Research paper

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Supramolecular rectangles and ladders constructed from Ni(II), Cu(II) and Zn(II) mononuclear complexes with bicompartmental ligands and 4-aminopyridine as tectons

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Dedicated to Professor Ionel Haiduc on the occasion of his 80th anniversary

Abstract

By reacting [M^{II}(valpn)] or [M^{II}(valdmpn)] mononuclear complexes with 4-aminopyridine in different molar ratios, five [M^{II}(valXpn)(4-NH_2-py)] and one [Ni^{II}(valdmpn)(4-NH_2-py)$_2$] complexes were obtained and structurally characterized (M^{II} = Ni^{II}, Cu^{II}, Zn^{II}; valpnH_2 and valdmpnH_2 are the Schiff bases resulted from the condensation of *o*-vanillin with 1,3-propylenediamine and 2,2-dimethyl-1,3-propylenediamine respectively). In the [Cu(valpn)(4-NH_2-py)], [Ni(valpn)(4-NH_2-py)], [Zn(valpn)(4-NH_2-py)] and [Ni(valdmpn)(4-NH_2-py)] complexes the metal ions are pentacoordianated with a square pyramidal geometry. The specific hydrogen bond interactions of the amino group belonging to the 4-aminopyridine with the free $O_2O'_2$ compartment of the Schiff base ligands led to various supramolecular architectures: rectangles, chains, and ladders. The spectroscopic properties of the compounds were also investigated.

Keywords: hydrogen bonding, supramolecular rectangles, supramolecular ladders, bicompartmental ligands, 4-aminopyridine, photoluminescence

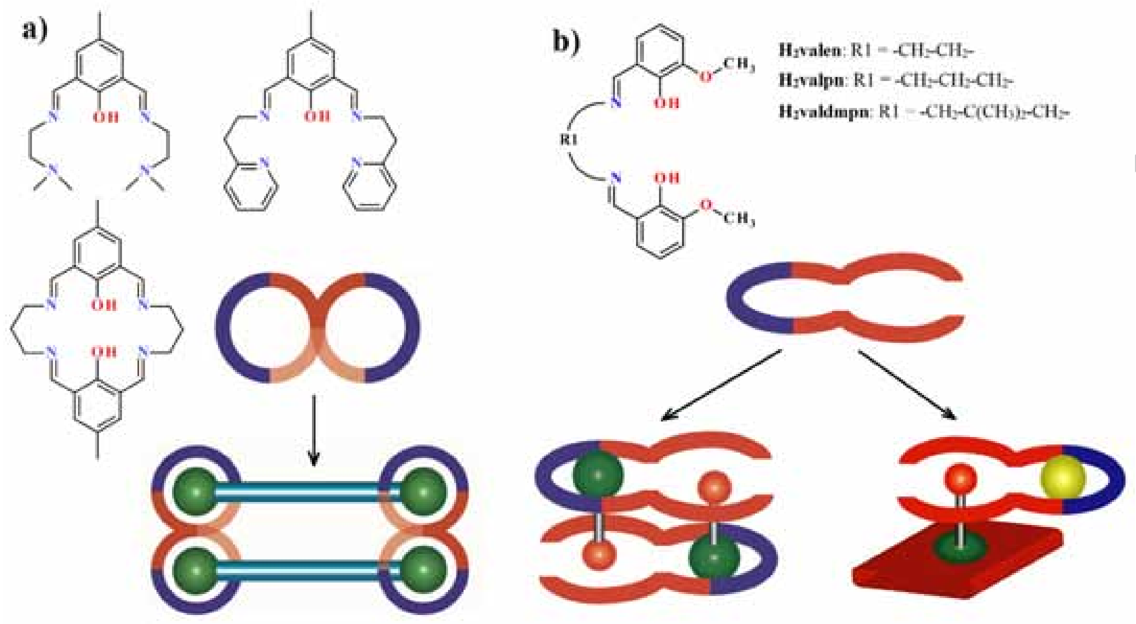
Introduction

In metallosupramolecular chemistry, the construction of molecular objects originates from the processing of the structural information stored within the ligands by the metal ions which operate through their coordination algorithm [1]. Depending on morphology of the ligands and stereochemical preferences of the metal ions, the self-assembly processes involving these species can lead to various structural motifs such as grids [2], helicates [3], cubes [4], prisms or octahedrons [5]. From the specific interactions of the metal ions with the ligands result interesting redox [6], optical [7], and magnetic properties [8].

Schiff-bases are easily accessible ligands which offer the possibility of controlling the nuclearity of their complexes by accommodating each metal ion into a well-defined coordination environment (compartment). Two types of bicompartmental ligands will be emphasised here: one derived from 2,6-diformyl-*p*-cresol and the other from *o*-vanillin. Thus, the macrocyclic and end-off ligands resulted from the condensation of 2,6-diformyl-*p*-cresol with various diamine (Scheme 1a) can generate binuclear complexes with divalent transitional metal ions (Ni^{II}, Cu^{II}, Zn^{II}). The preference of the Cu^{II} and Zn^{II} metal ions for coordination number 5 was exploited for synthesizing molecular rectangles by connecting the binuclear nodes with *exo*-bidentate ligands: 4,4'-bipyridine, bis(4-pyridyl)ethane, bis(4-pyridyl)ethylene or isonicotinato anion [9].

Schiff-bases derived from *o*-vanillin and diamines usually behave as bicompartmental ligands, allowing the synthesis of heterobinuclear 3d-4f complexes [10] or 3d-3d' complexes [10c, 11]. In the 3d-4f complexes, the 3d metal ion is hosted into the N_2O_2 compartment, while the oxophilic lanthanide cation occupies the larger, open $O_2O'_2$ compartment. In the binuclear complexes, the phenoxo oxygen atoms act as bridges between the two metal ions. In mononuclear complexes with the metal ion hosted into the N_2O_2 compartment, the larger vacant $O_2O'_2$ compartment can act as a receptor not only toward other metal ions, but also toward hydrogen bond donors (e.g. the aqua ligand arising from another complex, identical [12] or different [13] – Scheme 1b). Ammonium cation [14] or bis-protonated diamines [15] can be also used as guest, directing the crystalline organisation of such mononuclear complexes by co-crystallisation.

In this paper, we report on the syntheses, structural characterization, and optical properties of new supramolecular architectures based on [M^{II}(valpn)] or [M^{II}(valdmpn)] mononuclear complexes and 4-aminopyridine as tectons (where M^{II} = Ni^{II}, Cu^{II}, Zn^{II}; and valpnH_2 and valdmpnH_2 are the Schiff bases resulted from the condensation of *o*-vanillin with 1,3-propylenediamine and 2,2-dimethyl-1,3-propylenediamine respectively, in a 2:1 molar ratio).



Scheme 1 (a) Formation of molecular rectangles by connecting symmetrical binuclear Cu^{II} or Zn^{II} complexes with *exo*-bidentate ligands; (b) supramolecular recognition by hydrogen interactions of coordinated water molecules (donor) into the external $O_2O'_2$ free compartment of $[M^{II}(valXn)]$ mononuclear complexes (acceptor)

2. Experimental part

2.1. Syntheses

The [Cu(valpn)], [Ni(valpn)], [Zn(valpn)] and [Ni(valdmpn)] precursors were synthesized following the same general procedure: 5 mmol of $Cu(NO_3)_2{\cdot}3H_2O$, $Zn(NO_3)_2{\cdot}6H_2O$ or $Ni(NO_3)_2{\cdot}6H_2O$, were added to an ethanolic solution (20 mL) of 3-methoxysalycilaldeyde (10 mmol), 1,3-propylenediamine or 2,2-dimethyl-1,3-propylenediamine respectively (5 mmol), and triethylamine (20-30 mmol). The mixtures were boiled for 15-30 min. The precipitates resulted by cooling were filtered off and washed with ethanol and diethyl ether.

2.1.1. *[Cu(valpn)(4-NH_2-py)]·0.33CH_3CN –* ***1***

0.1 mmol of [Cu(valpn)] and 0.15 mmol of 4-aminopyridine were dissolved in 30 ml of acetonitrile. The slow evaporation at room temperature of the resulting mixture affords dark green single crystals after 4-5 days. Yield: 75%. As a general rule, we collect crystals prior total evaporation of the solvents in order to avoid contamination with the excess of 4-aminopyridine. All the crystals were washed with a 1:1 mixture of ethanol-diethyl ether.

Selected IR data (KBr pellet, cm^{-1}): 3437(m), 3237(w-br), 3095(w-br), 2998(w), 2930(w), 2841(w), 1629(vs), 1603(s), 1552(w), 1510(w), 1476(s), 1453(s), 1331(m), 1227(vs), 1079(m), 991(w), 823(w), 739(s), 631(w).

2.1.2. [Ni(valpn)(4-NH$_2$-py)]·0.33CH$_3$CN – ***2***

0.1 mmol of [Ni(valpn)] and 0.15 mmol of 4-aminopyridine were dissolved in 40 ml of acetonitrile-chloroform (1:1) mixture. The slow evaporation at room temperature of the resulting mixture affords dark green single crystals. Yield: 65%. Selected IR data (KBr pellet, cm^{-1}): 3362(m-w), 3228(m), 3052(w), 2921(w), 2851(w), 1662(m), 1619(vs), 1541(m-w), 1521(w), 1474(s), 1449(s), 1406(m-w), 1335(m), 1241(m), 1222(vs), 1075(m-w), 973(w), 821(w), 734(m), 626(w).

2.1.3. [Ni(valpn)(4-NH$_2$-py)] – ***3***

0.1 mmol of [Ni(valpn)] and 0.15 mmol of 4-aminopyridine were dissolved in 40 ml of acetonitrile-methanol (1:1) mixture. The slow evaporation at room temperature of the resulting mixture affords green single crystals. Yield: 70%. Selected IR data (KBr pellet, cm^{-1}): 3380(m-w), 3329(m), 3236(m), 3048(w), 2930(m-w), 2827(w), 1656(s), 1614(vs), 1540(m-w), 1529(m-w), 1477(s), 1451(s), 1409(m-w), 1340(m), 1240(s), 1221(vs), 1070(m-w), 1019(m-w), 734(s), 647(w).

2.1.4. [Zn(valpn)(4-NH$_2$-py)]·xCH$_2$Cl$_2$ – ***4***

0.1 mmol of [Zn(valpn)] and 0.12 mmol of 4-aminopyridine were dissolved in 40 ml of dichloromethane. The slow evaporation at room temperature of the resulting mixture affords yellow single crystals. Yield: 60%. Selected IR data (KBr pellet, cm^{-1}): 3352(m), 3223(m), 3053(w), 2923(w), 2849(w), 1665(m), 1620(vs), 1543(m), 1522(m-w), 1477(s), 1451(s), 1408(m), 1335(m), 1240(s), 1219(vs), 1076(m), 1021(m), 855(w), 735(s), 625(w).

2.1.5. [Ni(valdmpn)(4-NH$_2$-py)] – ***5***

0.1 mmol of [Ni(valdmpn)] and 0.15 mmol of 4-aminopyridine were dissolved in 30 ml of acetonitrile. The slow evaporation at room temperature of the resulting mixture affords dark green single crystals. . Yield: 60%. Selected IR data (KBr pellet, cm^{-1}): 3377(m), 3332(m-w), 3192(m-w), 2999(w), 2951(w), 2835(w), 1662(m), 1612(vs), 1545(m-w), 1522(m-w), 1475(s), 1450(s), 1412(m), 1334(m), 1220(vs), 1069(m), 1020(m-w), 856(w), 736(m), 641(w).

*2.1.6. [Ni(valdmpn)(4-NH_2-py)$_2$]·0.5CH_3CN – **6***

0.1 mmol of [Ni(valdmpn)] and 0.25 mmol of 4-aminopyridine were dissolved in 40 ml of acetonitrile-chloroform (1:1) mixture. The slow evaporation at room temperature of the resulting mixture affords light green single crystals. Yield: 70%. Selected IR data (KBr pellet, cm^{-1}): 3344(m), 3236(m), 3051(w), 2953(w), 2895(w), 2831(w), 1615(vs), 1563(w), 1541(w), 1516(w), 1473(s), 1450(s), 1335(m), 1218(vs), 1068(m), 1008(m-w), 855(w), 736(m), 639(w).

2.2. Physical measurements

The IR spectra (KBr pellets) were collected on a Bruker Tensor 37 spectrophotometer in the 4000-400 cm^{-1} range. The UV-Vis-NIR spectra (diffuse reflectance technique) were recorded on a JASCO V-670 spectrophotometer. The fluorescence spectra of solid samples were collected on a JASCO FP-8300 spectrofluorometer.

2.4. X-ray crystallography

Single crystal X-ray diffraction measurements were performed on a STOE IPDS II diffractometer operating with Mo-Kα (λ = 0.71073 Å) X-ray tube with graphite monochromator. The structures were solved by direct methods and refined by full-matrix least squares techniques based on F^2. The non-H atoms were refined with anisotropic displacement parameters. In the case of the compound **4,** we could not find a good model to refine the disordered dichloromethane solvent molecules and the SQUEEZE procedure was used for the final refinement. The solvent accessible volume found was 618 Å^3 with a count of 131 electrons per unit cell. Calculations were performed using SHELX-2014 crystallographic software package. A summary of the crystallographic data and the structure refinement for crystals **1** - **6** is given in Table 1. CCDC reference numbers: 1547885-1547890.

The X-ray powder diffraction measurements (XRPD) included in the Supplementary Information were carried out on a Proto AXRD Benchtop using the Cu-Kα radiation with a wavelength of 1.540593 Å in the range 5-35º 2θ.

Table 1. Crystallographic data, details of data collection and structure refinement parameters for compounds **1-6**

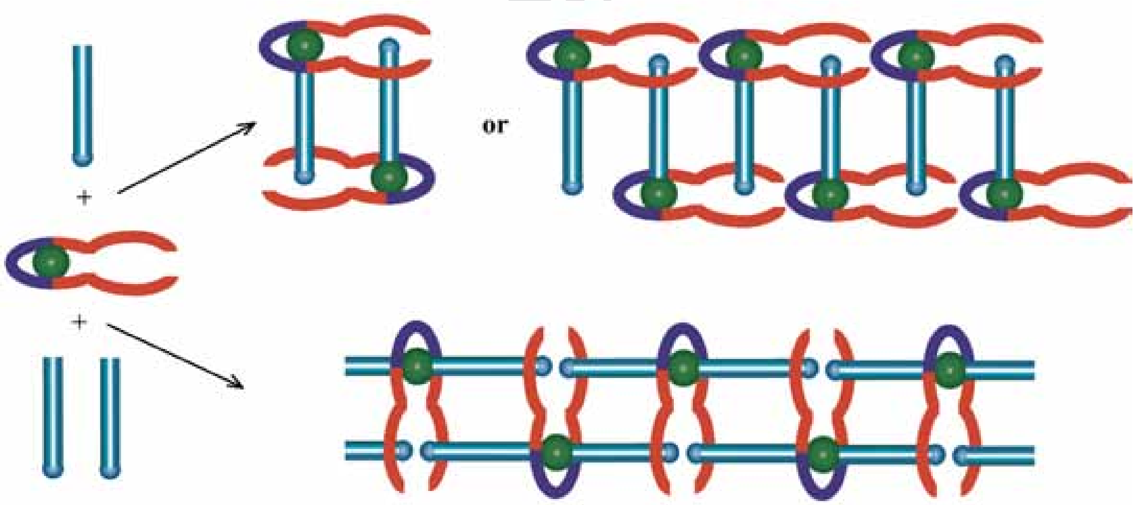
Compound	**1**	**2**	**3**
Chemical formula	$C_{24.67}H_{27}CuN_{4.33}O_4$	$C_{24.67}H_{27}NiN_{4.33}O_4$	$C_{24}H_{26}N_4NiO_4$
M (g mol^{-1})	511.71	506.88	493.20
Temperature (K)	173(2)	173(2)	173(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	*Trigonal*	*Trigonal*	*Orthorhombic*
Space group	*R-3*	*R-3*	*Pnma*
a (Å)	22.6015(7)	22.642(2)	8.3646(17)
b (Å)	22.6015(7)	22.642(2)	19.495(4)
c (Å)	23.8497(7)	23.799(3)	13.261(3)
α (°)	90	90	90
β (°)	90	90	90
γ (°)	120	120	90
V (Å^3)	10550.9(7)	10566(2)	2162.4(8)
Z	18	18	4
D_c (g cm^{-3})	1.450	1.434	1.515
μ (mm^{-1})	0.972	0.866	0.938
F(000)	4794	4776	1032
Goodness-of-fit on F^2	1.039	0.927	0.948
Final R_1, wR_2 [I>2σ(I)]	0.0262, 0.0694	0.0795, 0.1575	0.0711, 0.1628
R_1, wR_2 (all data)	0.0344, 0.0731	0.1891, 0.2006	0.1289, 0.2014
Largest difference in peak and hole (e Å^{-3})	0.307, -0.399	0.765, -0.535	1.267, -0.539

Compound	**4**	**5**	**6**
Chemical formula	$C_{24}H_{26}N_4O_4Zn$	$C_{26}H_{30}N_4NiO_4$	$C_{32}H_{37.50}N_{6.50}NiO_4$
M (g mol^{-1})	499.86	521.25	635.89
Temperature (K)	173(2)	293(2)	173(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	*Trigonal*	*Monoclinic*	*Monoclinic*
Space group	*R-3*	$P2_1/c$	$P2_1/c$
a (Å)	22.7562(16)	11.0981(12)	14.9173(7)
b (Å)	22.7562(16)	17.7273(13)	16.0180(6)
c (Å)	23.8969(17)	13.3789(17)	26.7592(14)
α (°)	90	90	90
β (°)	90	107.636(9)	90.288(4)
γ (°)	120	90	90
V (Å^3)	10717.0(17)	2508.4(5)	6393.9(5)
Z	18	4	8
D_c (g cm^{-3})	1.394	1.380	1.321
μ (mm^{-1})	1.068	0.813	2680
F(000)	4680	1096	2680
Goodness-of-fit on F^2	0.660	0.778	1.066
Final R_1, wR_2 [I>2σ(I)]	0.0439, 0.1033	0.0651, 0.1647	0.0852, 0.2101
R_1, wR_2 (all data)	0.1158, 0.1366	0.1015, 0.1723	0.1447, 0.2336
Largest difference in peak and hole (e Å^{-3})	0.342, -0.506	0.928, -0.342	0.741, -0.490

3. Results and discussion

3.1. Description of crystal structures

4-aminopyridine molecule, by its functional groups, has a dual behaviour: coordinating ligand and hydrogen bonds donor and/or acceptor. For the compounds reported herein, both features were exploited to build supramolecular architectures. The pyridyl nitrogen atom can coordinate to a metal ion, while the amino group can act as a hydrogen bonds donor. In [M^{II}(valpn)] or [M^{II}(valdmpn)] mononuclear complexes (M^{II} = Ni^{II}, Cu^{II} or Zn^{II}), the axial positions of the metal ion are available for coordination and the larger $O_2O'_2$ free compartment is a potential receptor for hydrogen bond donors. By combining these two tectons, a number of supramolecular architectures can be imagined, depending on the molar ratio between the mononuclear complexes and 4-aminopyridine (Scheme 2). For a 1:1 molar ratio supramolecular rectangles or supramolecular zigzag chains can be obtained, while for a 1:2 stoichiometry one possible arrangement is represented by a supramolecular ladder.



Scheme 2 Formation of supramolecular rectangles, zigzag chains or ladders by reacting [M^{II}(valXn)] mononuclear complexes with 4-aminopyridine in different molar ratios

The reactions of [Cu(valpn)] or [Ni(valpn)] with 4-aminopyridine (4-NH_2-py) in the same complex-to-ligand molar ratio (1:1.5), but different solvents (acetonitrile for the copper derivative and an acetonitrile-chloroform mixture for the nickel derivative) afforded the isostructural mononuclear compounds [Cu(valpn)(4-NH_2-py)]·0.33CH_3CN – **1** and [Ni(valpn)(4-NH_2-py)]·0.33CH_3CN – **2**, respectively.

Further we will describe the crystal structure of compound **1** mentioning the differences in **2** when present. The metal ion displays a square-pyramidal geometry (Figure 1a). The basal plane is formed by the two imino nitrogen atoms and the two phenoxo oxygen atoms of the Schiff base ligand. In the apical position is coordinated the pyridyl nitrogen atom of 4-aminopyridine. The basal bond lengths are Cu1-N1 = 2.0216(13), Cu1-N2 = 2.0042(14), Cu1-O2 = 1.9575(11), and Cu1-O3 = 1.9660(11) Å, shorter than the apical one, Cu1-N3 = 2.2101(13) Å. By contrast, the apical bond length in compound **2** is shorter, Ni1-N3 = 2.004(8) Å, and very similar to the basal ones, Ni1-N1 = 2.034(7), Ni1-N2 = 2.047(8), Ni1-O2 = 1.994(6), and Ni1-O3 = 2.002(6) Å.

The neutral mononuclear complexes generate supramolecular dimers through hydrogen bond interactions established between the amino groups of the 4-aminopyridine and the phenoxo and methoxy oxygen atoms of the free compartment of the Schiff base ligands (Figure 1b). The hydrogen interactions are donating bifurcated and the N4’···O1-4 distances are 3.024(3), 2.992(2), 2.949(3), and 2.982(3) Å respectively (’ = 2-x, 1-y, -z).

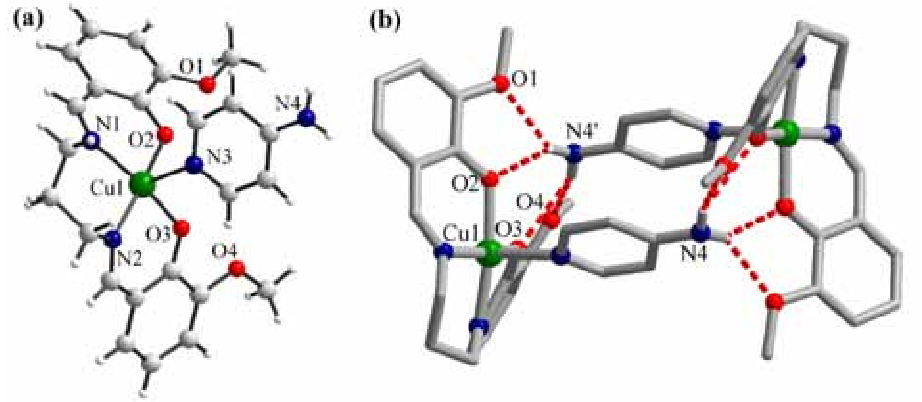


Figure 1. Perspective views of the mononuclear complexes [Cu(valpn)(4-NH$_2$-py)] (a) and of the supramolecular dimers (b) in the crystal structure of **1** (symmetry code: ’ = 2-x, 1-y, -z)

In the lattice of crystal **1,** six supramolecular dimers delimit cages hosting disordered acetonitrile solvent molecules. Each cage contains two solvent molecules disordered on three crystallographic positions (Figure 2).

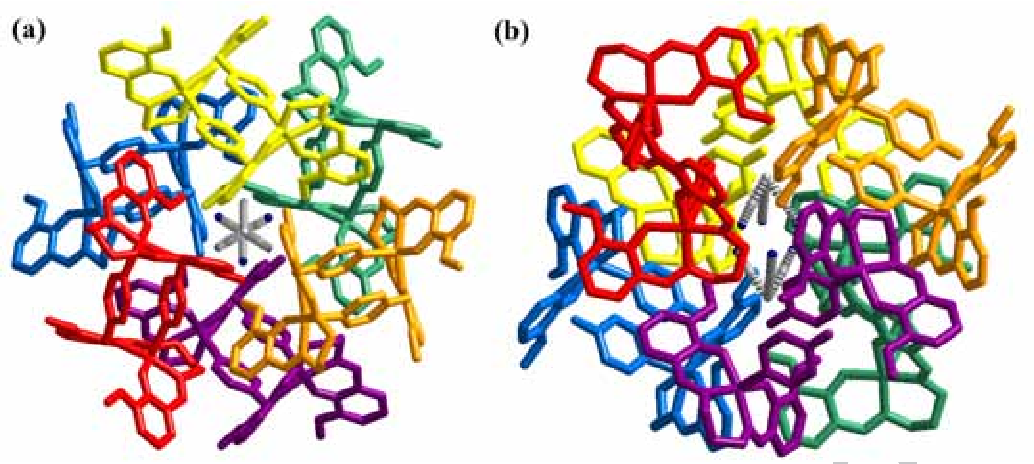


Figure 2. (a) Top (along the crystallographic *c* axis) and (b) side views of the cages formed by six supramolecular dimers in crystal **1**

By using [Ni(valpn)] and 4-aminopyridine in the same molar ratio (1:1.5), but with a different solvent combination, i.e. acetonitrile-methanol (1:1), another type of crystals was obtained, [Ni(valpn)(4-NH_2-py)] – **3**. The structural investigation of the compound **3** by X-ray diffraction on single crystal reveals also the presence of mononuclear complexes [Ni(valpn)(4-NH_2-py)], but a completely different lattice organization. The nickel ion is placed in a square-pyramidal environment also with the apical bond length very close to the basal ones, Ni1-N2 = 2.027(6), Ni1-N1 = 2.055(5), and Ni1-O2 = 2.004(4) Å (Figure 3a). Each mononuclear complex is involved in hydrogen bonding with other two complexes through the free compartment O1O2O2'O1' of the Schiff base (acceptor) and the amino group of the 4-aminopyridine (donor), generating in this way a supramolecular zigzag (castellated) chain (Figure 3b). The N3"···O1 and N3"···O2 distances are 3.090(5) and 2.869(7) Å respectively (" = 0.5+x, 0.5-y, -0.5-z).

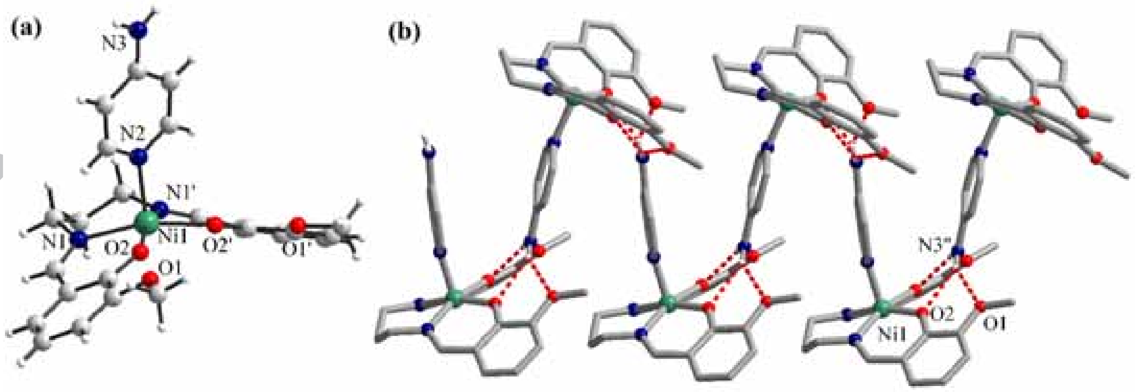


Figure 3. Perspective views of the mononuclear complexes [Ni(valpn)(4-NH_2-py)] (a) and of a supramolecular chain (b) in the crystal structure of **3** (symmetry codes: ' = x, 0.5-y, z; " = 0.5+x, 0.5-y, -0.5-z)

The supramolecular chains are parallel, running along the crystallographic *a* axis (Figure 4). In the *ac* plane, the CH moieties of the iminic groups establish weak CH···π interactions with the neighbouring chains. The non-covalent interactions between chains extend along the crystallographic *b* axis through π–π contacts (3.46-3.65 Å) involving the phenyl rings of the Schiff base ligands.

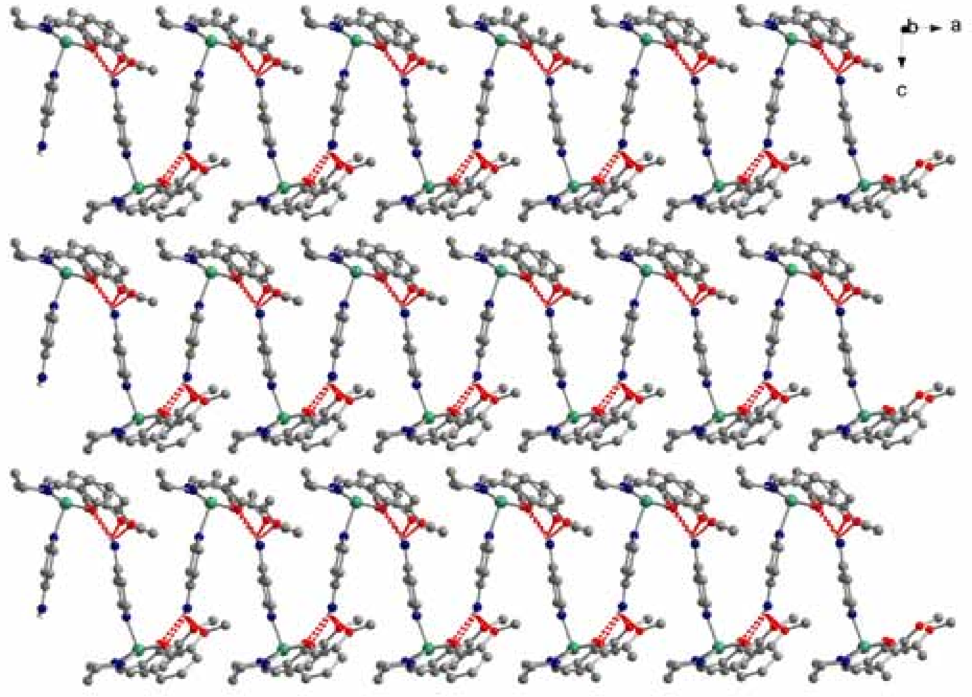


Figure 4. Packing diagram in crystal **3**, view along the crystallographic *b* axis

The reaction of [Zn(valpn)] with 4-aminopyridine in 1:1.2 molar ratio, in dichloromethane, gave the compound [Zn(valpn)(4-NH$_2$-py)]·xCH$_2$Cl$_2$ – **4**, isomorphous with the compounds **1** and **2**. The stereochemistry of the zinc ion is similar to that of the nickel ion in compound **2** with the apical bond length very close to the basal ones: Zn1-N3 = 2.038(4) , Zn1-N1 = 2.127(3), Zn1-N2 = 2.122(5), Zn1-O2 = 2.007(3) and Zn1-O3 = 2.019(3) Å (we used the same labelling scheme for the organic ligands in the compounds **1**, **2**, and **4**). Compound **4** crystallizes with dichloromethane solvent molecules in the lattice (replacing the acetonitrile from the compounds **1** and **2**), but we could not find a good model to refine the disordered dichloromethane solvent molecules. SQUEEZE procedure was used for the final refinement of the crystal structure. The count of 131 electrons per unit cell found by SQUEEZE procedure is consistent with about 0.17 molecules of dichloromethane per mononuclear complex of Zn(II).

Another pentacoordinated Ni(II) mononuclear complex, [Ni(valdmpn)(4-NH$_2$-py)] – **5**, was also obtained by reacting [Ni(valdmpn)] with 4-aminopyridine in molar ratios 1:1.5 in acetonitrile (Figure 5a). The bond lengths for the coordination surrounding of the Ni(II) ions are Ni1-N1 = 2.064(4), Ni-N2 = 2.050(4), Ni-N3 = 2.036(4), Ni1-O2 = 2.011(3) and Ni1-O3 = 1.997(3) Å. Supramolecular rectangles are formed by donating bifurcated hydrogen interactions between the amino groups and the phenoxo and methoxy oxygen atoms of the bicompartmental ligands (Figure 5b). The N4'···O1-4 distances are 2.999(6), 2.972(7), 2.952(7), and 2.995(7) Å respectively (' = -x, 1-y, 1-z). In compound **5**, the supramolecular dimers are also reinforced by π–π interactions established between the two 4-aminopyridine ligands (3.36-3.42 Å). In the compounds **1**-**4** this type of interactions were not evidenced between the 4-aminopyridine ligands.

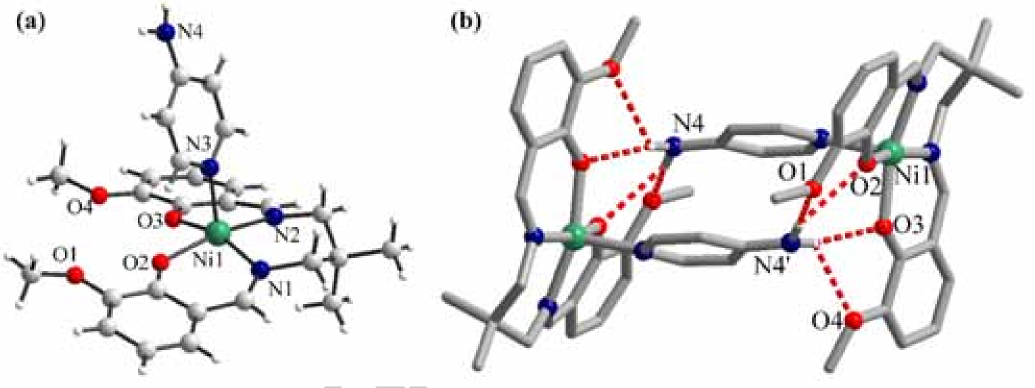


Figure 5. Perspective views of the mononuclear complexes [Ni(valdmpn)(4-NH$_2$-py)] (a) and of the supramolecular dimers (b) in the crystal structure of **5** (symmetry code: ' = -x, 1-y, 1-z)

By increasing the molar ratio in reaction between the 4-aminopyridine and [Ni(valdmpn)] to 2.5:1, we obtained [Ni(valdmpn)(4-NH$_2$-py)$_2$]·0.5CH$_3$CN (**6**) in which the two 4-aminopyridine ligands occupy the axial positions of the metal ions. Compound **6** crystallizes in the monoclinic *P2$_1$/c* space group with two crystallographically independent mononuclear complexes in the asymmetric unit. In both mononuclear complexes, the nickel ions exhibit an elongated octahedral stereochemistry with the donor atoms of the Schiff base ligand placed in the equatorial plane and the pyridyl nitrogen atoms of the 4-aminopyridine molecules coordinated in the axial positions (Figure 6). The bond lengths defining the equatorial planes are: Ni1-N1 = 2.070(7), Ni1-N2 = 2.089(6), Ni1-O2 = 2.051(4), Ni1-O3 = 2.046(5), Ni2-N7 = 2.107(6), Ni2-N8 = 2.060(7), Ni2-O6 = 2.030(5), and Ni2-O7 = 2.049(5) Å. The Ni-N bond lengths for the axial positions are: Ni1-N3 = 2.147(6), Ni1-N5 = 2.186(6), Ni2-N9 = 2.171(6), and Ni2-N11 = 2.133(6) Å respectively.

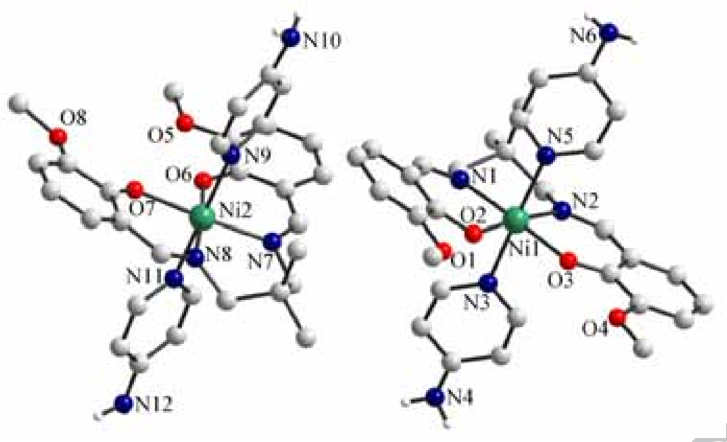


Figure 6. Perspective view of the two crystallographically independent mononuclear complexes [Ni(valdmpn)(4-NH_2-py)$_2$] in the crystal structure of compound **6**

The amino groups of the 4-aminopyridine ligands from the two crystallographically independent mononuclear complexes establish hydrogen bonds with $O_2O'_2$ free compartments of adjacent complexes. These hydrogen bonds generate supramolecular ladder-like chains (Figure 8), each $O_2O'_2$ free compartment of the [Ni(valdmpn)] moieties interacting with two 4-aminopyridine ligands from two different complexes. The rungs are formed by the [Ni(valdmpn)] fragments and the side rails by the 4-aminopyridine ligands. The chains are parallel, running along the crystallographic *b* axis. The N···O distances for the N-H···O hydrogen interactions range between 2.96 and 3.40 Å. The 4-aminopyridine molecules within the ladders are also involved in π–π interactions (3.35-3.53 Å).

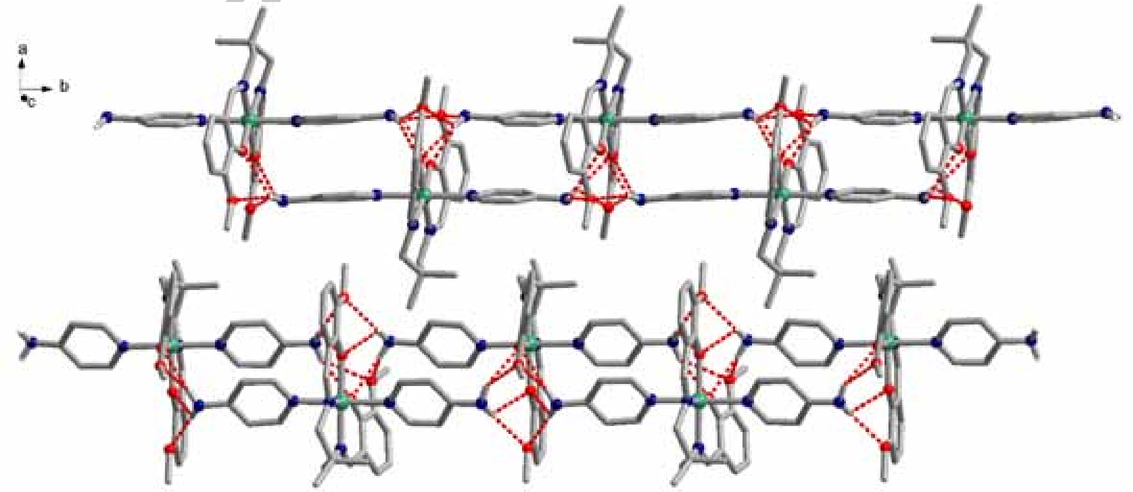


Figure 7. View of the supramolecular ladders generated by hydrogen bonding between [Ni(valdmpn)(4-NH_2-py)$_2$] mononuclear complexes in the crystal structure of compound **6**

3.2. Spectroscopic studies

The electronic spectra of compounds **1**-**6** were acquired over a wavelength range spanning UV to NIR (from 200 to 1800 nm). As the Ni(II) complexes form the majority of the compounds presented herein, let us first analyse their spectra. Considering the general case of octahedral nickel(II) species, three spin allowed transition originating from the $^3A_{2g}$ ground state are expected: to $^3T_{2g}$(F) (7000-13000 cm^{-1}), to $^3T_{1g}$(F) (11000-20000 cm^{-1}), and to $^3T_{1g}$(P) (19000-27000 cm^{-1}). In addition, a spin forbidden transition can usually be seized near the second spin allowed one and corresponds to the transition from $^3A_{2g}$ to ^1E_g(D) [16]. Only compound **6**, [Ni(valdmpn)(4-NH$_2$-py)$_2$]·0.5CH$_3$CN, contains a hexacoordinated Ni(II) ion and its geometry is a tetragonally distorted octahedron (D$_{4h}$) as the basal Ni-O and Ni-N bonds are virtually equal. It is obvious then that the spectrum appearance of compound **6** should not strongly differ from the one expected for O$_h$ symmetry. Thus, two bands of low intensity can be distinguished at higher wavelengths: one with a maximum at around 920 nm (10870 cm^{-1}) and a shoulder at around 790 nm (12658 cm^{-1}) and the other one with a maximum at around 610 nm (16393 cm^{-1}) (Figure 8). Taking into account that the ground term $^3A_{2g}$ becomes $^3B_{1g}$ and, at the same time, the degeneracy of the excited triplet states is lifted when O$_h$ changes to D$_{4h}$ symmetry, the corresponding transitions are presumptively from $^3B_{1g}$ to ^3E_g and $^3B_{2g}$ [both derived from $^3T_{2g}$(F)], to $^1A_{1g}$ and/or $^1B_{2g}$(^1E_g), and to $^3A_{2g}$ and/or ^3E_g [$^3T_{1g}$(F)], respectively [17]. As for the higher energy transitions [i.e. from $^3B_{1g}$ to $^3A_{2g}$ and ^3E_g terms resulting from $^3T_{1g}$(P)], they are most probably embedded into the intraligand and/or CT intense band with a maximum at around 380 nm (26316 cm^{-1}). Actually, this latter band together with the split one having a similar intensity and ranging between 200 and 300 nm can be found in the spectra of all the nickel(II) and copper(II) derivatives gathered herein and, therefore, are more likely to originate from intraligand transitions within both ligands.

The other Ni(II) compounds are very similar: crystals **2** and **3** are pseudopolymorphs, whereas the complex unit in **5** differs from the former two only by the diamine residue included into the Schiff base ligand. The Ni(II) ion is pentacoordinated in all these three complexes and its geometry is square pyramidal. Actually, this polyhedron can be obtained by the removal of one 4-aminopyridine from the octahedral array specific to compound **6**. As the nickel - donor atom bonds are almost equal in the basal plane, the symmetry can be assumed as C$_{4v}$ rather than C$_{2v}$. Consequently, the corresponding spectral terms derive from those specific to the tetragonally distorted octahedron (D$_{4h}$) by slightly lowering this symmetry [18]. The spectra of compounds **2**, **3**, and **5** display the same contour with four evident bands arising from d-d transitions. Thus, the large band spreading towards the NIR end corresponds to the transition from $^3B_1$ to ^3E [$^3T_{2g}(F)$] (1690, 1650, and 1740 nm for compounds **2**, **3**, and **5**, respectively). The two closely disposed maxima at around 800 and 870 nm are due to the transitions from $^3B_1$ to $^3B_2$ and to $^3A_2$, but their order cannot be stated. The band at 650 (for complexes **2** and **3**) or at 635 nm (for complex **5**) is assigned to the transition from $^3B_1$ to ^3E [$^3T_{1g}(F)$]. The intraligand bands at around 380 nm should mask the higher energy d-d transitions.

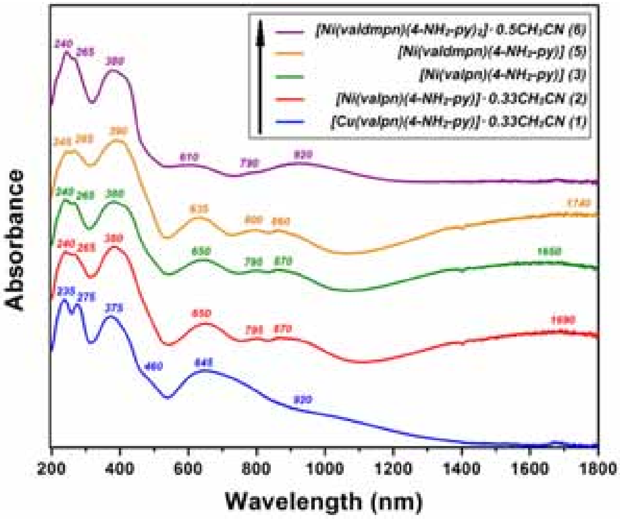


Figure 8. Electronic spectra of nickel(II) and copper(II) complexes

As for the copper(II) complex (**1**), the d-d transitions build up the absorption envelope between 540 and 1400 nm with a maximum at around 645 nm and a shoulder at around 920 nm (this asymmetric shape of the d-d transitions band with a shoulder in the lower energy region was frequently stated as characteristic for the square pyramidal stereochemistry of Cu^{2+} ion). The intense bands at 235, 275, and 375 nm are probably due to intraligand transitions. However, the shoulder at 460 nm is specific to this complex and can originate from a LMCT transition.

The room temperature photoluminescence of compound [Zn(valpn)(4-NH_2-py)]·xCH_2Cl_2 (**4**) was investigated using different wavelengths for excitation in the 350-430 nm range. The resulting emission spectrum displays an asymmetric band (tailed to the lower energy side) with a maximum at 470 nm. The highest intensity of this band is obtained when λ_{ex} = 420 nm. The corresponding excitation spectrum (λ_{em} = 470 nm) reveals a complex band within the 240-460 nm domain (Figure 9).

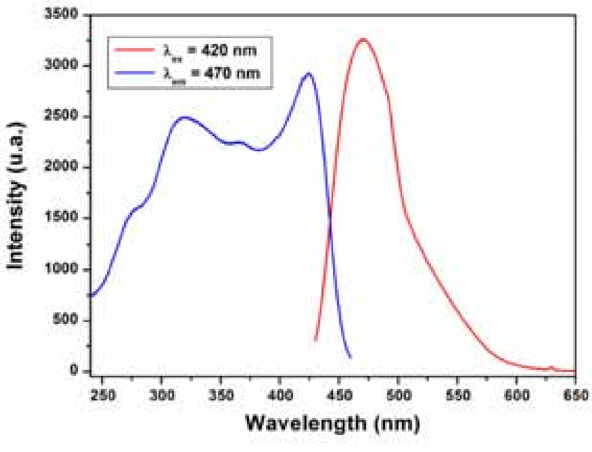


Figure 9. Emission (right) and excitation (left) spectra for the compound [Zn(valpn)(4-NH_2-py)]·xCH_2Cl_2 – **4**

The examples presented herein show that various supramolecular objects or architectures can be obtained by combining bimodal tectons which are able to establish both coordinative bonds and non-covalent interactions. The mononuclear complexes belonging to the [M(valXn)] family have the axial positions of the metal ion available for coordination and they can effectively act as receptors towards a large variety of hydrogen bond donors. Reacting [M(valXn)] complexes with 4-aminopyridine, we obtained supramolecular rectangles, zigzag chains or ladders depending on stoichiometry and reaction conditions. In the [M^{II}(valXpn)(4-NH_2-py)] complexes, the metal ions exhibit a square pyramidal geometry, coordination number five being still rare for the nickel (II) ion.

Acknowledgements. Financial support from University of Bucharest (project 72/2013) is highly acknowledged.

[1] (a) J.-M. Lehn, Supramolecular Chemistry - Concepts and Perspectives, VCH, Weinheim (1995); (b) J.-M. Lehn, Chem.–Eur. J. 6 (2000) 2097; (c) M. Fujita, Chem. Soc. Rev. 27 (1998) 417; (d) B. Champin, P. Mobian, J.-P. Sauvage, Chem. Soc. Rev. 36 (2007) 358.

[2] (a) M. Ruben, J. Rojo, F.J. Romero-Salguero, L.H. Uppadine, J.-M. Lehn, Angew. Chem., Int. Ed. 43 (2004) 3644; (b) K. Petukhov, M.S. Alam, H. Rupp, S. Strömsdörfer, P. Müller, A. Scheurer, R.W. Saalfrank, J. Kortus, A. Postnikov, M. Ruben, L.K. Thompson, J.-M. Lehn, Coord. Chem. Rev. 253 (2009) 2398; (c) L.N. Dave, T.S.M. Abedin, L.K. Thompson, Dalton Trans. (2008) 1661.

[3] (a) J.-M. Lehn, Angew. Chem., Int. Ed. 29 (1990) 1304; (b) C. Piguet, G. Bernardinelli, G. Hopfgartner, Chem. Rev. 97 (1997) 2005; (c) M. Albrecht, Chem. Rev. 101 (2001) 3457.

[4] S. Roche, C. Haslam, H. Adams, S.L. Heath, J.A. Thomas, Chem. Commun. (1998) 1681.

[5] M. Fujita, M. Tominaga, A. Hori, B. Therrien, Acc. Chem. Res. 38 (2005) 371.

[6] (a) L.H. Uppadine, P. Gisselbrecht, J.-M. Lehn, Chem. Commun. (2004) 718; (b) D.M. Bassani, J.-M. Lehn, S. Serroni, F. Puntoriero, S. Campagna, Chem. Eur. J. 9 (2003) 5936; (c) M. Boiocchi, L. Fabbrizzi, Chem. Soc. Rev. 43 (2014) 1835.

[7] (a) A.-S. Chauvin, S. Comby, M. Baud, C. De Piano, C. Duhot, J.-C.G. Bünzli, Inorg. Chem. 48 (2009) 10687; (b) N. André, T.B. Jensen, R. Scopelliti, D. Imbert, M. Elhabiri, G. Hopfgartner, C. Piguet, J.-C.G. Bünzli, Inorg. Chem. 43 (2004) 515; (c) P. Cucos, F. Tuna, L. Sorace, I. Matei, C. Maxim, S. Shova, R. Gheorghe, A. Caneschi, M. Hillebrand, M. Andruh, Inorg. Chem. 53 (2014) 7738.

[8] (a) L.N. Dawe, L.K. Thompson, Angew. Chem., Int. Ed. 46 (2007) 7440; (b) M. U. Anwar, L.K. Thompson, L.N. Dawe, F. Habib, M. Murugesu, Chem. Commun. 48 (2012) 4576; (c) A.M. Madalan, X.-Y. Cao, G. Rogez, J.-M. Lehn, Inorg. Chem. 53 (2014) 4275; (d) P. Cucos, M. Pascu, R. Sessoli, N. Avarvari, F. Pointillart, M. Andruh, Inorg. Chem. 45 (2006) 7035; (e) A.K. Mondal, H.S. Jena, A. Malviya, S. Konar, Inorg. Chem. 55 (2016) 5237.

[9] (a) D. Visinescu, M. Andruh, A. Müller, M. Schmidtmann, Y. Journaux, Inorg. Chem. Commun. 5 (2002) 42; (b) D. Visinescu, G.I. Pascu, M. Andruh, J. Magull, H.W. Roesky, Inorg. Chim. Acta 340 (2002) 201; (c) D. Visinescu, A.M. Madalan, V. Kravtsov, Yu. A. Simonov, M. Schmidtmann, A. Müller, M. Andruh, Polyhedron 22 (2003) 1385; (d) G. S. Papaefstathiou, Z. Zhong, L. Geng, L. R. MacGillivray, J. Am.

Chem. Soc. 126 (2004) 9158; (e) G. Marinescu, G. Marin, A.M. Madalan, A. Vezeanu, C. Tiseanu, M. Andruh, Cryst. Growth Des. 10 (2010) 2096.

[10] (a) J.-P. Costes, F. Dahan, A. Dupuis, J.-P. Laurent, Inorg. Chem., 35 (1996) 2400; (b) M. Andruh, Chem. Commun., (2007) 2565; (c) M. Andruh, Chem. Commun., 47 (2011) 3025.

[11] (a) D.G. Branzea, A. Guerri, O. Fabelo, C. Ruiz-Pérez, L.-M. Chamoreau, C. Sangregorio, A. Caneschi, M. Andruh, Cryst. Growth Des. 8 (2008) 941; (b) D. G. Branzea, L. Sorace, C. Maxim, M. Andruh, A. Caneschi, Inorg. Chem. 47 (2008) 6590; (c) M. Nayak, R. Koner, H.-H. Lin, U. Flörke, H.-H. Wei, S. Mohanta, Inorg. Chem. 45 (2006) 10764.

[12] (a) S. Nastase, F. Tuna, C. Maxim, C.A. Muryn, N. Avarvari, R.E.P. Winpenny, M. Andruh, Cryst. Growth Des. 7 (2007) 1825; (b) M.Á. Vázquez-Fernández, M.I. Fernández-García, A.M. González-Noya, M. Maneiro, M.R. Bermejo, M.J. Rodríguez-Doutón, Polyhedron 31(2012) 379; (c) C.D. Ene, S. Nastase, C. Maxim, A.M. Madalan, F. Tuna, M. Andruh, Inorg. Chim. Acta 363 (2010) 4247.

[13] (a) A.M. Madalan, N. Avarvari, M. Andruh, New J. Chem. 30 (2006) 521; (b) S. Harza, R. Koner, M. Nayak, H.A. Sparkes, J.A.K. Howard, S. Mohanta, Cryst. Growth Des. 9 (2009) 3603.

[14] A. Cucos, A. Ursu, A.M. Madalan, C. Duhayon, J.-P. Sutter, M. Andruh, CrystEngComm 13 (2011) 3756.

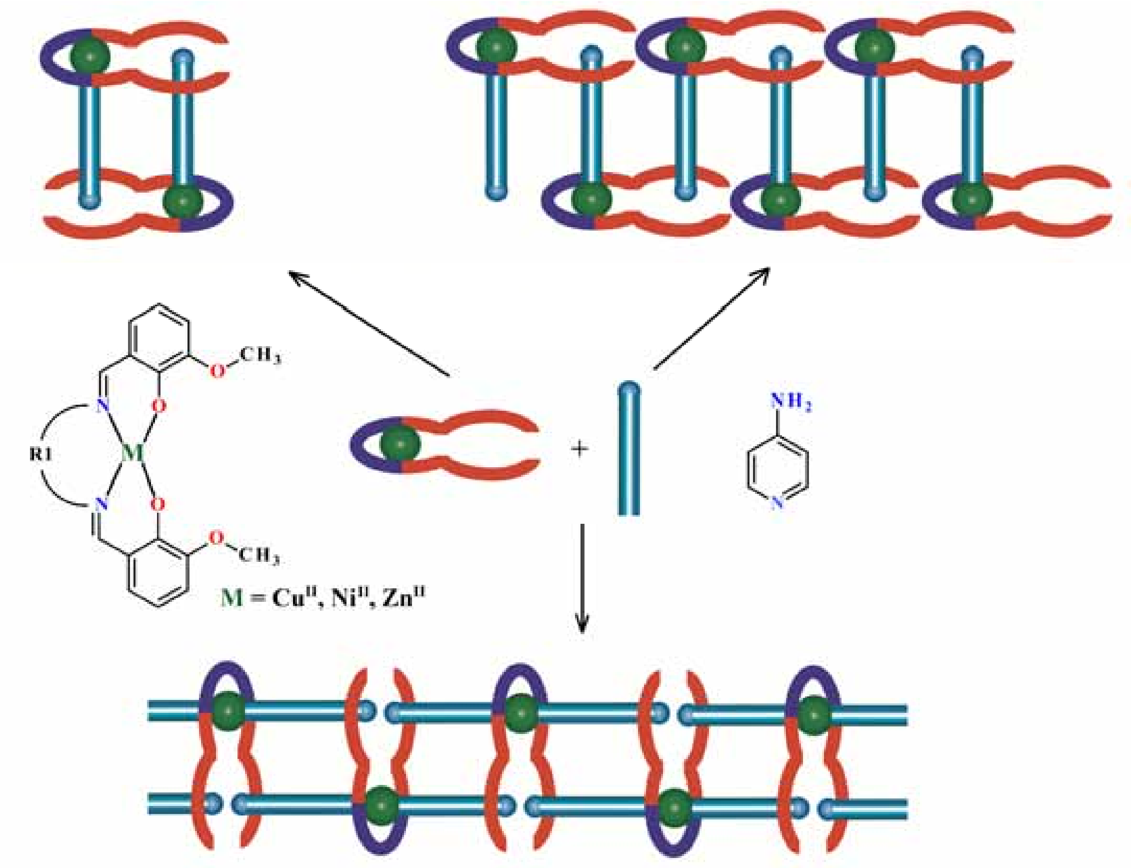
[15] (a) M. Nayak, S. Sarkar, P. Lemoine, S. Sasmal, R. Koner, H.A. Sparkes, J.A.K. Howard, S. Mohanta, Eur. J. Inorg. Chem. (2010) 744; (b) S. Sarkar, M. Fleck, S. Mohanta, J. Mol. Struct. 1021 (2012) 174.

[16] E.I. Solomon, A.B.P. Lever, Inorganic Electronic Structure and Spectroscopy, John Wiley & Sons, Inc., New York (1999).

[17] C.E. Taylor, A.E.Underhill, J. Chem. Soc. A (1969) 368.

[18] M. Gerloch, J. Kohl, J. Lewis, W. Urland, J. Chem. Soc. A (1970) 3269.

- Six Ni(II), Cu(II) and Zn(II) mononuclear complexes with bicompartmental Schiff base and 4-aminopydine ligands were synthesised;
- The crystal structure of the Ni(II), Cu(II) and Zn(II) mononuclear complexes were determined;
- Hydrogen bond interactions generate supramolecular rectangles, zigzag chains and ladders;
- The spectroscopic properties of the compounds were investigated.



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