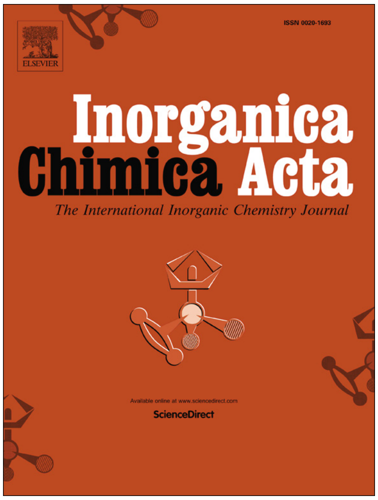


Research paper

Construction of one dimensional Co(II) and Zn (II) coordination polymers based on expanded N,N'-donor ligands

Mansoureh Zahedi, Behrouz Shaabani, Muhittin Aygün, Canan Kazak

PII: S0020-1693(17)30782-X
DOI: http://dx.doi.org/10.1016/j.ica.2017.09.023
Reference: ICA 17879

To appear in: *Inorganica Chimica Acta*

Received Date: 17 May 2017
Revised Date: 17 August 2017
Accepted Date: 8 September 2017

Please cite this article as: M. Zahedi, B. Shaabani, M. Aygün, C. Kazak, Construction of one dimensional Co(II) and Zn (II) coordination polymers based on expanded N,N'-donor ligands, *Inorganica Chimica Acta* (2017), doi: http://dx.doi.org/10.1016/j.ica.2017.09.023

Construction of one dimensional Co(II) and Zn (II) coordination polymers based on expanded N,N'-donor ligands

Mansoureh Zahedi[a], **Behrouz Shaabani***[, a], **Muhittin Aygün**[b] **and Canan Kazak**[c]

[a]*Department of Inorganic Chemistry, Faculty of Chemistry, University of Tabriz, Tabriz , Iran*

**Email:* shaabani.b@gmail.com (*shaabani@tabrizu.ac.ir)*

[b]*Department of Physic, Faculty of Arts & Sciences Dokuz Eylul University, Izmir, Turkey*

[c]*Department of Physics, Faculty of Arts and Sciences, Ondokuz Mayıs University, Kurupelit, Samsun , Turkey*

Abstract

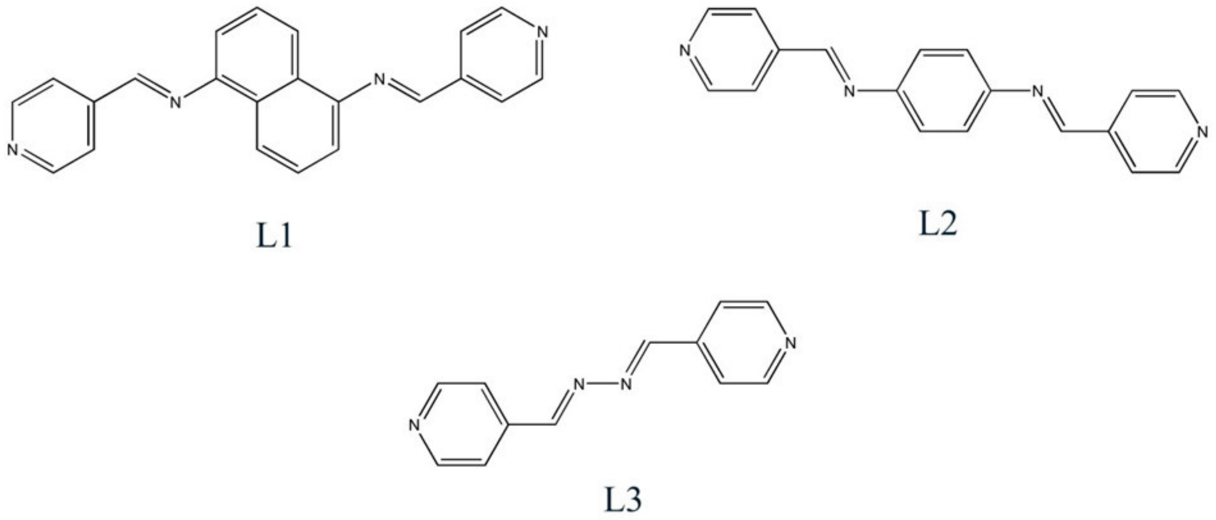
Four new 1-D coordination polymers $[Zn(acac)_2(L1)]_n$ **(1)**, $[Co(acac)_2(L1)]_n$ **(2)**, $[Co(acac)_2(L2)]_n$ **(3)** and $[Co(acac)_2(L3)]_n$ **(4)** were afforded by the complexation reaction of appropriate zinc and cobalt metal salts, acetylacetone co-ligand as well as three linear electron rich and bi-functional *N,N′*-bipyridyl-base ligands of *N,N′*-bis(pyridin-4-ylmethylene)naphthalene-1,5-diamine (L1), *N,N′*-bis(pyridin-4-ylmethylene) phenylene-1,4-diamine (L2) and *N,N′*-bis(pyridin-4-ylmethylene)hydrazine (L3). The structures of these compounds were characterized by FT-IR spectroscopy, elemental analysis, X-ray powder and single crystal X-ray diffractions. X-ray crystallography analyses revealed that these compounds have 1-D linear chain structures a containing $\{N_2O_4\}$ metal coordination environment in which the *N*-donor Lx (x=1–3) bridges occupy *trans* positions. The acetylacetone (acac) ancillary ligands control the coordination number of the metal cation and adopt chelating binding mode on octahedral metal center. Furthermore, 1-D chains are held together with their neighboring ones by C–H···O, C–H···π and π-π stacking intermolecular interactions to stabilize 2-D supramolecular networks. The two former cases **1** and **2**, containing same L1 spacer ligand generate isomorphous structures. Theoretical calculations invoking electronic properties, frontier molecular orbital description and the strength of interactions between metal ion and coordinated atoms via second order perturbation energies were carried out using natural bond orbital analysis (NBO). Finally, thermal stability of compound **2–4** was examined by thermogravimetric (TGA) analysis.

Keyword: Coordination polymers, Expanded *N,N′*-donor ligand, Crystal structure, NBO study, Thermogravimetric analyses (TGA).

1. Introduction

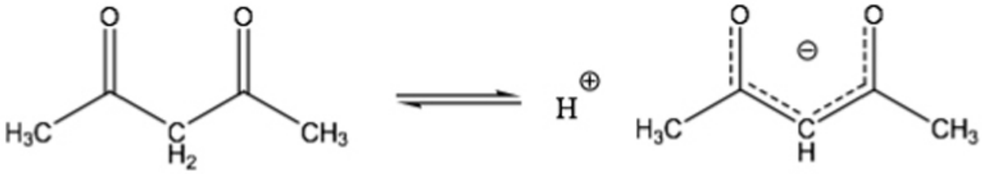
In recent decades, coordination polymers have been a popular research topic in crystal engineering, solid-state chemistry and supramolecular chemistry due to their intriguing diverse architectures and increasing demand of functional materials with potentially controllable properties. These materials can be used in various fields such as catalysts, optical, magnetic and electronic devices and biological applications [1–7]. Structural properties of the organic ligands are one of the main factors which can dramatically influence the topology and composition of the coordination polymers [7–10]. Tailored derivatives of *N,N′*-bipyridyl-base ligands are good candidates for designing and constructing of metal organic networks based on their significant structural properties such as versatility in spacers between the pyridine rings, rigidity or flexibility, rod-like shape and angular orientation of the donor atoms. These properties can exhibit several particular features upon coordination to metal cations: a) Appropriate bridging ability; two pyridyl *N*-donor atoms can coordinate to metal centers as a bidentate ligand. b) The dihedral angles between the pyridyl rings can vary and adapt to meet the requirements for constructing diverse frameworks. c) The ability to engage in intermolecular interactions like π-π stacking due to the completely or partly participation of aromatic groups, which can also affect crystal packing. These structural features can allow to construct diverse coordination polymers with interesting one, two and three-dimensional structures [11–13]. Among the vast number of bidentate *N*-donor ligands, *N,N′*-bis(pyridin-4-ylmethylene)naphthalene-1,5-diamine (L1), *N,N′*-bis(pyridin-4-ylmethylene) phenylene-1,4-diamine (L2) and *N,N′*-bis(pyridin-4-ylmethylene)hydrazine (L3) (Scheme 1) have attracted our attention, since they also can easily be synthesized and have not been used very frequently for the design of extended structures. A search in CSD data base [14] revealed that 18 structurally characterized complexes derivatives of L1 have been identified [15–21]. 1-D ladder-shaped coordination polymer $[Co_2(L1)_3(NO_3)_4]_n$ [15], two and three dimensional structure $[Co(L1)_{1.5}(NO_3)_2]$ and $[Co(L1)(bpdc)]\cdot(EtOH)$ (H_2bpdc = biphenyl-4,4'-dicarboxylic acid, H_2ndc= 2,6-naphthalene dicarboxylic acid) [21] can be mentioned as ones which involve Co(II) cation metal center and L1 linker ligand.

Investigations concerning the coordination polymers generated from L2 displayed that only 5 complexes have been characterized [22–27] and none of them contain cobalt cation as a metal center. Constructing of metal-organic frameworks including L3 in their structures exhibit more interests [28–32]; extended structures of $\{[Co(L3)(tp)(H_2O)_2]\cdot 3H_2O\}_n$ and $\{[Co(L3)(ip)]\cdot(L3)_{0.5}\}_n$ (H_2tp = terphetalic acid, H_2ip = isophethalic acid) can be addressed as examples [29].



Scheme 1. Expanded bipyridyl-base linkers used in this work.

Furthermore, coordination modes of β-diketone and its diversities are well known to rely on the pH of the environment and the nature of the substituents and their relative positions to other moieties in the β-diketones. Moreover, the $-CH_2-$ group readily deprotonates to form anionic tautomeric species (Scheme 2) with new coordination properties. Different types of β-diketones can be very attractive because of their considerable applications in variable fields such as metal-extracting agents [33], design of luminescent compounds [34] and manufacturing of red OLED devices [35]. According to the hot topic of metal-organic hybrid materials and applicable properties of compounds containing β-diketones, special attention has been devoted to the design, synthesis and topological investigation of coordination polymers containing β-diketones in their structures [36–40].



Scheme 2. Schematic of acetylacetone ligand

In addition to the fact that covalent bonds are impetus in the self-assembly of metal centers and organic ligands for construction of robust coordination polymers, weak intermolecular interactions such as classical hydrogen bonds as well as C–H···O/···π and π-π stacking have significant effects on topology and architecture of supramolcular networks. As a continuation of our work in synthesis of coordination polymers based on the expanded *N,N'*-donor linker ligands [19, 27, 41], we carried out the synthesis and detailed crystallographic characterization of four new coordination polymers $[M(acac)_2(L1)]_n$ (M = Zn (**1**), Co (**2**) and L1=(4-py)-CH=N-$C_{10}H_6$-N=CH-(4-py)), $[Co(acac)_2(L2)]_n$ **(3)** (L2=(4-py)-CH=N-C_6H_4-N=CH-(4-py)) and $[Co(acac)_2(L3)]_n$ **(4)** (L3=(4-py)-CH=N-N=CH-(4-py)), respectively. Compounds **1–4** were structurally characterized by elemental analysis, X-ray powder diffraction, FT-IR spectroscopy and single crystal X-ray diffraction. In addition, thermal stability and NBO analyses using the DFT method were investigated.

2. Experimental

2.1. Materials and Physical Measurements

$Co(acac)_2{\cdot}2H_2O$ was prepared according to the literature method [42] . All other reagents and solvents were commercially available and used without further purification. NMR spectra were recorded on a Bruker Avance II Ultrashield Plus 400. Elemental analyses were performed with a

Heraeus CHNO-Rapid VarioEL. FT-IR spectra were recorded on a Bruker Tensor 27 Perkin-Elmer FT-IR. TG analyses were measured in air with a heating rate of 5 $K.min^{-1}$ in the temperature range 25–800 °C on a Mettler Toledo TGA/SDTA 851e instrument. X-ray powder diffraction patterns were obtained at ambient temperature on flat samples with a Stoe Image plate Detector IP-PSD with Cu $K_{\alpha1}$ radiation.

2.2. Synthesis of the Spacer Ligands L1, L2 and L3

Synthesis of L1. We used a modified synthesis adapted from Lee *et al.* [16] : An ethanol (10 mL) solution of 4-pyridinecarboxaldehyde (1.88 mL, 20.0 mmol) was added dropwise to an ethanol solution (10 mL) of 1,5-diaminonaphthalene (1.58 g, 10.0 mmol) and the mixture was refluxed for 3 h. The resulting yellow crystalline solid was washed with ethanol (3×5 mL) and hexane (3×5 mL) and crystallized from CH_2Cl_2–hexane to give the pure ligand. Yield: 83%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.84 (d, 4H), 8.61 (s, 2H), 8.29 (d, 2H), 7.90(d, 4H), 7.56 (m, 2H), 7.18 (d, 2H). FT-IR (KBr, cm^{-1}): 3025(w), 1622 (s), 1590 (s), 1405 (s), 1316 (m), 1229 (m), 977 (m), 923 (m), 788 (s), 648 (w). Anal. Calc. for $C_{22}H_{16}N_4$: C, 78.5; H, 4.7; N, 16.6. Found: C, 78.7; H, 4.8; N, 16.5%.

*Synthesis of L2***.** A modified synthesis producer adapted from ref [43] was used: An acetonitrile solution (5mL) of 4-pyridinecarboxaldehyde (1.88 mL, 20.0 mmol) was added drop wise to a solution of 1, 4-phenylendiamine (1.08 g, 10.0 mmol) dissolved in the same solvent and the mixture was stirred for three hours at room temperature. The resulting yellow solid was filtered off and washed with acetonitrile (3×5 mL) and hexane (3×5 mL) to give the pure ligand L2. Yield: 78%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.80 (d, 4H), 8.54 (s, 2H), 7.79 (d, 4H), 7.36(s, 4H). FT-IR (KBr, cm^{-1}): 3028 (w), 2921 (w), 2888 (w), 2855 (w), 1627 (s), 1595 (s), 1551 (s), 1486 (s), 1412 (s), 1323 (s), 1221 (m), 1191(s), 1100 (m), 984 (w), 891 (m), 815 (s), 603 (m). Anal. Calc. for $C_{18}H_{14}N_4$: C, 75.50; H, 4.93; N, 19.57. Found: C, 75.66; H, 4.89; N, 19.53%.

Synthesis of L3. According to the synthetic procedure of zur Loye *et al*. [44]. 1 mL (11 mmol) of hydrazine hydrate was added dropwise to a solution of 4-pyridinecarboxaldehyde (2.2

mL, 22 mmol) dissolved in ethanol (15 mL). Two drops of formic acid were added and the mixture was stirred at room temperature for 24 h. The yellow solid product was filtered and washed several times with ethanol/ether (1:1). Yield: 86%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.75 (d, 4H), 8.54 (s, 2H), 7.69 (d, 4H). FT-IR (KBr, cm^{-1}): 2941 (w), 1623 (s), 1595 (s), 1552 (m), 1417(s), 1309 (s), 1207 (m), 1082 (m), 1058 (w), 975 (s), 814 (s), 678 (s), 508 (s). Anal. Calc. for $C_{12}H_{10}N_4$: C, 68.56; H, 4.79; N, 26.65. Found: C, 68.53; H, 4.81; N, 26.61%.

2.3. Preparation of Coordination Compounds

$[Zn(acac)_2(L1)]_n$ (1). A mixture of dichloromethane and methanol (1:1, 2 ml) was gently layered on the top of a dichloromethane solution (6 ml) of L1 (33.6 mg, 0.10 mmol) in a test tube. A solution of $Zn(OAc)_2 \cdot 2H_2O$ (21.95 mg, 0.10 mmol) and acetylacetone (20.0 mg, 0.20 mmol) in methanol (6 ml) was added carefully as a third layer. Yellow block crystals formed within two days, yield~8%. FT-IR (KBr, cm^{-1}): 3037(w), 2923(w), 2854(w), 1585(s), 1518(s), 1463 (s), 1403 (s),1361(m), 1313(w), 1228(w), 1060(w), 1007(m), 923(m), 835(m), 786 (m), 655 (w), 510(m).

We note that in contrast to **2–4** only few isolated crystals and no appreciable quantity of the target compound could be obtained; no data from elemental and thermal analysis are available.

$[Co(acac)_2(L1)]_n$ (2). A dichloromethane solution (6 mL) of L1 (33.6 mg, 0.10 mmol) was allowed to diffuse slowly into a methanol solution (6 mL) of $Co(acac)_2 \cdot 2H_2O$ (29.5 mg, 0.10 mmol) through an intermediate layer of methanol/dichloromethane (1:1, 4 ml). Orange block crystals formed within 2 days, yield 63%. IR (KBr, cm^{-1}): 3038(w), 2954(w), 2916(w), 1582(s), 1516(s), 1461(s), 1407(s), 1362(m), 1315(w), 1230 (w), 1060(w), 1008(m), 923(m), 834 (m), 786 (m), 656(w), 509(m). Anal. Calc. for $C_{32}H_{30}N_4O_4Co$: C, 64.75; H, 5.09; N, 9.44. Found: C, 64.63; H, 5.12; N, 9.53%.

$[Co(acac)_2(L2)]_n$ (**3**). To a tetrahydrofuran (THF) solution (5 mL) of L2 (28.6 mg, 0.10 mmol) was carefully introduced a methanol solution (5 mL) of $Co(acac)_2 \cdot 2H_2O$ (29.5 mg, 0.10 mmol) as a second layer. Orange block crystals formed within 4 days, yield 57%. FT-IR (KBr, cm^{-1})

3043(w), 2922(w), 2854(w), 1587(s), 1521(s), 1457(m), 1404(s), 1364(m), 1326(m), 1228(w), 992(w), 926(w), 785(m), 652(s), 510(m). Anal. Calc. for $C_{28}H_{28}N_4O_4Co$: C, 61.80; H, 5.19; N, 10.31. Found: C, 61.72; H, 5.26; N, 10.47%.

$[Co(acac)_2(L3)]_n$ (**4**). This compound was prepared following a similar procedure to that used for the synthesis of **2**, except that L3 (21 mg, 0.10 mmol) was added instead of L1. Orange block crystals formed within 1 day, yield 68%. FT-IR (KBr, cm^{-1}): 3040(w), 2946 (w), 2871 (w), 1583 (s), 1514 (s), 1459(s), 1408 (s), 1371 (s), 1319 (m), 1251 (m), 1228(w), 1202 (w), 1055 (w), 1001 (m), 930 (m), 838 (m), 788 (m), 650(w), 508(m). Anal. Calc. for $C_{22}H_{24}N_4O_4Co$: C, 56.50; H, 5.18; N, 11.99. Found: C, 56.27; H, 5.28; N, 11.78%.

2.4. X-ray Data Collection and Structure Determinations

Intensity data for all compounds were collected at 293 K with Mo-K_α radiation (λ = 0.71073 Å) on an Xcalibur four-circle diffractometer equipped with an EOS CCD detector. The CrysAlisPro software [45] was used for data collection, cell refinement and data reduction. The structures were solved by direct methods (SHELXS-97) [46] and refined by full matrix least squares procedures based on F^2 as implemented in SHELXL-97 [47]. Moreover, for compound **3**, the OLEX2 Solvent Mask routine was used to remove the contribution of the disordered solvent molecule, which can be attributed to THF solvent with a total void of 159 Å³(37 electrons) per unit cell as a filled space. Anisotropic displacement parameters were applied to all non-hydrogen atoms and hydrogen atoms bonded to C were positioned geometrically and refined with a riding model with isotropic displacement parameters set at 1.2 times U_{eq} of appropriate carrier atoms. The crystal data and refinement parameters are presented in Table 1. Selected bond lengths and angles are given in Tables S1 and S2.

CCDC 1550484, 1550482, 1550483 and 1550481 contains the supplementary crystallographic data for **1–4**, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/contsretrieving.html, or 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.

Table 1. X-ray data collection and structure refinement detail.

Compound	1	2	3	4
Chemical formula	$C_{32}H_{30}N_4O_4Zn$	$C_{32}H_{30}CoN_4O_4$	$C_{28}H_{28}CoN_4O_4$	$C_{22}H_{24}CoN_4O_4$
Mr	599.97	593.53	543.47	467.38
Crystal system, space group	Triclinic, *P*-1	Triclinic, *P*-1	Triclinic, *P*-1	Triclinic, *P*-1
Temperature (K)	293	293	295	293
a, b, c (Å)	8.5618 (5), 8.9827 (5), 10.5511 (5)	8.5565 (6), 8.9574 (7), 10.5780 (7)	8.6267 (7), 11.5515 (13), 14.6400 (17)	6.3638 (7), 9.1119 (10), 10.3267 (13)
α, β, γ (°)	80.711 (4), 75.387 (5), 64.918 (5)	80.924 (6), 75.696 (6), 65.030 (7)	102.644 (10), 94.647 (8), 94.940 (8)	95.379 (10), 107.630 (11), 90.588 (9)
V ($Å^3$)	709.79 (6)	710.85 (9)	1410.7 (3)	567.70 (12)
Z	1	1	2	1
μ (mm^{-1})	0.91	0.65	0.65	0.79
Crystal size (mm)	0.34 × 0.22 × 0.12	0.29 × 0.23 × 0.16	0.32 × 0.15 × 0.11	0.42 × 0.22 × 0.13
Absorption correction	Analytical	Analytical	Analytical	Analytical
Diffractometer	Xcalibur, Eos	Xcalibur, Eos	Xcalibur, Eos	Xcalibur, Eos
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	5477, 2902, 2505	5035, 2900, 2537	8856, 5710, 2803	2020, 1596, 1363
R_{int}	0.045	0.019	0.048	0.022
($\sin \theta/\lambda$)max ($Å^{-1}$)	0.625	0.625	0.625	0.625
R_1, wR_2, S	0.041, 0.148, 1.23	0.038, 0.092, 1.06	0.072, 0.167, 0.92	0.040, 0.082, 1.07
No. of reflections	2902	2900	5710	1596
No. of parameters	189	189	338	144
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
Δρmax, Δρmin (e $Å^{-3}$)	0.81, −0.98	0.26, −0.23	0.34, −0.34	0.37, −0.20

2.5. Theoretical Calculation Method

The density functional theory (DFT) according to the Kohn–Sham scheme was applied to study the natural atomic charges, wiberg bond index, frontier molecular orbitals and second-order perturbation energies from natural bond orbital (NBO) analysis. The starting atomic coordinates and molecular structure parameters for single point calculations were those from the crystal structures data of the compounds **1–4**. All the computational results reported in this work were obtained using the GAUSSIAN 03 package [48] at hybrid functional B3LYP level [49]. Basis set of 6-31G* [50] was employed for all non-metal atoms and the effective core potential basis set Lanl2dz [51] was used for metal atoms.

3. Result and Discussion

3.1. Synthesis and characterization

Relatively long and rigid conjugated nitrogen-donor Schiff-base linker ligands L1–L3 were prepared by condensation of 4-pyridinecarboxaldehyde and required diamine reagents such as 1,5-naphtalinediamine, 1,4-phenylenediamine or hydrazine hydrate, in the mole ratio of 1:2. Single crystals of $[Zn(acac)_2(L1)]_n$ **(1)** were synthesized by the reaction of L1, $Zn(OAc)_2 \cdot 2H_2O$ and acetylacetone in a methanol/dichloromethane layer-separation diffusion approach with a molar ratio of 1:1:2. In summary, Metanol/dichloromethane and Metanol/tetrahydrofuran solvent diffusion of $Co(acac)_2 \cdot 2H_2O$ and the appropriate biprydyl-base spacer ligands, in 1:1 molar ratio, easily led to the formation of $[Co(acac)_2(Lx)]_n$ (x= 1, 2 and 3) **2–4** coordination polymers.
The Fourier Transform Infrared spectrum of the free Schiff base ligands display the absorption peaks of imine ν(C=N) in 1622, 1623 and 1627 cm^{-1} for L1, L2 and L3, respectively. Consistent with this assignment, vibrations of the imine ν(C=N) groups are encountered in the range 1600-1680 cm^{-1} [52]. These absorption bands in coordination polymers appear in lower frequency range of 1587–1582 cm^{-1}. In all compounds, sharp and strong characteristic bands of 1587–1514 cm^{-1} can be attributed to ν(C=O) or ν(C=C) stretching of the acetylactone ligand [53]. It has to be mentioned that the azomethine (C=N) stretching frequencies overlap with νC=O in acac.

The results of our single crystal diffraction experiments are also supported by microanalytical data, except for compound **1**. Powder diffraction confirms that our samples are phase-pure (Figs. S1-S4).

3.2. Description of the crystal structures

$[M(acac)_2(L1)]_n$ (M = Zn (1), Co (2)). Isomorphous compounds **1** and **2** crystallized in the triclinic *P*-1 space group. Zinc and cobalt metal centers in **1** and **2** are located in an octahedral sphere consisting of two bidentate acetylacetone in the equatorial position and L1 bridging ligand in the axial position, bound through terminal 4-pyridyl groups. This kind of octahedral coordination environment is frequently observed for Zn(II) and Co(II) complexes [54–56]. The average values of metal-ligand distance are 2.05 Å, 2.25 Å, 2.04 Å and 2.20 Å for Zn–O, Zn–N, Co–O, Co–N, respectively. Each bridging ligand connects two $M(acac)_2$ centers, resulting in the formation of infinite 1D chains as given in Fig. 1a and Fig. S5. The observed octahedral coordination geometry and bond lengths around the Zn(II) and Co(II) centers are close to the reported 1-D structures of $[Zn(lig)(ttfa)_2]_n$, $[Zn(lig)(btfa)_2]_n$ and $[Co(lig)_2(pyz)]_n$ (Httfa = 2-thenoyltrifluoroacetone, Hbtfa = benzoyltrifluoroacetone and lig = pyrazine) [57, 58]. The separation between next-neighbour metal(II) cations connected by a spacer ligand L1 amounts to 20.1 Å. The aromatic rings in the L1 spacer ligand are subtend with interplanar angles of ca. 40°.

The adjacent chains are arranged in an alternate mode through the π-π stacking interactions between L1 ligands with the C···C distance of 3.2 Å and a non-classical inter strand C–H···O hydrogen bonds of 2.6 Å among the H atoms of L1 ligand and the oxygen atom of acetylacetone from neighbor chains, which are significant and likely contribute to the assembly process and stabilization of the 2-D supramolecular polymeric structures (Fig. 1b).

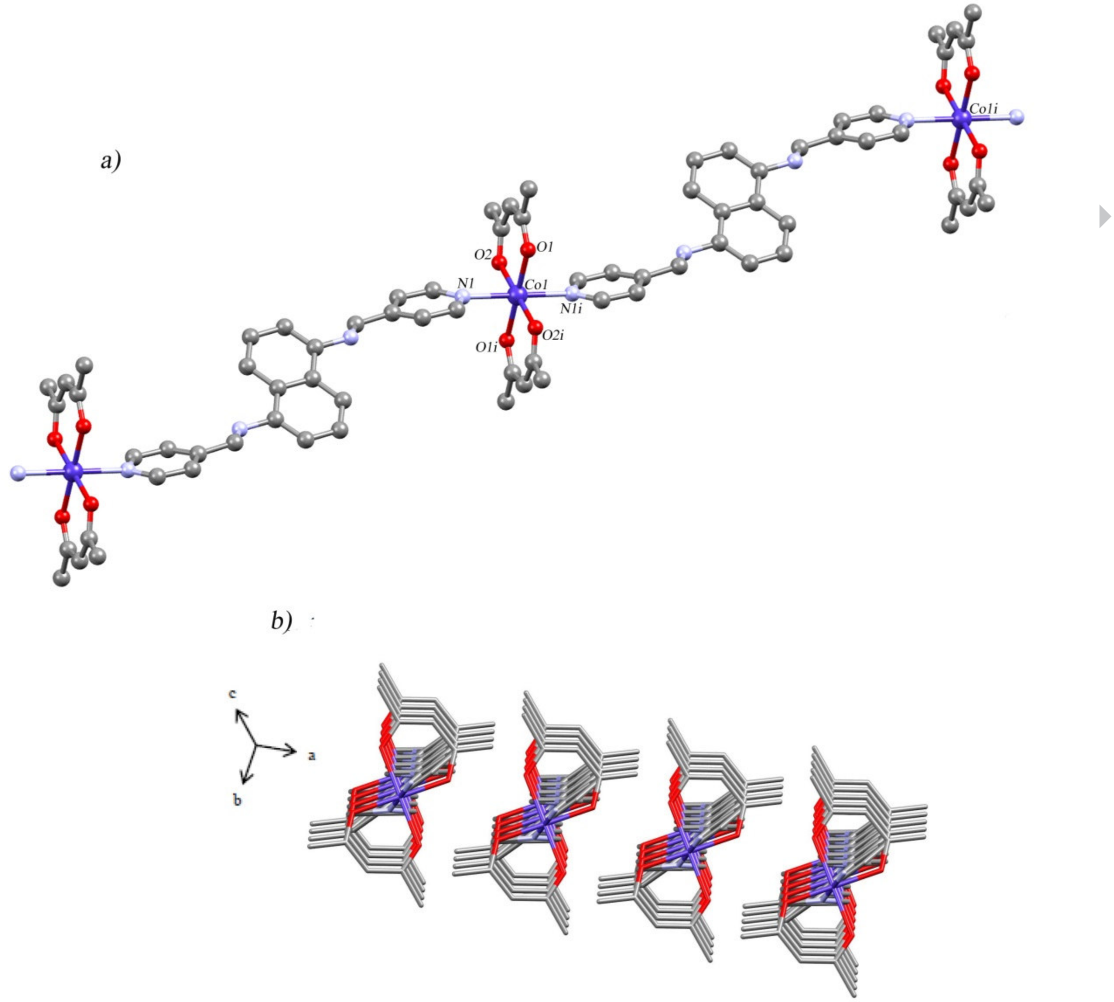


Figure 1. (a) 1-D linear chain structure **2** resulting from L1 ligand and Co(acac)$_2$. Symmetry operators $i= -x, -y+1, -z+1$. (b) Packing in polymer direction along [1-1-1]. H atoms have been omitted for clarity.

[Co(acac)$_2$(L2)]$_n$ (3), [Co(acac)$_2$(L3)]$_n$ (4). The Co(II) atoms are located in a distorted octahedral coordination geometry in **3** and the octahedral one in **4**. They have a coordination sphere similar to that of compound **2**. Thus *N*-donor atoms of two L2 and L3 bridges occupy *trans* positions around the metal center in **3** and **4**, respectively and oxygen atoms of two acetylacetone co-ligands are coordinated equatorially. The 4,4'-bipyridyl-base ligands and Co(II) cations are linked alternately to form a one-dimensional (1-D) linear chain running parallel to *ab* plane and along [11-1] direction (body diagonal) in **3** and **4,** respectively (Fig. 2a and Fig. S6a).

The average bond lengths of 2.20 Å for Co−N and 2.03 Å for Co−O lie in the normal range observed in structures such as a 1-D zigzag chain $[Co(dbm)_2(4ptz)]_n \cdot n$THF (4ptz =2,4,6-tris-(4-pyridyl)-1,3,5-triazine, dbm=1,3-diphenylpropane-1,3-dione) and a molecular complex $[Co(acac)_2(lig)_2]\cdot 2CH_3CN$ (lig = ethylenedioxotetrathiafulvalene-pyridine). The related compounds demonstrate same coordination environment of $\{N_2O_4\}$ as in compounds **3** and **4,** either [59, 60].

The Co···Co distance subtended by a single spacer L2 amounts to 19.92 Å. This linker ligand has arranged in a tilt conformation in which two pyridine rings display dihedral angles of ca. 30° and 148° around phenyl ring. Meanwhile, presence of shorter spacer ligand **L3**, in which adopts a $C(6)=N(2)–N(2)^i=C(6)^i$ torsion angle of 180° and is exactly coplanar, led to the significantly shorter separation of next-neighbour Co cations (15.92 Å) in **4**.

Finally, in **3** two non-classic C−H···O hydrogen bonds interaction [2.66 and 2.69 Å] between carbon atoms of L2 spacer ligand and oxygen atoms of the acetylacetone with C−H···π [2.83 and 2.88 Å] interaction of adjacent linker ligands and interaction of methylene group of acetylacetone with aromatic rings of the spacer ligand are found in the structure and play an important role in stabilizing of 2D structure (Fig. 2b). Whereas, non-classic C−H···O hydrogen bonds of pyridine ring with acetylacetone co-ligand [2.69 Å] is the only intermolecular interaction which assembled compound **4** in two dimensional network (Fig. S6b).

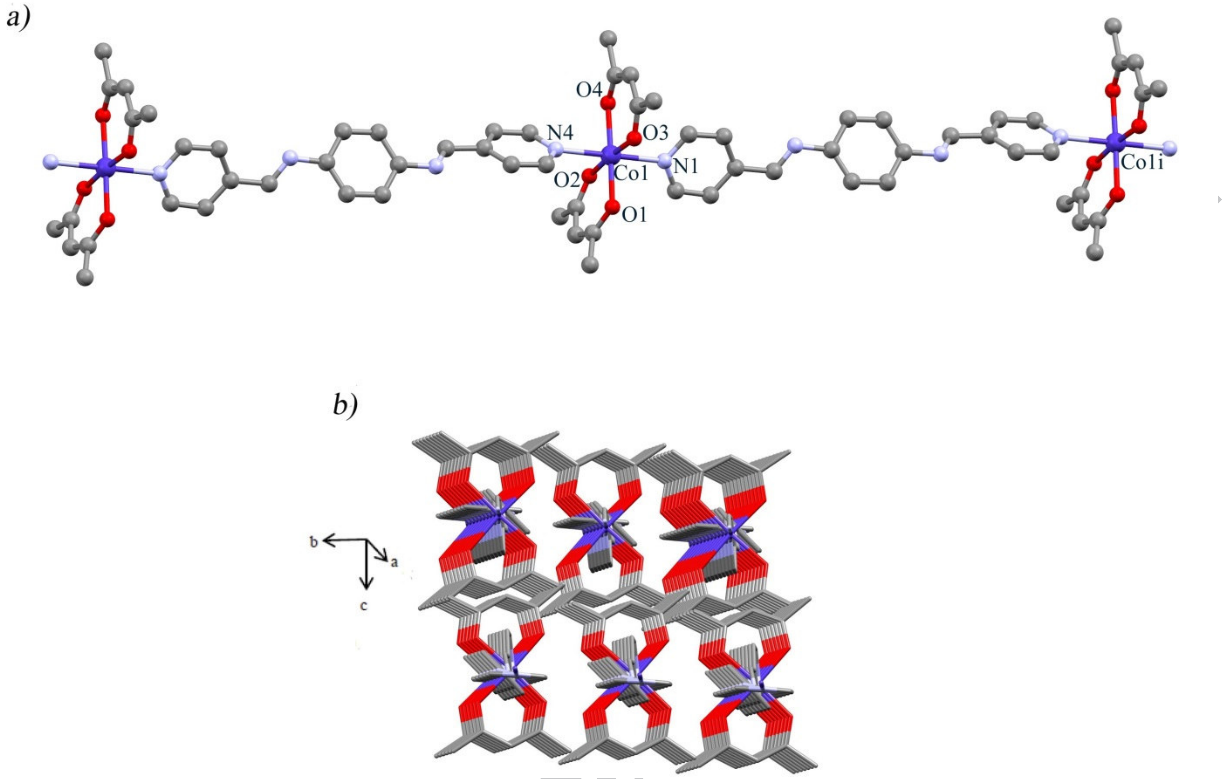


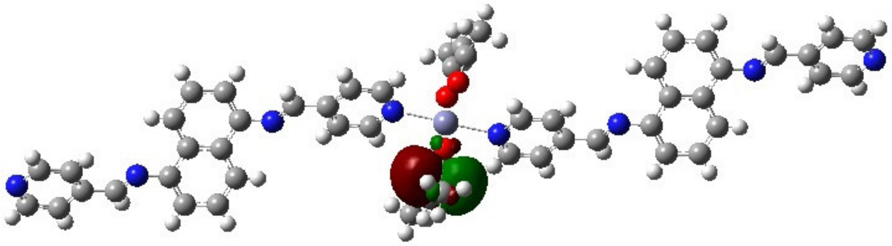
Figure 2. (a) 1-D linear chain structure **3** resulting from L2 ligand and Co(acac)$_2$. Symmetry operators *i*= *x*+*2, y*+*1, z;* (c) Packing in polymer direction along [1-1-1] in **3**.

3.3. Natural Bond Orbital (NBO) Analysis

The NBO analysis was used to investigate the electronic properties of compounds **1–4**. The selected natural atomic charges, electron configuration and wiberg bond index for compounds **1–4** are shown in Tables S3-S6. Base on the electron configuration results, it can be concluded that Zn^{2+} and Co^{2+} ions are coordinated mainly via 4s, 3d and 4p orbitals. All *O*- and *N*-donor atoms supply electrons of 2s and 2p to form the coordination bonds with metal cations. The affinity of charge transfer from ligand to metal ion can be deduced from natural charge of metal ions (1.30 for Zn^{2+}, 0.77 for Co^{2+} in **2,4** and 0.75 for Co^{2+} in **3**), which are much smaller than +2. The differences of the NBO wiberg bond index among M–O and M–N bonds, that expresses the bond order, make their bond lengths be different and are in good agreement with the X-ray crystal structural data of reported compounds [61], in which the corresponding index shows a shorter bond distance.

All possible interactions between donor (Lewis-type NBOs) and acceptor (non-Lewis NBOs) are investigated by NBO analysis. The stabilization energy ΔE_{ij} related to this delocalization is given by second-order perturbative correction [62]. These interactions are named as 'delocalization' corrections to the zeroth-order natural Lewis structure. The most important values that have resulted from *n-n** interactions between lone-pair of oxygen and nitrogen orbitals with anti-lone-pair of metal orbitals are summarized in table S3-S6. The larger ΔE_{ij} is due to the more intensive interaction between metal cations and coordinated atoms. This interaction is one of the most important factors in the self-assembly of coordination polymers. Generally, the bond lengths of donor and acceptor atoms are in good agreement with stabilization energies, which means decreasing in bond distance is caused by increasing in stabilization energy.

As depicted in figure 3, both lowest unoccupied and highest occupied molecular orbital of structure **1** are composed of the acetylacetone ligand, but they are not belong to the same co-ligand; so, the charge transfer of ligand-to-ligand may be inferred from some contours of molecular orbital. Highest occupied molecular orbitals (HOMO) of **2** consists of π orbitals of naphthalene rings, meanwhile, α and β lowest unoccupied molecular orbitals (LUMO) are centralized on metal center and contrary naphthalene ring, respectively (Fig. S7). Hence, metal-to-ligand and ligand-to-metal charge transfer can be supposed for this coordination polymer. The 3D plots in structure **3** show that metal cation has the main contribution in HOMO_α orbitals, while pyridine ring in spacer ligand constructs the LUMO orbitals, which means metal-to-ligand charge transfer is expected (Fig. S8). The β frontiers orbitals of **3** are mainly include acetylactone ancillary ligand in which intra-ligand charge transfer can be possible. The lowest α unoccupied molecular orbital (LUMO) of **4** is localized on acetylacetone ligand and cobalt(II) constructs its LUMO orbital, which means ligand-to-metal charge transfer (LMCT) is expected. For HOMO_β and LUMO_β orbitals, the metal center is the main contributor to these orbitals (Fig. S9).


Lumo

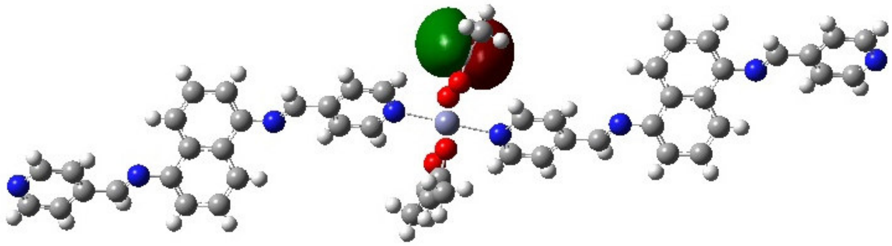

Homo

Figure3. Graphical presentation of calculated frontier orbitals $[Zn(acac)_2L1]_n$ **(1)**

3.4 Thermal stabilities

To examine the stability of the coordination polymer **2–4**, thermogravimetric analyses (TGA) of these compounds were performed on polycrystalline samples at a heating rate of 5 $°C\cdot min^{-1}$ in the temperature range of 25–800 °C in air (Fig. S10-S12). The TGA curves show no weight loss up to about 190 °C demonstrating that the frameworks of **2–4** are retained up to this temperature and the solvent molecules are absent. Coordination polymer **2** displays two weight loss steps. The first discrete weight loss occurs between 190 and 315˚C, presumably due to the decomposition of naphthalene spacer of L1 ligand (found 24.53%, calc 25.87%). Acetylacetone co-ligands and pyridine rings of L1 has been lost in a continuous fashion in the range of 316–540˚C (found 64.26%, calc 65.05%). The solid residue composed after 540˚C can be attributed to CoO (found 11.66%, calc 12.79%). Framework **3** collapses in three steps. The first weight loss step in the temperature range of 190–306˚C is probably due to the removal of phenyl fragment of L2 ligand (found 18.15%, calc 19.03%). This decomposition is continued by the elimination of one acetylacetone co-ligand up to 395˚C (found 18.40%, calc 18.50%). The last step followed by release of residual part of L2 and the second co-ligand (found 48.86%, calc 49.62%). The final remnant mass in 500˚C can be assigned to CoO (found 13.97%, calc 13.78%). The TGA curve compound **4** exhibits consecutive two stages of thermal decomposition. The first obvious and sharp weight loss can be associated to destruction of two acetylacetone and also the spacer part of pyridine rings in L3 (found 49.63%, calc 48.74%). Continuously, a less sharp region is observed over 275–420°C accompanying the complete decomposition of linker ligand (found 38.76%, calc 39.85%). These data indicate that the synthesized compounds not only have acceptable stability but also display the same thermal stability, which can be attributed to the presence of the same metal cation and analogous coordination environment and 1-D linear structures in all. While, Differences in decomposition modes appear to depend, at least partially, on the variation of intermolecular interactions among the adjacent 1-D linear chains and usage of different expanded *N,N′*-donor linker ligands contain various spacers.

4. Conclusion

In the present paper, four new coordination polymers, $[Zn(acac)_2(L1)]_n$ **(1)**,$[Co(acac)_2(L1)]_n$ **(2)**, $[Co(acac)_2(L2)]_n$ **(3)** and $[Co(acac)_2(L3)]_n$ **(4)** were synthesized and their structural characterization has been done by single crystal X-ray diffraction. It gave evidence that the rigid and long *N,N′*-bipyridyl-base linker ligands are able to join the $Zn(acac)_2$ and/or $Co(acac)_2$ nodes through their 4-pyridyl nitrogen-donor atoms to create infinite 1-D linear chain coordination polymers. The ability of *N,N′*–donor ligands to participate in intermolecular interactions via the completely or partly engagement of aromatic groups may help stabilizing of 2-D supramolcular networks through $\pi\cdots\pi$ stacking and C−H···O/π non-classic hydrogen bond between adjacent chains. Different Co···Co distances subtended by a single linker ligand and various intraligand geometry among these synthesized compounds declare the remarkable effect of spacers between pyridine rings on the extended structures. Thermogravimetric analysis has shown common features with a few differences which reflect the architecture of each individual compound; analysis showed high thermal stability and same starting decomposition temperature in all coordination polymers which can be attributed to the structural similarity, but display different weight loss steps that can probably be due to the influence of the different spacers in the linker ligands and also variations in the intermolecular interactions. At the end, theoretical calculation of natural charge, Wiberg bond index and delocalization of charge from lone-pair of donor orbitals to anti-lone-pair of metal orbitals confirm the stabilization of these compounds and show the obvious covalent interaction between the coordinated atoms and metal(II) ions.

5. Reference

[1] J.-m. Hao, B.-y. Yu, K. Van Hecke, G.-h. Cui, A series of d^{10} metal coordination polymers based on a flexible bis(2-methylbenzimidazole) ligand and different carboxylates: synthesis, structures, photoluminescence and catalytic properties, CrystEngComm, 17 (2015) 2279-2293.
[2] Y. Hasegawa, T. Nakanishi, Luminescent lanthanide coordination polymers for photonic applications, RSC Adv. 5 (2015) 338-353.
[3] A.M. Kirillov, Hexamethylenetetramine: An old new building block for design of coordination polymers, Coord. Chem. Rev., 255 (2011) 1603-1622.
[4] M.D. Allendorf, A. Schwartzberg, V. Stavila, A.A. Talin, A Roadmap to Implementing Metal–Organic Frameworks in Electronic Devices: Challenges and Critical Directions, Chem. Eur. J, 17 (2011) 11372-11388.
[5] S. Gupta, M.V. Kirillova, M.F.C. Guedes da Silva, A.J.L. Pombeiro, A.M. Kirillov, Alkali Metal Directed Assembly of Heterometallic Vv/M (M = Na, K, Cs) Coordination Polymers: Structures, Topological Analysis, and Oxidation Catalytic Properties, Inorg. Chem, 52 (2013) 8601-8611.
[6] P. Smolenski, S.W. Jaros, C. Pettinari, G. Lupidi, L. Quassinti, M. Bramucci, L.A. Vitali, D. Petrelli, A. Kochel, A.M. Kirillov, New water-soluble polypyridine silver(i) derivatives of 1,3,5-triaza-7-phosphaadamantane (PTA) with significant antimicrobial and antiproliferative activities, Dalton Trans, 42 (2013) 6572-6581.
[7] J.-Z. Gu, A.M. Kirillov, J. Wu, D.-Y. Lv, Y. Tang, J.-C. Wu, Synthesis, structural versatility, luminescent and magnetic properties of a series of coordination polymers constructed from biphenyl-2,4,4[prime or minute]-tricarboxylate and different N-donor ligands, CrystEngComm, 15 (2013) 10287-10303.
[8] E.C. Constable, Expanded ligands—An assembly principle for supramolecular chemistry, Coord. Chem. Rev., 252 (2008) 842-855.

[9] X.-H. Chang, J.-H. Qin, L.-F. Ma, J.-G. Wang, L.-Y. Wang, Two-and three-dimensional divalent metal coordination polymers constructed from a new tricarboxylate linker and dipyridyl ligands, Cryst. Growth Des., 12 (2012) 4649-4657.
[10] Ł. Jaremko, A.M. Kirillov, P. Smoleński, T. Lis, A.J.L. Pombeiro, Extending the Coordination Chemistry of 1,3,5-Triaza-7-phosphaadamantane (PTA) to Cobalt Centers: First Examples of Co-PTA Complexes and of a Metal Complex with the PTA Oxide Ligand, Inorg. Chem., 47 (2008) 2922-2924.
[11] S.A. Barnett, N.R. Champness, Structural diversity of building-blocks in coordination framework synthesis—combining M(NO3)2 junctions and bipyridyl ligands, Coord. Chem. Rev., 246 (2003) 145-168.
[12] J.-L. Dong, D.-Z. Wang, Y.-Y. Jia, D.-H. Wang, Three coordination polymers based on 9,10-di(pyridine-4-yl)anthracene ligand: Syntheses, structures and fluorescent properties, J. Mol. Struct., 1142 (2017) 304-310.
[13] W. Bauer, C. Lochenie, B. Weber, Synthesis and characterization of 1D iron (II) spin crossover coordination polymers with hysteresis, Dalton Trans, 43 (2014) 1990-1999.
[14] C.R. Groom, F.H. Allen, The Cambridge Structural Database in retrospect and prospect, Angew. Chem. Int. Ed., 53 (2014) 662-671.
[15] C.-Y. Su, A.M. Goforth, M.D. Smith, H.-C. zur Loye, Assembly of large simple 1D and rare polycatenated 3D molecular ladders from T-shaped building blocks containing a new, long N, N′-bidentate ligand, Chem. Commun., (2004) 2158-2159.
[16] D. Min, B.-Y. Cho, S.W. Lee, Novel long bipyridine-type linking ligands containing an intervening naphthalene fragment:[Zn (L 1)(NO 3) 2],[Zn (L 2)(NO 3) 2], and [Cd (L 1) 1.5 (NO 3) 2](L 1=(4-py)–CH N–C 10 H 6–N CH–(4-py); L 2=(3-py)–CH N–C 10 H 6–N CH–(3-py)), Inorg. Chim. Acta, 359 (2006) 577-584.
[17] Y.O. Jang, S.W. Lee, Homoleptic silver-bis (pyridine) coordination polymers:[Ag (L 1) 2]·(PF 6),[Ag (L 1) 2]·(SbF 6),[Ag (L 1) 2]·(BF 4),[Ag (L 2)]·(PF 6), and [Ag (L 3) 1.5]·(CF 3 SO 3)·(H 2 O) 2 {L 1=(4-py)–CH N–C 10 H 6–N CH–(4-py); L 2=(2-py)–CH N–C 10 H 6–N CH–(2-py); L 3=(3-py)–CH N–C 14 H 12–N CH–(3-py)}, Polyhedron, 29 (2010) 2731-2738.
[18] F. Li, J.K. Clegg, C.J. Kepert, Structural diversity in coordination polymers constructed from a naphthalene-spaced dipyridyl ligand and iron (II) thiocyanate, J Incl Phenom Macrocycl Chem, 71 (2011) 381-388.
[19] B. Shaabani, N. Rad-Yousefnia, M. Zahedi, Ş. Ertan, G.R. Blake, M.S. Zakerhamidi, Construction of new 1D and 2D coordination polymers generated from rigid N, N′-bis (4-pyridylmethylene)-1, 5-naphthalenediamine ligand: Syntheses, crystal structures and luminescence properties, Inorg. Chim. Acta, 455 (2017) 158-165.
[20] Y.-M. Jung, S.W. Lee, Relative Coordinating Abilities of Bis (pyridine)-Type Ligands When Forming Mixed-Ligand Coordination Polymers: Preparation and Structure of $[Cd_2(L1)_2(L2)(NO_3)_4]_\infty$ {(n-py)-CH= $NC_{10}h_6$-N= CH-(n-py)[n= 3 (L1), 4 (L2)]}, Bull. Korean Chem. Soc., 31 (2010) 2668.
[21] S.H. Kim, H.S. Huh, S.W. Lee, Cobalt (II) coordination polymers based on dicarboxylates and dipyridyl-type ligands:$[CoL_{1.5}(NO_3)_2]$,$[Co_{1.5}(bpdc)_{1.5}(dma)]\cdot(dma)\cdot(EtOH)$,$[Co_{1.5}(ndc)_{1.5}(dma)_2]$,$[Co_3(ndc)_3(dmf)_4]$, and $[CoL(bpdc)]\cdot(EtOH)$($bpdcH_2$= biphenyl-4,4′-dicarboxylic acid, ndcH 2= 2,6-naphthalene dicarboxylic acid, L= py $CHNC_{10}H_6NCHpy$), J. Mol. Struct., 841 (2007) 78-87.
[22] T. Moriuchi, S. Bandoh, M. Kamikawa, T. Hirao, Palladium Homobimetallic Complexes with Bridging π-Conjugated Ligands, Chem. Lett., 29 (2000) 148-149.

[23] Y. Diskin-Posner, G.K. Patra, I. Goldberg, Supramolecular assembly of metalloporphyrins in crystals by axial coordination through amine ligands, Journal of the Chemical Society, Dalton Trans, (2001) 2775-2782.
[24] J.-J. Jiang, S.-R. Zheng, Y. Liu, M. Pan, W. Wang, C.-Y. Su, Self-Assembly of Triple Helical and meso-Helical Cylindrical Arrays Tunable by Bis-Tripodal Coordination Converters, Inorg. Chem., 47 (2008) 10692-10699.
[25] J.-J. Jang, L. Li, T. Yang, D.-B. Kuang, W. Wang, C.-Y. Su, Self-assembly of 2D Borromean networks through hydrogen-bonding recognition, Chem. Commun., (2009) 2387-2389.
[26] M.Y. Masoomi, S. Beheshti, A. Morsali, Mechanosynthesis of new azine-functionalized Zn(ii) metal-organic frameworks for improved catalytic performance, J. Mater. Chem. A, 2 (2014) 16863-16866.
[27] N. Rad-Yousefnia, B. Shaabani, M. Kubicki, M.S. Zakerhamidi, A.M. Grzeskiewicz, 2D holodirected lead (II) halide coordination polymers based on rigid N, N′-bis (4-pyridylmethylidyne) phenylene-1,4-diamine ligand: Syntheses, crystal structures, NBO studies and luminescence properties, Polyhedron, 129 (2017) 38-45.
[28] S. Mistri, E. Zangrando, P. Vojtíšek, S.C. Manna, 1D, 2D, and 2D Parallel Interpenetrated Dicarboxylato Bridged Co (II) Metal Organic Frameworks: Synthesis, Crystal Structure, Fluorescence Sensing and Band Gap Calculation, ChemistrySelect, 2 (2017) 2634-2642.
[29] S. Sanda, S. Parshamoni, A. Adhikary, S. Konar, A family of metal–organic frameworks based on carboxylates and a neutral, long, and rigid ligand: their structural revelation, magnetic, and luminescent property study, Cryst. Growth Des., 13 (2013) 5442-5449.
[30] Q.H. Zhao, Y.Q. Liu, R.B. Fang, Synthesis, crystal structures and magnetic properties of a coordination polymer containing the $[Mn_5(\mu_{1,1}-N_3)_8(N_3)_2(bpd)_5(H_2O)_2]$ repeat cluster units (bpd= 1,4-bis (4-pyridyl)-2,3-diaza-1,3-butadiene), Inorg Chem Commun, 9 (2006) 699-702.
[31] A.R. Kennedy, K.G. Brown, D. Graham, J.B. Kirkhouse, M. Kittner, C. Major, C.J. McHugh, P. Murdoch, W.E. Smith, Chromophore containing bipyridyl ligands. Part 1: supramolecular solid-state structure of Ag(i) complexes, New J. Chem, 29 (2005) 826-832.
[32] N. Kundu, P.B. Chatterjee, M. Chaudhury, E.R.T. Tiekink, A binuclear iminodiacetato-copper(II) complex with the N,N'-bis(pyridin-4-ylmethylene)hydrazine ligand as spacer, Acta Crystallogr., Sect. E, 61 (2005) m1583-m1585.
[33] G.F. Gagabe, K. Satoh, K. Sawada, Effect of substituent of β-diketones on the synergistic extraction of lanthanoids with linear polyether, Talanta, 84 (2011) 1047-1056.
[34] K. Buczko, M. Karbowiak, Co-fluorescence enhanced tuneable emission of lanthanide β-diketonate complexes in solid thin films, JOL, 136 (2013) 130-140.
[35] N.T. Kalyani, S. Dhoble, Organic light emitting diodes: Energy saving lighting technology—A review, Renew. Sustainable Energy Rev., 16 (2012) 2696-2723.
[36] F. Perdih, CuII and ZnII β-diketonate coordination polymers based on pyrimidin-2-amine, pyrazine and 1, 2-bis (4-pyridyl) ethane, Acta Crystallogr., Sect. B: Struct. Sci., 72 (2016).
[37] F. Marandi, S. Teimouri, H.-K. Fun, Cd (II) and Zn (II) Coordination Polymers Assembled from Benzoyltrifluoroacetone and 1, 2-Bis (4-Pyridyl) Ethane Ancillary ligands, Acta Chim. Slov, 60 (2013) 328-334.
[38] J. Yoshida, S.-i. Nishikiori, R. Kuroda, Construction of supramolecular complexes by use of planar bis (β-diketonato) cobalt (II) complexes as building blocks, Chem. Lett., 36 (2007) 678-679.

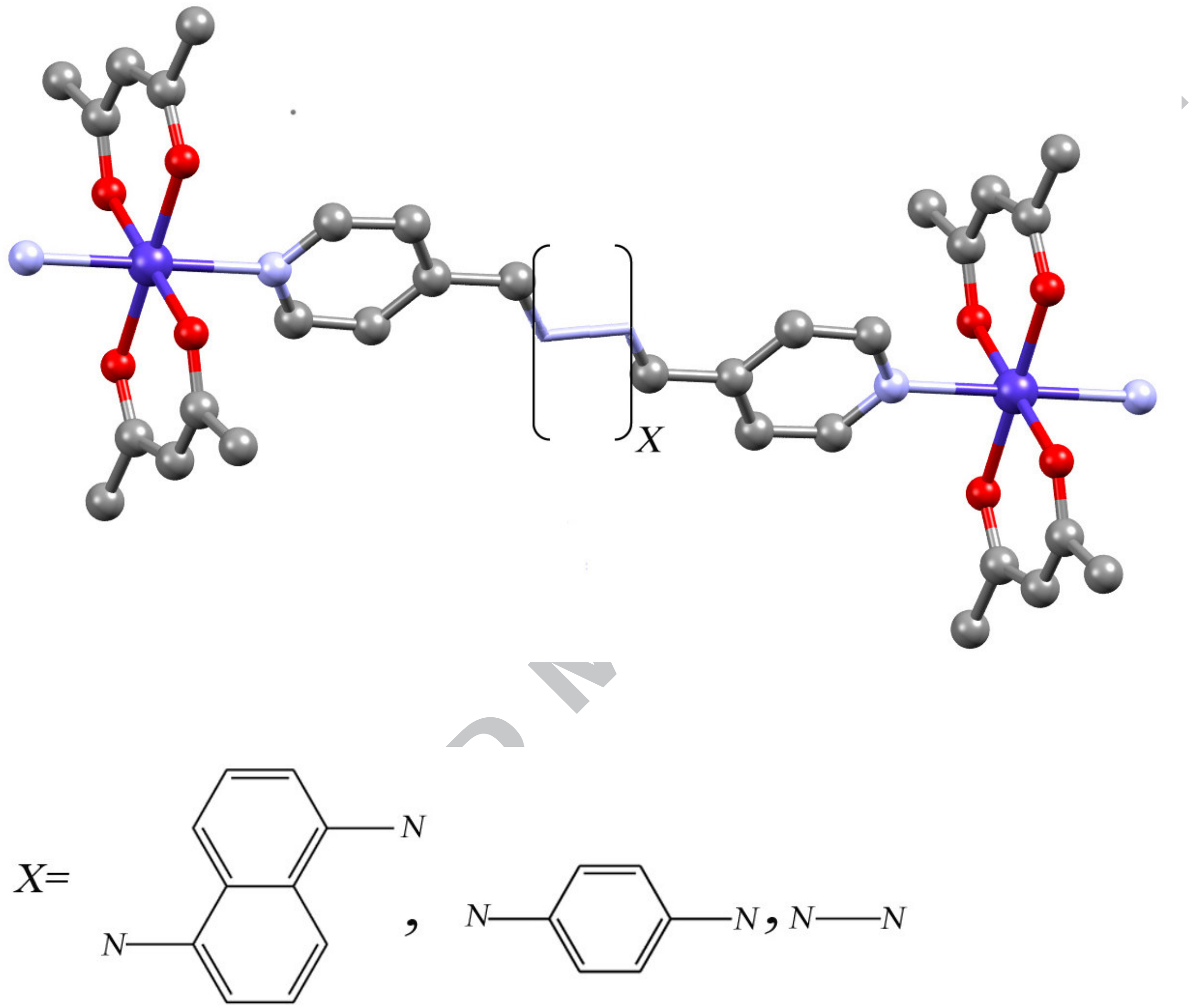
[39] Y. Liu, A.H. Lam, F.W. Fowler, J.W. Lauher, The squaramides. A new family of host molecules for crystal engineering, Mol. Cryst. Liq. Cryst., 389 (2002) 39-46.
[40] M.N. Kopylovich, Y.Y. Karabach, K.T. Mahmudov, M. Haukka, A.M. Kirillov, P.J. Figiel, A.J.L. Pombeiro, Heterometallic Copper(II)–Potassium 3D Coordination Polymers Driven by Multifunctionalized Azo Derivatives of β-Diketones, Cryst. Growth Des., 11 (2011) 4247-4252.
[41] M. Zahedi, B. Shaabani, U. Englert, N. Rad-yousefnia, G.R. Blake, C. Kazak, Cd (II) Coordination Polymers based on Expanded N, N'-Heteroaromatic Donor Ligands, Polyhedron, (2017).
[42] H.M. Goff, J. Hines, J. Griesel, C. Mossman, Synthesis, characterization, and use of a cobalt (II) complex as an NMR shift reagent: an integrated laboratory experiment, J. Chem. Educ, 59 (1982) 422.
[43] D. Grasso, G. Buemi, S. Fasone, C. Gandolfo, ELECTRONIC SPECTRA AND DIPOLE MOMENTS OF P-PHENYLENEDIAMINE-N, N′-DIBENZYLIDENE AND ITS AZA-DERIVATIVES, ChemInform, 12 (1981).
[44] D.M. Ciurtin, Y.-B. Dong, M.D. Smith, T. Barclay, H.-C. zur Loye, Two Versatile N, N ‘-Bipyridine-Type Ligands for Preparing Organic– Inorganic Coordination Polymers: New Cobalt-and Nickel-Containing Framework Materials, Inorg. chem., 40 (2001) 2825-2834.
[45] P. CrysAlis, Agilent Technologies Ltd: Yarnton, Oxfordshire, UK, (2013).
[46] G. Sheldrick, SHELXS-97-A program for automatic solution of crystal structures, University of Goettingen, Goettingen, Germany, (1997).
[47] G. Sheldrick, SHELXL-97, Program for structure refinement, University of Göttingen, Germany, (1997).
[48] M. Frisch, G. Trucks, H. Schlegel, G. Scuseria, M. Robb, J. Cheeseman, J. Montgomery Jr, T. Vreven, K. Kudin, J. Burant, Gaussian 03, revision C. 02; Gaussian, Inc.: Wallingford, CT, (2013).
[49] P. Stephens, F. Devlin, C. Chabalowski, M.J. Frisch, Ab initio calculation of vibrational absorption and circular dichroism spectra using density functional force fields, J. Phys. Chem. A, 98 (1994) 11623-11627.
[50] a. Petersson, A. Bennett, T.G. Tensfeldt, M.A. Al-Laham, W.A. Shirley, J. Mantzaris, A complete basis set model chemistry. I. The total energies of closed-shell atoms and hydrides of the first-row elements, J. Chem. Phys, 89 (1988) 2193-2218.
[51] W.J. Hehre, R.F. Stewart, J.A. Pople, self-consistent molecular-orbital methods. i. use of gaussian expansions of Slater-type atomic orbitals, J. Chem. Phys, 51 (1969) 2657-2664.
[52] P.A. Vigato, S. Tamburini, The challenge of cyclic and acyclic Schiff bases and related derivatives, Coord. Chem. Rev., 248 (2004) 1717-2128.
[53] S.F. Tayyari, F. Milani-Nejad, Vibrational assignment of acetylacetone, Spectrochim. Acta Mol. Biomol. Spectrosc., 56 (2000) 2679-2691.
[54] D. Hermann, C. Näther, U. Ruschewitz, (MII = Mn, Co, Ni, Zn): Four new coordination polymers with acetylenedicarboxylate (ADC_2^-) as bridging ligand, Solid State Sci., 13 (2011) 1096-1101.
[55] X.-S. Tai, H.-Y. You, A new 1D chained coordination polymer: Synthesis, crystal structure, antitumor activity and luminescent property, Crystals, 5 (2015) 608-616.
[56] Y. Zhao, K. Li, J. Li, Solvothermal Synthesis of Multifunctional Coordination Polymers, Z. Naturforsch. B Chem. Sci., 65 (2010) 976-998.
[57] F. Marandi, Synthesis, spectral, X-ray diffraction and thermal studies of new Zn II–pyrazine coordination polymers, J. Mol. Struct., 1059 (2014) 75-80.

[58] B.-Q. Ma, S. Gao, T. Yi, G.-X. Xu, One-dimensional coordination polymers [Co (acac) 2 pz] n and [Co (acac) 2 (4, 4′-bipy)] n (acac= acetylacetone, pz= pyrazine, bipy= 4, 4′-bipyridine): Synthesis, structures and magnetic properties, Polyhedron, 20 (2001) 1255-1261.
[59] L.A. Barrios, J. Ribas, G. Aromí, J. Ribas-Ariño, P. Gamez, O. Roubeau, S.J. Teat, Preparation and structure of three solvatomorphs of the polymer [Co (dbm) 2 (4ptz)] n: spin canting depending on the supramolecular organization, Inorg. Chem., 46 (2007) 7154-7162.
[60] D. Xiao, L. Meng, G. Zhou, Y. Liang, Z. Wang, X. Xiao, Synthesis and Electrochemical Properties of Two Transition Metal Coordination Complexes Based on 4-Pyridyl-Substituted TTF Ligand, Synth. React. Inorg. Met.-Org. Chem., 46 (2016) 1059-1064.
[61] Z.-P. LI, Y.-H. XING, Y.-H. ZHANG, F.-Y. BAI, X.-Q. ZENG, M.-F. GE, Synthesis, structure and quantum chemistry calculation of scorpionate oxovanadium complexes with benzoate, ACTA PHYS-CHIM SIN, 25 (2009) 741-746.
[62] A.E. Reed, L.A. Curtiss, F. Weinhold, Intermolecular interactions from a natural bond orbital, donor-acceptor viewpoint, Chem. Rev., 88 (1988) 899-926.

- ★ four new Zn(II) and Co(II) MOCPs have been prepared by reacting of various electron rich and expanded N,N'-bipyridyl-base spacer ligands with M(acac)$_2$, where acac= acetylacetone, yielding novel supramolecular networks with 2-D structures and divers architectures.

- ★ thermogravimetric analysis displayed that the synthesized compounds have similar thermally stable and exhibit no decomposition up to 190˚C, approximately.

- ★ Electronic properties, frontier molecular orbital description and the strength of interactions between metal ion and coordinated atoms were done using NBO analysis.


X
X=
N
N
N
N
N
N