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Evolution from discrete mononuclear complexes to trinuclear linear cluster and 2D coordination polymers of Mn(II) with dihydrazone Schiff bases: Preparation, structure and thermal behavior

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ABSTRACT

Four Mn(II) coordination compounds based on the 2,6-diacetylpyridine bis(isonicotinoylhydrazone) (H₂L¹) and 2,6-diacetylpyridine bis(nicotinoylhydrazone) (H₂L²), were prepared using different synthetic conditions and starting manganese salts: discrete mononuclear [Mn(H₂L¹)₂(H₂O)₂](NO₃)₂ (1) and trinuclear [Mn₃(H₂L¹)₂(NCS)₂Cl₄(H₂O)₂] (2) complexes and two 2D coordination polymers {[Mn₃(L¹)₃(H₂O)₂] · 1.5C₂H₅OH₃_n (3) and {[MnL²]·dmf₃_n (4), where dmf = N,N-dimethylformamide. Single-crystal X-ray diffraction study shows that H₂L¹ and H₂L², which differ only by para- or meta- position of radicals with respect to the nitrogen atoms in the terminal pyridyl fragments, demonstrate chelate or chelate-bridging coordination mode with N₃O₂, or N₄O₂ and N₅O₂ donor atoms, respectively. The planar-chelate coordination of these ligands provides the pentagonal-bipyramidal surrounding of Mn(II) and the terminal pyridyl moieties promote bridging function and structure expansion in 2–4 as well as octahedral Cl₂N₄ coordination geometry for one of Mn(II) atoms in the trinuclear complex **2**. All compounds have been investigated in the solid state by IR spectroscopy and thermal analysis in order to understand the influence of the inorganic anion presence/absence on the stability of synthesized compounds.

1. Introduction

Hydrazones ($R_1R_2C = NNR_2R_4$) represent a class of organic ligands capable to coordinate with diverse metal centers generating varied molecular architectures. The possibility of keto-enol tautomerization [1–4], the conformational flexibility, pharmacological activity [5,6] due to the presence of azomethine moiety and their use in medicine make them being of great interest. Thus, the development of Schiff base ligands with the hydrazone fragment allowed the synthesis of new metal complexes, which have been employed in numerous fields of scientific research, due to their chemical, physical, biological and structural properties, as well as their applications [7–10].

The addition of functional groups with potentially donor atoms to hydrazones leads to the new Schiff base ligands capable of forming stable chelates [11]. The 2,6-diacetylpyridine (dap) is a suitable candidate for preparation of dihydrazone Schiff bases with multiple coordination sites, giving rise to metal complex compounds with exclusive geometries. The opportunities for generating new molecular architectures can be possible by condensation of dap with isonicotinic/nicotinic acid hydrazides (Scheme 1) [12,13] and by suitable substitution of their pyridine rings in order to provide additional donor atoms.

Coordination compounds with the 2,6-diacetylpyridine bis(isonicotinoylhydrazone) (H_2L^1) ligand are obtained both from direct and template synthesis. Analysis of the Cambridge Structural Database (CSD) [11] revealed twenty coordination compounds of transition metals where this ligand predominately acts as a pentadentate N_3O_2 ligand and surrounding metal ion in the equatorial plane. The examination of published examples showed that the L^1 moiety forms homoand heterometallic complexes coordinating in the neutral, biprotonated and bideprotonated fashions on nitrogen atoms of the terminal pyridine

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Scheme 1. Graphic representation of the H₂L¹ and H₂L² ligands synthesis.

fragments (Fig. S1) in consequence providing eleven mononuclear and two binuclear compounds, as well as one 2D coordination polymer. It is noteworthy that only five coordination compounds [8,14] were prepared through one-pot template synthesis, while the rest of the compounds - by direct reaction between H_2L^1 and transition metal salts.

Our previous study of transition metals coordination compounds with 2,6-diacetylpyridine bis(nicotinoylhydrazone) (H_2L^2) ligand [14–18] also showed that this ligand can coordinate in neutral, biprotonated, mono- and bideprotonated modes (Fig. S2), revealing six mononuclear, two binuclear, and one tetranuclear coordination compounds, as well as one 1D and five – 2D coordination polymers. Six compounds [15,18] were obtained by exploring direct synthetic method, while the others were obtained by template synthesis.

The interest in Mn(II)-based coordination compounds arise not only from its biomimetic roles [16,19] or as a cofactor for some enzymes (decarboxylase, hydrolase and kinase) [20–23], but also because they are good precursors for magnetic materials (due to a large number of unpaired electrons of manganese complexes) [24–28], as well as for its intricate structures. This transition metal ion easily coordinates with nitrogen, oxygen and chloride atoms that provide versatile coordination abilities with the preparation of exciting mono- and polynuclear compounds [11] with effective biomedical applications [29].

The crystals of discrete coordination compounds $[Mn(H_2L^1)_2(H_2O)_2]$ (NO₃)₂ (1) and $[Mn_3(H_2L^1)_2(NCS)_2Cl_4(H_2O)_2]$ (2) suitable for singlecrystal diffraction analysis were obtained by template assembly of components, while 2D coordination polymers { $[Mn_3(L^1)_3(H_2O)_2]$. 1.5C₂H₅OH}_n (3) and { $[MnL^2]$ ·dmf}_n (4) by the direct reaction between pre-synthesized H₂L¹ and H₂L² ligands and manganese sulfate salt. Compounds were characterized by single crystal X-ray diffraction method, IR spectroscopy and thermal analysis.

2. Experimental

2.1. Materials and methods

All reagents (dap, inaH, naH, all Mn(II) salts, KSCN) and solvents (ethanol, dmf) were obtained from commercial sources and were used without further purification. Elemental analysis was performed on an Elementar Analysen systeme GmbH Vario El III elemental analyzer. The IR spectra were obtained in Vaseline oil (400–4000 cm⁻¹) and ATR (650–4000 cm⁻¹) on a FT IR Spectrum-100 Perkin Elmer spectrometer.

Thermal analysis was performed on Derivatograph Q-1000 system in nitrogen atmosphere (100 cm³/min) at a heating rate of 10 °C/min in the temperature range of 20 – 1000 °C. Thermogravimetric (TG), derivative weight loss (DTG) and differential thermal (DTA) curves were simultaneously registered.

2.2. Synthesis

2.2.1. Synthesis of H_2L^1 and H_2L^2 .

The ligands 2,6-diacetylpyridine bis(isonicotinoylhydrazone) (H_2L^1) and 2,6-diacetylpyridine bis(nicotinoylhydrazone) (H_2L^2) were prepared by the condensation of the respective carbonyl compound and amines using similar methods as described earlier [12,13].

2.2.2. Synthesis of $[Mn(H_2L^1)_2(H_2O)_2](NO_3)_2$ (1)

2,6-diacetylpyridine (0.16 g, 1 mmol) in ethanol (10 mL), isonicotinic acid hydrazide (0.14 g, 1 mmol) in ethanol (10 mL) and KSCN (0.1 g, 1 mmol) in ethanol (10 mL) were added to $Mn(NO_3)_2\cdot 4H_2O$ (0.25 g, 1 mmol) in ethanol (10 mL). The yellow solution was refluxed on a water bath for 3 h until the solution was coloured in orange. After 24 h yellow crystals were obtained (0.209 g). The product was filtered off and washed with ethanol and air dried. Yield: 34%. Anal. Calcd. for 1, $C_{21}H_{23}MnN_9O_{10}$: C, 40.92; H, 3.76; N, 20.45. Found: C, 40.85; H, 3.80; N, 20.35. IR data (cm⁻¹): 3500-3600br, 1656m, 1645m, 1604m, 1556m, 1492w, 1323vs, 1299s, 1230m, 1137m, 1074m, 1041w, 1014m, 1006m, 844m, 826m, 752m, 666w, 552w, 524w, 473w.

2.2.3. Synthesis of $[Mn_3(H_2L^1)_2(NCS)_2Cl_4(H_2O)_2]$ (2)

The mixture of MnCl₂·4H₂O (0.011 g, 0.05 mmol), KSCN (0.004 g, 0.025 mmol), isonicotinic acid hydrazide (0.007 g, 0.05 mmol) and 2,6diacetylpyridine (0.009 g, 0.05 mmol) was dissolved in ethanol (8 mL) was sealed in a Teflon-lined autoclave and heated at 80 °C for 72 h under autogenous pressure. Cooling to room temperature at the rate of 0.6 °C/ min afforded the product as yellow acrylic crystals were collected by filtration (0.001 g) and washed with ethanol and ethylic ether. Yield: ~3%. Anal. Calcd. for **2**, $C_{22}H_{21}Cl_2Mn_{1.50}N_8O_3S$: C, 41.89; H, 3.36; N, 17.76. Found: C, 41.23; H, 3.13; N, 17.70. IR data (cm⁻¹): 3610-3290br, 3193br, 2070vs, 1693s, 1623s, 1605s, 1491m, 1462m, 1235m, 1171s, 1064m, 1012s, 846s, 814s, 751m, 655m, 559m, 528w, 467m, 441w.

Table 1

Crystallographic data and structure refinement details for compounds 1–4.

	1	2	3	4
Empirical formula	C21H23MnN9O10	$C_{22}H_{21}Cl_2Mn_{1.50}N_8O_3S$	C ₆₆ H ₆₄ Mn ₃ N ₂₁ O _{9.50}	C24H24MnN8O3
Formula weight	616.42	630.84	1468.20	527.45
Crystal system	Triclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	P-1	P2 ₁ /c	C2/c	$P2_{1}2_{1}2$
Z	2	4	4	2
a(Å)	8.3541(5)	19.741(3)	25.6486(10)	12.9449(4)
b(Å)	10.2910(6)	8.1600(10)	9.4136(3)	9.5117(4)
c(Å)	16.2970(9)	17.245(2)	28.4353(11)	9.9745(4)
α(deg)	73.649(5)	90	90	90
β (deg)	83.224(5)	112.140(10)	99.968(4)	90
γ(deg)	73.874(5)	90	90	90
V (Å ³)	1290.32(14)	2573.1(6)	6761.9(4)	1228.14(8)
$D_{\rm c}~({\rm g/cm}^{-3})$	1.587	1.628	1.442	1.426
$\mu(mm^{-1})$	0.585	1.079	0.626	0.581
F(000)	634	1282	3032	546
Crystal size (mm ³)	$0.30\times0.20\times0.07$	$0.30\times0.20\times0.02$	$0.40\times0.40\times0.30$	$0.40 \times 0.40 \times 0.20$
Reflections collected/unique	7848/4535	5922/5922	12951/6285	3030/1825
	[R(int) = 0.0237]		[R(int) = 0.0328]	[R(int) = 0.0259]
Reflections with $[I > 2\sigma(I)]$	3662	2371	4896	1688
Data/restraints/parameters	4535/0/386	5922/72/348	6285/9/470	1825/0/155
GOF on F^2	0.999	0.918	1.000	1.003
R_1 , w R_2 [$I > 2\sigma(I)$]	0.0505, 0.1329	0.0629, 0.0875	0.0485, 0.1195	0.0412, 0.1097
R_1 , w R_2 (all data)	0.0647, 0.1449	0.1646, 0.0968	0.0661, 0.1290	0.0460, 0.1136

2.2.4. Synthesis of $\{[Mn_3(L^1)_3(H_2O)_2] \cdot 1.5C_2H_5OH\}_n$ (3)

A mixture of MnSO₄·5H₂O (0.012 g, 0.05 mmol), 2,6-diacetylpyridine bis(isonicotinoylhydrazone) (0.03 g, 0.075 mmol), dimethylformamide (5 mL), ethanol (3 mL) and water (1 mL) was sealed in a Teflon-lined autoclave (10 mL) and heated at 120 °C for 48 h under autogenous pressure. Cooling to room temperature at the rate of 0.6 °C/min afforded the product as ruby crystals and separated (0.011 g). Yield: ~5%. Anal. Calcd. for 3, $C_{66}H_{64}Mn_3N_{21}O_{9.50}$: C, 53.99; H, 4.39; N, 20.03. Found: C, 53.80; H, 4.32; N, 20.12. IR data (cm⁻¹): 3245m, 1668m, 1602m, 1567s, 1500m, 1219m, 1158s, 1087w, 1066w, 1007m, 799m, 761m, 670m, 586w, 518w, 461w.

2.2.5. Synthesis of $\{[MnL^2] \cdot dmf\}_n$ (4)

A mixture of $MnSO_4 \cdot 5H_2O$ (0.012 g, 0.05 mmol), 2,6-diacetylpyridine bis(nicotinoylhydrazone) (0.03 g, 0.075 mmol), dimethylformamide (5 mL), ethanol (3 mL) and water (1 mL) was sealed in a Teflonlined autoclave and heated at 120 °C for 48 h under autogenous pressure. Cooling to room temperature at the rate of 0.6 °C/min afforded the product as garnet crystals were separated (0.013 g). Yield: 52%. Anal. Calcd. for 4, C₂₄H₂₄MnN₈O₃: C, 54.65; H, 4.59; N, 21.24. Found: C, 54.59; H, 4.60; N, 21.30. IR data (cm⁻¹): 1672s, 1651m, 1594m, 1582m, 1551m, 1495m, 1257m, 1156s, 1136m, 1095m, 1049s, 818m, 754s, 562w, 534w, 418w.

2.3. X-ray crystallography

Diffraction measurements for compounds 1-4 were carried out at room temperature on an Xcalibur E diffractometer equipped with CCD area detector and a graphite monochromator using MoKa radiation. Determination of the unit cell parameters and processing of experimental data were performed using the CrysAlis Oxford Diffraction Ltd. [30]. All calculations to solve the structures and to refine the proposed models were carried out with the SHELXS97 [31] and SHELXL2014 program packages [32]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms attached to carbon and nitrogen atoms were positioned geometrically and treated as riding atoms. The O-bounded Hatoms in water molecule in 1-3 were found from differential Fourier maps at the intermediate stages of the refinement. Compound 2 was refined as a non-merohedral twin with the component ratio 0.785:0.215. Atoms Mn(2), Cl(2) and one pyridine ring of isonicotinic fragment in the H_2L^1 molecule in 2 is disordered over two positions with the 0.54 and 0.46 probabilities. The outer sphere ethanol molecule in 3 is disordered over three positions. The X-ray data and the details of the refinement for 1-4 are summarized in Table 1. Selected geometric parameters for 1-4 are given in Tables S1 and S2. The Figures were produced using the Mercury program [33]. The solvent accessible voids (SAVs) were calculated using PLATON [34]. Crystallographic data of the compounds reported herein were deposited with the Cambridge Crystallographic Data Centre and allocated the deposition numbers CCDC 2082304-2082307.

3. Results and discussion

A coherent variation of the synthetic methods (direct or template) and the reaction conditions, such as reflux the reactants at room temperature or under solvothermal conditions, taking into account the



Scheme 2. Experimental procedure for the preparation of the obtained coordination compounds.



Fig. 1. View of the structure of mononuclear $[Mn(H_2L^1)(H_2O)_2]^{2+}$ cation in **1** with partial atomic numbering scheme (a). Perspective view of the fragment of the H-bonded supramolecular network in **1** in which C-bound H atoms are omitted for clarity (b).

nature of the solvent and the anion has been undertaken. One-pot synthesis involving Mn(II) salts, dap, and iaH ligands, in C_2H_5OH solution results in orange and yellow crystals (Fig. S3) of mono- and trinuclear Mn(II) compounds 1 and 2 (Scheme 2). In both these cases, the reactions were carried out in the presence of the KSCN salt. When the corresponding Schiff base and the MnSO₄·5H₂O salt were taken as reagents under solvothermal conditions, ruby/garnet crystals of compounds 3 and 4 were obtained (Scheme 2, Fig. S3).

The results of this study and our recent publications showed that the addition of dmf solvent in the synthesis plays a significant role in the dimensionality extension of coordination compounds: reactions in the absence of dmf carry to the mononuclear coordination compounds formation (1, 2 and [14,17,35]), while the addition of dmf led to the fabrication of coordination compounds with higher dimensionality (3, 4 and [15,18]). It has been also observed that the chosen reaction conditions affect the obtaining of pure crystals: in the result of the solvothermal synthesis are obtained crystals with lower yield but with high purity (2–4), while the refluxing or stirring of the reactants leads to obtaining of impure crystals, which require additional recrystallization (1). Compounds 2–4 were aimed to be obtained by the same method as 1 and unfortunately, it failed.

Despite the low yields of some compounds, all syntheses are easily reproducible. The obtained crystals were checked on a single-crystal Xray diffractometer, which demonstrates their reproducibility through the coincidence of the unit cell parameters.

3.1. IR spectroscopy

The IR spectra of compounds **1–4** confirm the coordination of organic ligands H_2L^1 and H_2L^2 to Mn(II) ions (Fig. S4). The ν (C=O) stretching vibration bands represent the most important vibration bands and characteristic for the Schiff base ligands at 1671 cm⁻¹ in H_2L^1 and 1666 cm⁻¹ in H_2L^2 [12]. These bands are observed at 1645 cm⁻¹ in **1**, 1693 cm⁻¹ in **2**, 1668 cm⁻¹ in **3**, and 1651 cm⁻¹ in **4**.

In the IR spectrum of compound **1**, the strong absorption in the 3500–2600 cm⁻¹ region, represented by peaks at 3124, 3075 and 2731 cm⁻¹, indicates the stretching vibrations ν (OH) and ν (NH) associated by hydrogen bonds formation, as well as ν (CH). The absorptions in the region 3610–3290 cm⁻¹ and the broad band at 3193 cm⁻¹ in spectrum **2** are attributed to ν (OH) and ν (NH) oscillations, while the δ (OH) and δ (NH) oscillations are manifested to 1623 cm⁻¹.

In the spectra of complexes **3** and **4** is absent the band ν (NH) observed in free ligands at 3184 cm⁻¹ and 3186 cm⁻¹, which demonstrates the dianionic nature of the ligands in compounds. In **3**, the wide absorption bands at 3510–3110 cm⁻¹ can be attributed to ν (OH) vibrations of coordinated water and lattice ethanol molecules. The

presence of the ν (C=N) stretching vibration bands in pure organic ligands was documented at 1569 cm⁻¹ and 1568 cm⁻¹ while in complexes these bands were observed at 1656 cm⁻¹ in **1**, 1623 cm⁻¹ in **2**, 1567 cm⁻¹ in **3**, and 1551 cm⁻¹ in **4**. The ν (C=C) absorption bands of the aromatic ring are manifested at 1601, 1495 and 1444 cm⁻¹ in H₂L¹, and 1594, 1484, 1443 cm⁻¹ in H₂L². These vibrations are observed in complexes at 1604, 1556, 1492 cm⁻¹ in **1**, at 1605, 1491 and 1462 cm⁻¹ in **2**, at 1602, 1591, 1500 cm⁻¹ in **3**, and at 1594, 1582, 1495 cm⁻¹ in **4** [36,37]. The solvent dmf molecule in **4** are represented by ν (C=O) band at 1672 cm⁻¹.

The highest intensity bands from 1323 and 1297 cm⁻¹, as well as the band from 826 cm⁻¹ in spectrum **1** are attributed to the NO₃⁻ anions oscillations [36,38]. The coordinated NCS⁻ anions through nitrogen atom are manifested via: ν (CN) – 2070 cm⁻¹ (the most intensive band in the spectrum **2**), ν (CS) – 814 cm⁻¹ and δ (NCS) – 467 cm⁻¹.

The type of substitutions in aromatic rings are distinguished by absorption bands that are manifested by $\delta(CH)_{planar}$ oscillations (in region 1275–1000 cm⁻¹ for 1,4- and 1175–1000 cm⁻¹ for 1,2,3- substitution type) and δ (CH)_{nonplanar} (860–800 cm⁻¹ for 1,4- and 810–750 cm⁻¹ for 1,2,3-substitution type) [36,37]. In our compounds the oscillations $\delta(CH)_{nlanar}$ manifested at: 1230, 1014 and 1006 cm⁻¹ in **1**, 1235 and 1012 cm^{-1} in **2**, 1219 and 1066 cm⁻¹ in **3**, 1257 and 1049 cm⁻¹ in **4** illustrate the 1,4- substitution (two neighbour hydrogen atoms), while those at 1137, 1074 and 1041 cm^{-1} in 1, 1171, 1064 and 1012 cm^{-1} in **2**, 1158, 1087, 1007 cm⁻¹ in **3**, and 1136, 1095, 1049 cm⁻¹ in **4** show the 1,2,3- substitution (three neighbour hydrogen atoms)) in the aromatic ring [36]. The absorption bands of the $\delta(CH)_{nonplanar}$ oscillation from the benzene rings are more pronounced and are manifested in the range 860–750 cm⁻¹ for 1,4- and 1,2,3- substitutions: at 826 cm⁻¹ in 1, 846 cm^{-1} in **2**, at 799 cm^{-1} in **3**, and at 818 cm^{-1} in **4** for two neighbour hydrogen atoms and at 753 cm⁻¹ in 1, 751 cm⁻¹ in 2, at 761 cm⁻¹ in 3, and at 754 cm^{-1} in 4 for 1,2,3- substitution type [36,37].

In the 700–400 cm⁻¹ region of all IR spectra ν (M-N) and ν (M–O) oscillations have been partially revealed [38,39]. Thus, the ν (Mn-N_{pyridine}) oscillations are manifested to 552 (1), 559 (2), 586 (3) and 562 cm⁻¹ (4), and ν (Mn-N_{azomethine}) – 524 (1), 528 (2), 518 (3) and 534 cm⁻¹ (4). The oscillations ν (Mn-O_{carbohydrazide}) are revealed by the absorption bands 473 (1), 441 (2), 461 (3) and 418 cm⁻¹ (4), while the ν (Mn-O_{water}) oscillations are observed at 666 (1), 655 (2) and 670 cm⁻¹ (3) [38].

3.2. X-ray study

The crystal structures of compound 1 comprises mononuclear complex cation $[Mn(H_2L^1)(H_2O)_2]^{2+}$ and NO_3^- anions. The coordination polyhedron of the metal attains an N_3O_4 pentagonal bipyramid provided



Fig. 2. View of the molecular structure of trinuclear $[Mn_3(H_2L^1)_2Cl_4(NCS)_2(H_2O)_2]$ compound with partial atomic numbering scheme (a). The fragments of H-bonded supramolecular layer (b) and network (c) in **2**. C-bound H atoms are omitted for clarity.

by the pentadentate ligand in the equatorial plane and water molecules in the axial vertices (Fig. 1a). The Schiff base acts as a neutral pentadentate ligand coordinating through pyridyl nitrogen atom (N4), two azomethine nitrogen atoms (N3 and N5) and two carbohydrazide oxygen atoms (O1 and O2), at usual for Mn(II) bond distances (Table S1). The coordinated ligand provides a pentagonal arrangement with four chelate angles in the range from 67.93(9) to 70.21(8)° and the nonchelate O–Mn–O angle 84.16(8)°. The sum of these angles equals 360.23° which indicates a coplanar arrangement of donor atoms. The axial water molecules and the metal ion demonstrate about a linear arrangement with O(1*w*)–Mn(1)–O(2*w*) angle 176.58(11)°. The coordinated pyridine ring forms dihedral angles with the two terminal pyridine rings equal to 9.92(12) and 15.24(13)°. In the crystal structure of **1**, the components form a 3D supramolecular network (Fig. 1b) by three types of intermolecular hydrogen bonds: O—H…O between a water molecule and nitrate anion; O—H…N between the same water molecule



Fig. 3. Fragment of 2D polymer in **3** with partial atomic numbering scheme illustrates the connectivity of the Mn(II) ions (a); Topology of the layer in the **3**: top view (b), view along two-fold screw axis (c) and simplified topology of net based only on Mn(2) atoms and considering Mn(1) atoms as a bisconnector (e). The packing of layers with the mode of enclathration of C_2H_5OH molecules in **3**; view along the *b* (b) and *c* (c) axis.

with the nitrogen atom of one terminal pyridine moiety, and N—H···O between the amide nitrogen atom and nitrate anion (Table S2).

The structure of compound **2** consists of discrete centrosymmetric trinuclear $[Mn_3(H_2L^1)_2(NCS)_2Cl_4(H_2O)_2]$ complexes (Fig. 2a). The Mn (1) cation adopts an N₃O₃Cl pentagonal bipyramidal geometry going from the pentadentate Schiff base ligand in the equatorial plane, while the axial vertices are occupied by Cl⁻ anion and water molecule. The H_2L^1 coordinates to Mn(1) in neutral form as a pentadentate ligand like in compound 1, and the environment of this metal presents an pentagonal arrangement, chelate N-Mn(1)-N/O bond angles in the equatorial plane are in the range from 67.9(2)-68.1(2)° (Table S1), the non-chelate O(1)–Mn(1)–O(2) bond angle is 86.68(18)°, sum of these angles 359.17° and Mn(1) atom displace on 0.157(3) Å from the mean plane of donor atoms in the direction of chloride anion (Table S1). The water molecule and chloride anion in the axial positions and the Mn(1) metal ion deviate from linearity, O(1w)-Mn(1)-Cl(1) 170.01(14)°. The coordinated central pyridine ring of H₂L¹ forms dihedral angles with the terminal pyridine rings equal to 22.3(3)° and 28.6(3) or 48.48(3)° for two positions of disordered pyridine ring, respectively. In this structure the H₂L¹ molecule act as a hexadentate ligand, involving one of the terminal nitrogen atoms to coordinate to Mn(2) of [MnCl₂(NCS)₂] moiety. The Mn (2) atom is six-coordinated with N_4Cl_2 square bipyramidal geometry provided by two nitrogen atoms from two H₂L ligands and another two N atoms from NCS⁻ anions in the equatorial plane, and two Cl⁻ anions in the apical positions. The self-association of trinuclear aggregates in 2 occurs via O(1w)-H...S and N(2)/(6)-H...Cl hydrogen bonds with the formation of the 2D supramolecular layer (Fig. 2b), which is further assembled into a 3D supramolecular network (Fig. 2c) through O(1w)-H...N hydrogen bonds (Table S2).

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Compound **3** { $[Mn_3(L^1)_3(H_2O)_2] \cdot 1.5C_2H_5OH$ }_n is a 2D coordination polymer isostructural to the solvatomorphic $\{[Mn_3(L^1)_3(H_2O)_2]\}$. $2dmso_n$ [8]. In this compound were distinguished two crystallographically different Mn(II) ions, Mn(1) - in general position and Mn(2) - on two-fold axis (Fig. 3a). All manganese atoms have pentagonal bipyramidal geometry with N_4O_3 and N_5O_2 environment for Mn(1) and Mn(2), respectively, provided by L1 ligand in equatorial plane and two monodentate ligands in axial positions which differ for these metal centres. The axial positions of Mn(1) are occupied by an oxygen atom of water molecule and an nitrogen atom from isonicotinic ring of the $(L^1)^{2-}$ coordinated to Mn(2), while the Mn(2) apical positions are occupied by the symmetry related nitrogen atoms N(7) of isonicotinic rings of the $(L^1)^{2-1}$ ligand coordinated to Mn(1). Thus, the $(L^1)^{2-}$ ligands show a hexadentate and heptadentate coordination mode, (Fig. 3a) and result in 2D coordination polymer with Mn...Mn separation 9.5538(7) and 9.6021 (7) Å.

The topology of this 2D layered polymer is shown in Fig. 3b and 3c, the Mn(1) serves as a bisconnected node, similar to Mn(2) in cluster 2, while Mn(2) serves as a four connected nodes. This layer can also be thought of as fused helices of the same chirality with common Mn(2) nodes (Fig. 3c), but if one considers the Mn(1) nodes as a linear bisconnector the topology of the layer may be simplified up to 4,4-net (Fig. 3d).

The layers are additionally stabilized by intramolecular hydrogen bonds between coordinated water molecules and the O-amide atoms of the (L^{1})²⁻ ligands (Table S2). The disordered polar protic ethanol solvent molecules are accumulated in the crystal compartments of **3**, held there by the electrostatic, van der Waals forces. The calculation of SAVs for the simulated solvent-free network yields the volume of 979.3 Å³ or 14.5%



Fig. 4. View of the coordination environment of the Mn(II) ion in 4 with partial numbering scheme (a). Fragment of polymeric layer (b) and packing of the layers which afford the channels filled with the dmf solvent shown in space-filling mode (c), Topology of the layer, top (d) and side (e) views.

of the total unit cell volume (Fig. 3b and c).

Compound 4 with 2,6-diacetylpyridine bis(nicotinoylhydrazone) L^{2-} anion reveals a 2D coordination polymer build-up from sevencoordinated (N₅O₂) manganese(II) complexes with symmetrical pentagonal bipyramidal environment. The metal atoms reside on twofold axis. In the equatorial plane the 2,6-diacetylpyridine bis(nicotinoylhydrazone) ligand surrounds the Mn(II) atom just like 2,6-diacetylpyridine bis(isonicotinoylhydrazone) in compounds 1–3, and the axial positions are occupied by two nitrogen atoms of terminal pyridine rings of adjacent symmetry related complexes (Fig. 4a). Similar to the compounds discussed above, the coordinated Schiff base ligand H₂L² provides an ideal pentagonal arrangement, chelate N–Mn(1)–N/O bond angle are 67.58(9) and 69.79(12)° (Table S1), the non-chelate O–Mn (1)–O bond angle is 85.72(16)°, and in sum give 360.46° attesting to the planarity of the structure. The axial nitrogen atoms of nicotinic rings and Mn(1) form a 176.5(2)° angle showing a little deviated linear

arrangement. The $(L^2)^{2-}$ ligand shows a twisted conformation proved by the dihedral angle between coordinated pyridine ring and nicotinic ring equal to $40.70(14)^{\circ}$, and is responsible for the linking of Mn(II) cations in the 2D coordination layer with 4,4-net topology and the diagonal dimensions of the meshes of 9.5117(4) \times 12.9449(4) Å (Fig. 4b). The Mn...Mn separations across the Schiff base ligand is 8.5867(6) Å. The layers are parallel to (ab) crystallographic plane and stack along the crystallographic *c*-axis forming the channels filled by the polar aprotic dmf solvent molecules (Fig. 4c), bonded through weak C-H···O hydrogen bonds with the nicotinic rings of $(L^2)^{2-}$ (Table S2). The SAVs calculated for the simulated solvent-free network gives a value of 317.5 ${\rm \AA}^3$ (~25.9% of the unit cell volume), thus indicating a high solvent uptake. It is noteworthy that compound **4** is isostructural and isomorphous with our recent presented homo-Zn(II)/Cd(II) and heterometallic Zn(II)M(II) (M(II) = Mn, Cd) coordination layers [18] obtained in a similar way and which show good luminescence responsiveness to the



Fig. 6. Thermoanalytical curves (TG-a, DTG-b and DTA-c) for compounds 1 (grey), 2 (green), 3 (red) and 4 (blue).

removal of guest solvent molecules.

3.3. Thermal analysis

To examine the thermal stability and decomposition of coordination compounds, simultaneous thermal analyses (TG-DTG-DTA) of the Schiff base ligands (H₂L¹ and H₂L²) (Fig. S5) and all complexes were carried out from 20 °C to 1000 °C in nitrogen atmosphere (Fig. 6).

The H_2L^1 ligand melts at 212 °C, remaining stable up to 254 °C when it begins to decompose. This ligand undergoes two decomposition steps: a loss of 42.4% of the mass is observed up to 382 °C, and the second step is up to 466 °C when another 12.0% mass is eliminated. The H_2L^2 ligand is slightly more stable that H_2L^1 as melts at 266 °C and immediately after melting it begins to decompose. As the previous ligand, the thermal degradation of H_2L^2 occurs in two steps: in the range 270–384 °C is identified a loss of 42.4% and in the range 384–475 °C is removed 10.2% of the mass of the compound. In both cases, the resulting residues undergo transformations with subsequent heating, processes that last up to 1000 °C.

The compound 1 begins to decompose at 110 °C by removing water molecules, the mass loss being 5.93% (5.84% calc.). The process is accompanied by endothermic effect in the range of 110–190 °C. In the range 220–280 °C there is an oxidative thermal degradation with a strong exothermic effect. This is explained by the presence of nitrate anions in the structure. The mass loss at this stage is 53.9% and as a result, a mixture of carbonaceous residue and Mn(III) oxide is obtained. Up to 840 °C the residue formed is stable and in the interval 840–995 °C on the TG curve a decrease of the mass is observed as a result of the transformation of the oxide of Mn(III) into Mn₃O₄. The process is accompanied by a weak endothermic effect, possibly due to the fact that the more reactive organic part of the ligand (aliphatic chains) has been oxidized by the nitrate ions and the aromatic residue is not oxidized during this temperature range (Fig. 6a).

Compound **2** is thermally stable up to 110 °C; subsequent heating leads to the loss of two coordinated water molecules, a process that ends at 180 °C. The mass loss represents 2.85% (2.85% calc.). Up to 290 °C this compound does not undergo other transformations, and in the range 290–377 °C there is a mass loss of 6.7%, which corresponds to the elimination of two inaH molecules (6.8% calc.). In the range 377–434 °C has observed another 18.1% mass loss, a process caused by the thermal degradation of the H_2L^1 ligand. Heating to 480 °C leads to a total loss of 40.5%, and the residue formed gradually degrades to 1000 °C. In the DTA curve at 654 °C is observed an endothermic effect without a mass change, which can be explained by the melting of Mn(II) chloride obtained at the decomposition of compound **2**.

Compound **3** begins to lose mass at 65 $^{\circ}$ C due to elimination of solvent molecules: up to 155 $^{\circ}$ C the mass of the compound decreases by 2.5% which corresponds to the elimination of 0.5 ethanol molecule

(2.45% calc.) and up to 255 °C the total loss is 7.8% which corresponds to the elimination of one ethanol molecule (7.20% calc.). Both processes are accompanied by endothermic effects. In the interval 255-370 °C from the TG curve there is no mass loss, at the same time on the DTA curve an exothermic maximum is observed which can be explained by the restructuring of the compound after the elimination of the solvent molecules. Decomposition of the ligand occurs in temperature interval 371-496 °C, process accompanied by an endothermic peak. The mass loss at this stage being 46.4%, which corresponds to 56.8% of the ligand mass. Because the thermal analysis was performed in an inert atmosphere, as a result of the thermal degradation, carbonic residue and Mn (III) oxide were formed, the latter decomposes at 820 °C into Mn₃O₄ and the removed oxygen partially oxidizes the carbon residue. As a result, on the DTA curve an exothermic peak is observed in the range 820–905 $^{\circ}$ C and it is found a larger mass decrease (3.17%) than calculated only for the decomposition of Mn(III) oxide (0.56%) (Fig. 6b).

The compound **4** is thermally stable up to 282 °C, when the thermal degradation of the ligand starts and occurs in two stages: first between 282 and 368 °C and second in interval 410–516 °C. Both stages are accompanied by endothermic effects and mass loss is 14.9% and 42.4% respectively. As in case of compound **3**, Mn_2O_3 and carbonaceous residue are formed as a result of thermal decomposition. Mn(III) oxide decomposes in the range of 830–925 °C to form Mn_3O_4 and the oxygen formed oxidizes the carbon residue. As a result, an exothermic peak is observed on the DTA curve (Fig. 6c).

4. Conclusion

Modifications of synthetic methods and reaction conditions led to the preparation of four Mn(II) samples, two discrete compounds and two coordination polymers, with hydrazone Schiff bases derived from 2,6diacetylpyridine and isonicotinic/nicotinic hydrazides. Schiff bases behave as neutral (1 and 2) and bideprotonated (3 and 4) ligands and coordinate to the Mn(II) ion through azomethine and central pyridyl nitrogen atoms, as well as through carbohydrazide oxygen atoms, while isonicotinic/nicotinic pyridine rings increase the structure dimensionality in 2-4. The thermal analysis has been established the influence of the inorganic anion on the stability of synthesized compounds, thus, compound **1** which contains the nitrate anion begins to decompose at a lower temperature (220 °C) than the H_2L^1 ligand (254 °C) due to the nitrate ion oxidizing effect. The chloride ion, on the other hand, increases the thermal stability of the coordination compound, so that 2 is the most thermally stable (290 °C). In the absence of the inorganic anions, it was noticed that compounds begin to decompose at a temperature close (compound **3** – 255 °C, H_2L^1 – 254 °C) or slightly higher (compound 4 – 282 °C, H_2L^2 – 266 °C) to the ligand.

CRediT authorship contribution statement

Lilia Croitor: Conceptualization, Investigation, Visualization, Writing - original draft, Supervision. Maria Cocu: Methodology, Investigation, Formal analysis, Writing - original draft. Ion Bulhac: Conceptualization, Investigation, Writing - original draft. Paulina N. Bourosh: Investigation, Visualization, Writing - original draft. Victor Ch. Kravtsov: Investigation, Visualization, Writing - review & editing. Oleg Petuhov: Investigation, Visualization, Writing - original draft. Olga Danilescu: Methodology, Investigation, Formal analysis, Writing original draft.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

CCDC 2082304–2082307 contain the supplementary crystallographic data for the new structures. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.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.

Supplementary data (Fig. S1: The registered modes in CSD and the present work of L¹ moiety coordination in the transition metal coordination compounds: neutral (a, b, c), biprotonated (d) and bideprotonated (e-h). The transition metal ion is shown by green ball. Fig. S2: Neutral (a-d), biprotonated (e), mono- (f) and bideprotonated (g, h) coordination modes of L² fragment to transition metal ions. The transition metal ion is shown by green ball. Table S1: Bond distances and bond angles in metal coordination cores in 1–4. Table S2: Hydrogen bond distances (Å) and angles (°) in 1–4. Fig. S3: Photographs of crystals' compound 1–4 selected for the single crystal X-ray experiment. Fig. S4: The IR spectra of compounds 1–3 and H₂L¹ ligand (a), as well as for compound 4 and H₂L² ligand (b). Fig. S5: TG (black), DTG (red) and DTA (blue) curves of Schiff base ligands H₂L¹ (a) and H₂L² (b)) to this article can be found online at https://doi.org/10.1016/j.poly.20 21.115329.

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