0˚. Whereas the 1D chains in the crystal structure of **1** pack in a manner such that the pyrazole rings of different bbd ligands from adjacent chains are strictly parallel (dihedral angle = 0˚) (Fig. 1b), though the centroid···centroid distances of 5.05 Å imply no significant π···π interaction between adjacent chains.

3. 2. 2. Crystal structure of $[Zn(NCS)_2(\mu\text{-bbd})]_n$ (2)

Compound **2** crystallizes in the monoclinic space group $P2_1/n$. The asymmetric unit contains two $Zn(NCS)_2$ fragments and two μ-bbd ligands (Fig. 2a). The Zn(II) ions are in the center of a distorted tetrahedral ZnN_4 arrangement coordinating two nitrogen atoms from two distinct μ-bbd ligands and two nitrogen atoms from two terminal N-bonded thiocyanate ions. The Zn-N(μ-bbd) distances are comprised in the range 2.009(2)-2.017(2) Å and are similar to those reported for $[Zn(SCN)_2(api)]_n$ [19] (api= 1-(3-aminopropyl)-imidazole). The other Zn-N(thiocyanate) bond distances are comprised in the range 1.952(3)-1.957(3) Å (Table 2). The NCS ligands in **2**, show very small distortions from linearity (N-C-S ca. 179°) and bind to the metal in a non-linear mode with Zn-N-C angles in the range 142.9(3)°-159.9(3)°. The bond angles around Zn(II) are slightly distorted from the ideal tetrahedral bond angle and range from 104.8(1)°to 116.8(1)°.

As in **1**, in the structure of **2**, the Zn(II) ions are connected via μ-bbd ligands to form a 1D zig-zag chain structure. In contrast to **1**,the μ-bbd ligands in **2** have two different

conformations with two different (Zn)N-to-N(Zn) distances: 6.48 Å for the *gauche-anti-gauche'* (red) and 7.54 Å for the *anti-anti-anti* (blue) conformations [Fig. 2b].This can be attributed to the effect of the counter ions on the conformation of the flexible μ-bbd ligands [10g,h]. The different conformations of the ligands cause two different Zn···Zn distances (7.55 and 8.08 Å) in the chain structure of **2**.

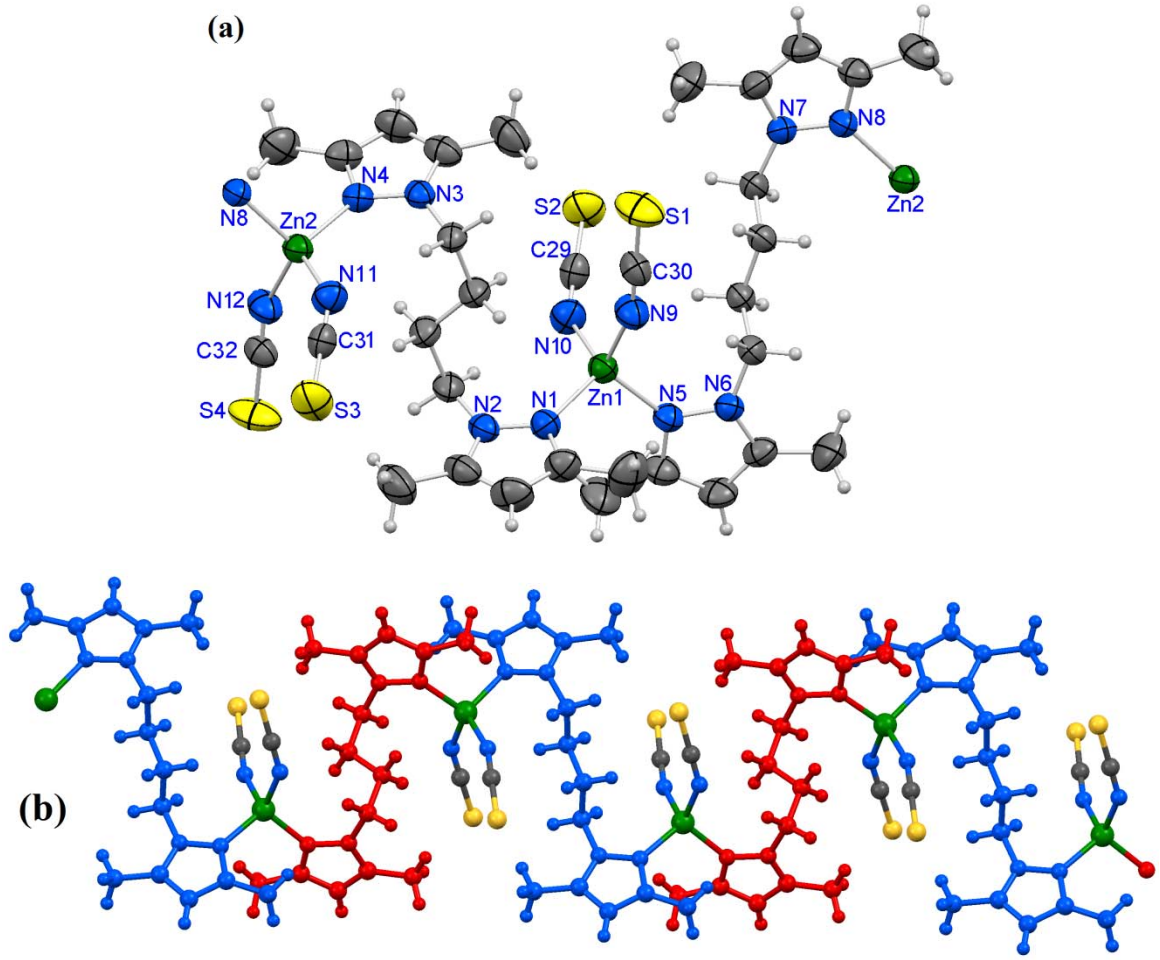


Fig. 2. The structure of $[Zn(NCS)_2(\mu\text{-bbd})]_n$ (**2**). (a) asymmetric unit of **2** with labeling scheme. (b) 1D zig-zag structure of **2** containing a sequence of μ-bbd ligands with two different conformations, *gauche-anti-gauche'* (red) and *anti-anti-anti* (blue).

The dihedral angle between the two pyrazole rings in both conformations are similar and equal to 3.2° and 3.7°, respectively. The μ-bbd ligands in **1** and the red colored ligands in **2**, exhibit the same structural conformations but with different N-to-N distances. This may be ascribed to the different torsion angles of $-(CH_2)_4-$ spacer in the structures (Table 4). The calculated dihedral angles between the ring mean planes for the bbd ligands in **1** and **2** are close to zero, because the usual convention is to report such dihedral angles in the range 0-90˚; however, the strictly parallel rings would be better described as antiparallel, with a dihedral angle of 180˚, resulting in Zn-N bonds that point in exactly opposite directions.As

for **1**, adjacent chains in the structure of **2** have no significant intermolecular interactions and there are no pyrazole ring-stacking interactions within or between chains; nevertheless the centroid···centroid distance of 4.88 Å between the pyrazole rings of the adjacent chains shows a closer proximity in the structure of **2**, compared to the packing of chains in **1**. Coordination polymers of Zn(II) ion with flexible bis(pyrazole-1-yl)alkane ligands are uncommon and only a few examples are reported in the literature [20].

Table 1. Crystallographic data and structure refinement details for **1-4**.

Compound	**1**	**2**	**3**	**4**
Formula	$C_{14}H_{22}I_2N_4Zn$	$C_{16}H_{22}N_6S_2Zn$	$C_{22}H_{33.5}Cl_2N_8O_{8.75}Zn$	$C_{24}H_{40}Cl_2N_8O_{10}Zn$
formula mass	565.53	427.89	686.34	736.91
T(K)	130(1) K	293(2) K	130(1) K	293(2) K
crystsyst	Monoclinic	Monoclinic	Orthorombic	Tetragonal
space group	*C*2/*c*	$P2_1/n$	*F*2*dd*	$I4_1/acd$
a(Å)	12.6785(6)	13.9476(9)	21.3477(15)	18.9727(7)
b(Å)	11.4031(6)	23.4840(16)	22.9862(16)	18.9727(7)
c(Å)	15.0587(8)	14.0807(10)	24.297(2)	17.9724(12)
β(°)	112.944(6)	116.1540(10)	90.00	90.00
V(Å^3)	2004.86(18)	4139.8(5)	11922.6(15)	6469.4(5)
Z	4	8	16	8
*D*calcd (g cm^{-3})	1.874	1.373	1.529	1.513
no. of reflns collected	5425	13296	10082	45502
no. of independentreflns	2227	6339	5262	2489
R_{int}	0.0247	0.0795	0.0808	0.1309
data/restraints/params	2227/0/98	6339/0/451	4794/155/363	2489/0/102
GOF on F^2/ Flack parameter	1.029	0.998	1.031 / 0.07(5)	1.023
R1[$I > 2\sigma(I)$]	0.0246	0.0474	0.1013	0.0740
wR_2(all data)	0.0336	0.1424	0.3121	0.2914

All of these compounds have been prepared by rigid or less flexible linker ligands. Zinc-based coordination polymers containing flexible pyrazole based ligands with -$(CH_2)_n$- (n≥4) as a spacer group have not been observed in any polymeric systems prior to this work. In contrast, the zinc complexes of this type of ligands with n=1, 2, 3 which have been published in the literature, have only monomeric or dimeric structures [21]. With the main objective to understand the effect produced on the structure of the coordination polymers by exchanging the halogen with the pseudo-halogen, we have been able to synthesize complexes **1** and **2** as the first examples of zinc(II) coordination polymers with the bis(pyrazole-1-yl)alkane ligands.

3. 2. 3. Crystal structure of $\{[Zn(\mu\text{-bib})_2](ClO_4)_2\cdot(Et_2O)_{0.5}\cdot(H_2O)_{0.25}\}_n$ (3)

Single crystal X-ray studies indicate that compound **3** crystallizes in the orthorhombic space group *F*2*dd*. The asymmetric unit consists of a $[Zn(bib)_2]^{2+}$ cation and two ClO_4^-counterions (Fig. 3a), together with a half of diethyl ether and a quarter of water as guest molecules. The Zn(II) center shows a slightly distorted ZnN_4 tetrahedral geometry by four coordinated nitrogen atoms from four distinct μ-bib ligands.The Zn-N bond distances and N-Zn-N bond angles (Table 3) are comparable to those observed for $\{[Zn(bib)_2](ClO_4)_2\}_n$ [11d] and are in the normal range for such coordination bonds.

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

(1)		**(2)**		**(2)**	
Bond lengths/Å					
Zn1-N1	2.053(2)	Zn1-N1	2.017(2)	Zn2-N4	2.009(2)
Zn1-I1	2.5908(4)	Zn1-N5	2.013(2)	Zn2-N8	2.013(2)
N1-N2	1.374(3)	Zn1-N9	1.957(3)	Zn2-N11	1.952(3)
		Zn1-N10	1.956(3)	Zn2-N12	1.956(3)
		S1-C30	1.605(3)	S3-C31	1.596(3)
		S2-C29	1.605(3)	S4-C32	1.602(3)
		C30-N9	1.144(4)	C31-N11	1.158(4)
		C29-N10	1.144(4)	C32-N12	1.140(4)
Bond angles/°					
I1-Zn1-N1	102.64(6)	N1-Zn1-N5	109.4(1)	Zn1-N9-C30	159.9(3)
I1-Zn1-I1a	110.76(2)	N1-Zn1-N9	104.9(1)	Zn1-N10-C29	142.9(3)
I1-Zn1-N1a	121.65(6)	N1-Zn1-N10	116.8(1)	N9-C30-S1	178.8(3)
N1a-Zn1-N1	98.25(13)	N5-Zn1-N9	115.1(1)	N10-C29-S2	179.4(3)
I1a-Zn1-N1a	102.64(6)	N5-Zn1-N10	106.1(1)	Zn2-N11-C31	145.0(3)
		N9-Zn1-N10	104.8(1)	Zn2-N12-C32	156.7(3)
		N4-Zn2-N8	108.5(1)	N11-C31-S3	179.4(3)
		N4-Zn2-N11	116.7(1)	N12-C32-S4	179.1(3)
		N4-Zn2-N12	106.1(1)		
		N8-Zn2-N11	105.1(1)		
		N8-Zn2-N12	115.7(1)		
		N11-Zn2-N12	105.1(1)		

Although the Zn(II) centers in complexes **2** and **3** have the same (ZnN_4) coordination environments, the structures of the final products are very different. In the structure of **3**, two neighboring Zn(II) ions are interconnected by a double bridge of μ-bib ligands, shown in blue color in Fig. 3b, to form a 22-membered macrocyclic $[Zn(bib)_2Zn]$ dimeric unit. The dimeric units are linked together by single bridge μ-bib ligands (red colored), to form an infinite 3D coordination network (Fig. 3c).

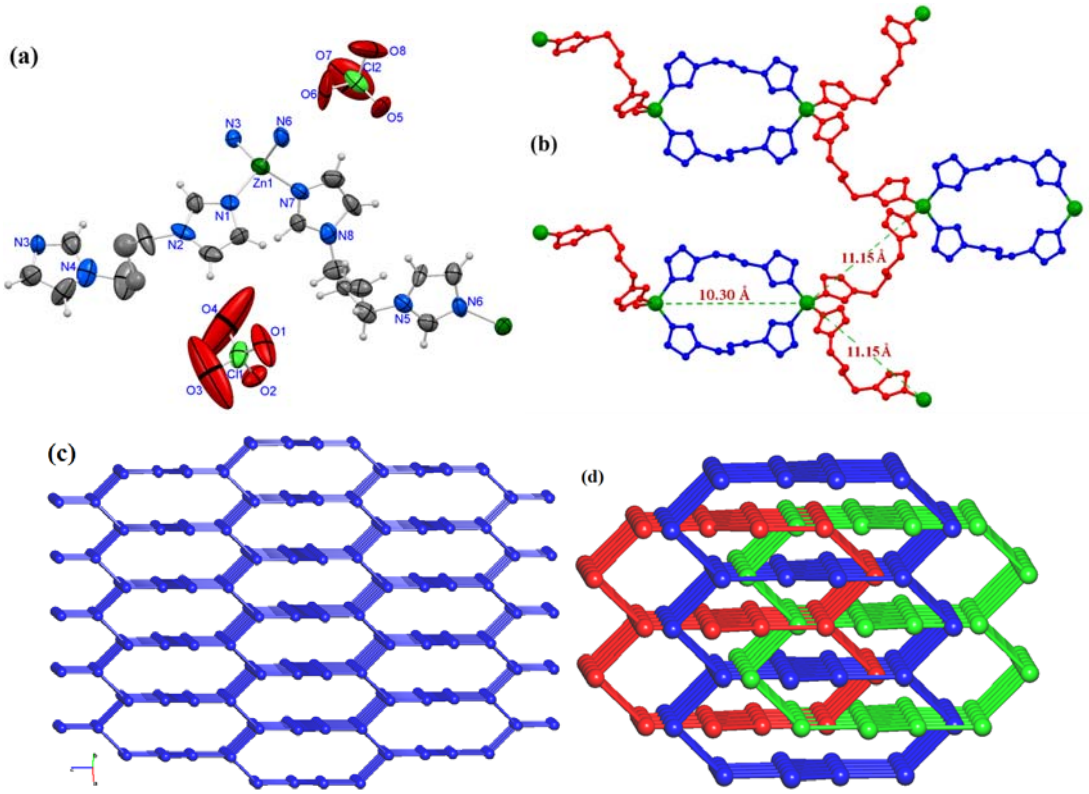


Fig. 3.(a) Coordination environment of Zn(II) in **3** with a labeling scheme for asymmetric unit without disordered guest molecules. (b) View of a section of the 3D net which show different ligand conformations and Zn···Zn distances. (c) Schematic illustration of a single 3D 10^3-**ths** network (d) Schematic representation of the 3-fold interpenetrating 10^3-**ths** topology of crystal **3**. All H atoms in (**a**) and (**b**) have been omitted for clarity.

Table 3.Selected bond lengths (Å) and angles (°) for **3** and **4**.

(3)		**(3)**		**(4)**	
Bond lengths/Å					
Zn1-N1	1.979(13)	Cl1-O3	1.386(8)	Zn1-N1	1.989(4)
Zn1-N3	1.981(12)	Cl1-O4	1.404(8)	Cl1-O1	1.381(5)
Zn1-N6	1.956(14)	Cl2-O5	1.394(7)	Cl1-O2	1.416(5)
Zn1-N7	1.989(13)	Cl2-O6	1.403(7)		
Cl1-O1	1.381(7)	Cl2-O7	1.377(7)		
Cl1-O2	1.394(7)	Cl2-O8	1.394(7)		
Bond angles/°					
N1-Zn1-N3	109.2(4)	O2-Cl1-O3	109.2(6)	N1-Zn1-N1	97.7(2)
N1-Zn1-N6	111.7(6)	O2-Cl1-O4	107.4(6)	N1-Zn1-N1	115.7(1)
N1-Zn1-N7	106.5(5)	O3-Cl1-O4	109.0(6)	O1-Cl1-O1	109.6(6)
N3-Zn1-N6	111.6(6)	O5-Cl2-O6	108.2(5)	O1-Cl1-O2	111.5(4)
N3-Zn1-N7	111.7(5)	O5-Cl2-O7	111.4(6)	O1-Cl1-O2	107.2(3)
N6-Zn1-N7	106.1(5)	O5-Cl2-O8	110.0(5)	O2-Cl1-O2	109.9(5)
O1-Cl1-O2	111.1(5)	O6-Cl2-O7	109.5(6)		
O1-Cl1-O3	110.4(6)	O6-Cl2-O8	108.2(6)		
O1-Cl1-O4	109.7(6)	O7-Cl2-O8	109.4(5)		

The alkyl chain of the blue colored μ-bib ligands adopts a *gauche-anti-gauche'* conformation.The dihedral angle between the mean planes of two imidazolyl rings is 1.86 °and the N-to-N distances is 8.06 Å (Table 4). The red colored μ-bib ligands show a *gauche-anti-gauche* conformation with the dihedral angle of 12.39° and the N-to-N distance of 7.69 Å which are different from those in the blue colored bib ligands. As shown in Fig. 3b, two different Zn···Zn distance (10.30 and 11.15 Å) are observed in the network, as a consequence of the two different types of arrangements for the bib ligands. From a topological point of view, each Zn(II) ion can be considered as a three-connected node. The 3D framework of **3** can be abstracted into a 10^3-**ths** network topology (Fig. 3c). Moreover, three identical 10^3-**ths** networks are interlocked with each other, forming a 3-fold interpenetrated 3D architecture (Fig. 3d). The adjacent 3D networks are interconnected by weak intermolecular C-H···O hydrogen bonds, formed between oxygen atoms of the perchlorate anions and the hydrogen atoms of imidazolyl rings of the μ-bib ligands (Fig. S1) [22]. In addition, significant imidazole ring stacking interactions occur in **3** (Fig. S2). The conformations of the blue colored bib ligands are such as to bring one ring of each ligand into close proximity and approximately parallel, with a centroid···centroid distance of 3.99 Å, an interplanar distance (defined as the perpendicular distance between one ring centroid and the mean plane of the other ring) of 3.35 Å and a dihedral angle of 1.81° between the two rings [23, 22b].

The packing of the 3D nets of **3** in the crystal structure leaves small voids, which are occupied by Et_2O and water guest molecules. The calculated guest free void is about 11% of the cell volume. Position of Et_2O guest molecules and perchlorate counteranions in the crystal structure is shown in Fig. S3.

3. 2. 4. Crystal structure of $\{[Zn(\mu\text{-bmib})_2](ClO_4)_2\cdot(H_2O)_4\}_n$ (4)

Complex **4** crystallizes in the tetragonal space group $I4_1/acd$ and has the same metal/ligand ratio and the same coordination environment as in **3**. The asymmetric unit of **4** contains one Zn(II) ion, half μ-bbd ligand and ClO_4^- on a 2-fold axis, together with a guest water molecule. In this complex, each Zn(II) ion is coordinated by four imidazole nitrogen atoms from four crystallographically equivalent μ-bmib ligands to give a tetrahedral ZnN_4 coordination geometry (Fig. 4a). The Zn-N bond distance is 1.989(4) Å and the N-Zn-N coordination angles are 97.7(2) and 115.7(1)° (Table 3). These values are different from those observed in complex **3**. It is likely that this observation is a consequence of the larger size and steric hindrance of the μ-bmib ligands in **4**. In contrast to **3**, in complex **4** neighboring Zn(II) ions

are interconnected by a double-bridging μ-bmib ligands to form an infinite 1D polymeric double chain along the *c* axis containing a centrosymmetricdinuclear 22-membered $[Zn_2(bmib)_2]$ metallacyclic units of C, N and Zn atoms. The dimeric units are arranged nearly perpendicularly to each other to reduce the steric hindrance between the methyl groups of the imidazole rings (Fig. 4b).

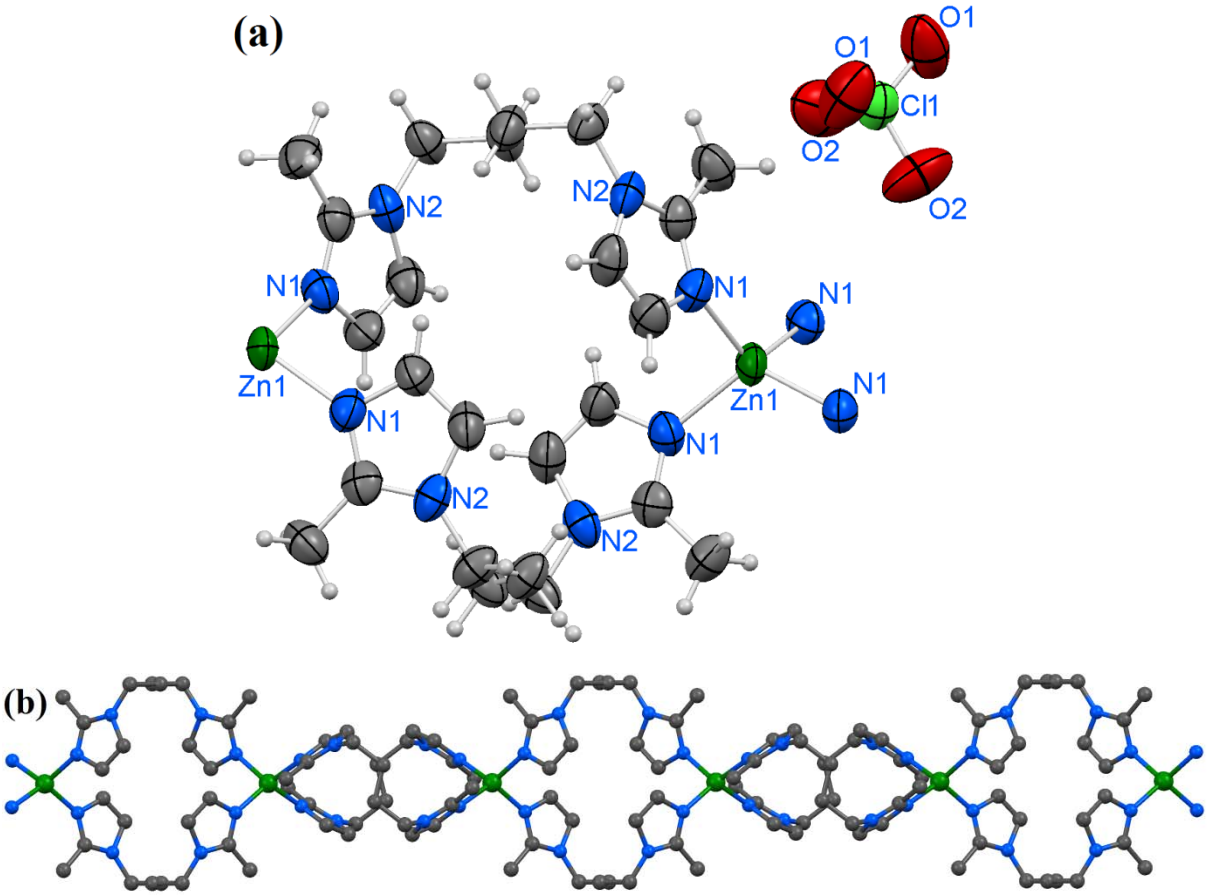


Fig. 4.(a) Coordination environment of Zn(II) in **4** with a labeling scheme for the asymmetric unit without disordered guest molecules. (b) Part of the cationic 1D double chain with alternating perpendicular 22-membered macrometallacyclicunits .All H atoms in (**a**) and (**b**) have been omitted for clarity.

The adjacent Zn···Zn distance in **4** is 8.99 Å, which is shorter than those observed in **3** (10.30 and 11.15 Å) and even in the homologue structure $\{[Zn(bib)_2](ClO_4)_2\}_n$ (10.85 Å) [11d].The difference between the Zn···Zn separations in these compounds can be attributed to the fact that, although the bib and bmib bridging bidentate ligands have the same spacer groups and *gag(g')* conformations for the saturated NCCCCN chains, their dihedral and torsion angles are quite different from each other (Table 4).In the structure of **4**, the μ-bmib ligands display an eclipsed conformation with N to N distances of 6.63Å, which is the shortest observed in a CSD search for the bmib ligand [24]. The 1D cationic chains are arranged parallel to each

other running along the tetragonal *c* direction with the perchlorate counterions located between the chains. Although, at the first glance the structure of **4** looks much similar to that of $\{[Zn(bib)_2](ClO_4)_2\}_n$ [11d], the X-ray analyses show that there are differences in the crystal packing of these compounds that can be attributed to the methyl group of the μ-bmib ligands. In contrast to the structure of $\{[Zn(bib)_2](ClO_4)_2\}_n$ [11d] in which there is no interaction between the adjacent 1D chains, in the structure of **4**, the neighboring chains extend to a single 3D supramolecular network by the C-H···O hydrogen bonds formed between the oxygen atoms of the perchlorate anions as a tetrahedral 4-connected node and an hydrogen atom of imidazole rings and methyl substituents with H···O distaces of 2.45 and 2.31 Å, respectively (Fig. S4) [22].

The parallel square packing of the 1D chains leave narrow channels along the *c* axis, containing disordered water guest molecules. The total void value of the channels without water guests is estimated (by Platon) [25] to be 460 $Å^3$, approximately 7.1% of the unit cell volume.

Table 4. Conformation, torsion, dihedral angles (˚), N-to-N and Zn···Zn separation (Å) for the linker ligands in the structures of **1-4** and $\{[Zn(bib)_2](ClO_4)_2\}_n$ [11d].

Compound	**1**	**2 (red)**	**2 (blue)**	**3 (blue)***	**3 (red)**	**4**	**$\{[Zn(bib)_2](ClO_4)_2\}_n$**
Conformation	*gag'*	*gag'*	*aaa*	*gag'*	*gag*	*gag*	*eae*†
NCCC	46.2	-64.0	-172.7	57.8/46.1	57.4	65.5	0.0
CCCC	180	180.0	177.2	159.1/180.0	168.1	180	-168.0
CCCN	-46.2	61.2	176.6	-72.1/-70.3	55.6	65.45	0.0
Dihedral angle	0	3.2	3.7	1.9	12.4	17.2	11.0
N-to-N	6.33	6.48	7.54	8.06	7.69	6.63	8.45
Zn···Zn	7.74	7.55	8.08	10.30	11.15	8.99	10.85

* the ligand is disordered 50%:50%. † *e* = eclipsed

3. 3. Thermal analyses

The thermal behaviours of compounds **1-4** were studied by TGA. A plateau in the temperature range of 50-300˚C indicates that the molecular architecture of **1** is stable up to 300˚C (Fig. S5). The structure of **1** begins to collapse at about 310˚C. The first total weight loss of 20.6% observed in the temperature range of 310-370˚C corresponds to the dissociation of μ-bbd ligands (calcd. 21.7%) and decomposition of 1D chain structure. Decomposition of the remaining parts takes place on further heating and the final weight at 800˚C is zero. The nearly complete weight loss of compounds **1** may come from the sublimation of the ZnI_2 component. This phenomenon was previously observed for similar cadmium and zinc coordination polymers [26]. Compound **2** is stable up to 210˚C; the dissociation of organic

components and architectural destruction occurs in several stages at higher temperatures. The remaining weight corresponds to the $Zn(NCS)_2$ as a final residue (obsd 41.6%, calcd 40.9%). In the TGA curve of **3**, the water and Et_2O guest molecules depart from the structure in the temperature range of 50-200˚C in two steps (obsd 7.0%, calcd 6.7%). Free of guests 3D architecture of **3** is stable up to 335˚C and the structure begins to collapse at about 345˚C. The weight loss of 57.3% in the range of 345-600˚C is consistent with the dissociation of μ-bib ligands (calcd. 57.3%). As in **3**, the first weight loss in the TGA curve of **4** corresponds to the departure of water guest molecules from the structure in the temperature range of 50-300˚C. Free of guests structure of **4** is stable up to 320˚C and begins to collapse at about 330˚C. Pyrolysis of the organic ligand and decomposition occurs in several stages at higher temperatures.

4. Conclusions

In conclusion, herein we report four new zinc 1D or 3D coordination polymers by facile one-pot reactions at room temperature. Complexes **1** and **2**have been synthesized with the same ligand and different counteranions while complexes **3** and **4** have the same counter anions but different ligands. It was observed that the counter anions and the steric hindrance at the metal centers have significant influence on the structural topology of the complexes. Compounds **1**, **2** and **4** consist of 1D polymeric chain, while **3** has 3D network structure. This observation is related to the greater steric hindrance at the metal centers in complexes **1** and **2** as compared with **3** and **4**. With decreasing the steric hindrance on the coordinating groups of the flexible ligands, we obtained more complex structures. As a result, the bbd ligand with two methyl substituents formed 1D chain structures while bmib with a methyl substituent formed 1D double chains and the bib ligand without steric hindrance around the nitrogen donor atoms, generated a 3-fold 3D network with 10^3-**ths** topology.

Acknowledgements

The authors thank Shahid Chamran and the UniversitàdegliStudi di Milano for financial support. DMP acknowledges the Ministry of Education and Science of Russia (Grant 14.B25.31.0005).

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