

DISCRETE AND POLYMERIC Mn(II)

COORDINATION COMPOUNDS WITH DIHYDRAZONE SCHIFF BASES



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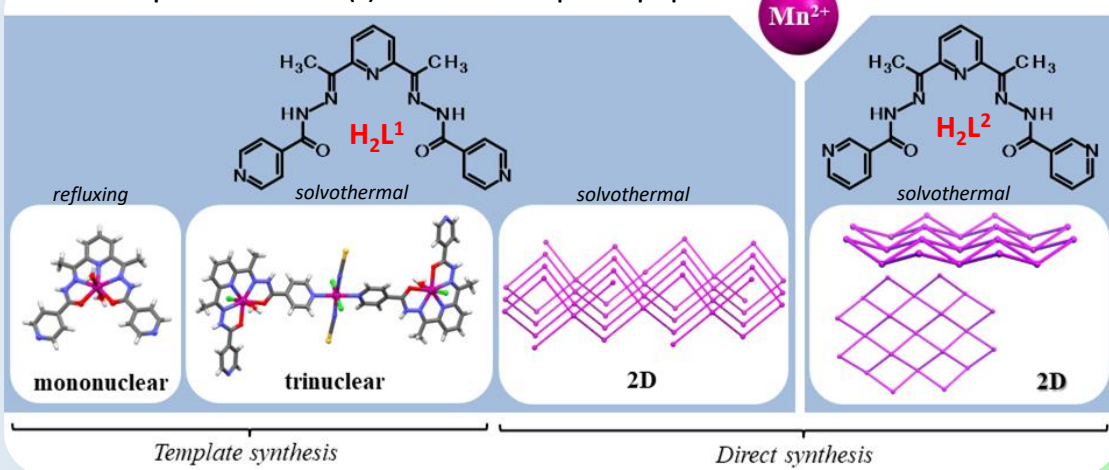


The Schiff base ($R_1R_2C = NNR_3R_4$) with the hydrazone fragment provide a good platform for generating a variety of new ligands their metal complexes with promising chemical, physical, biological properties useful for their practical applications. The 2,6-diacetylpyridine (dap) is a suitable candidate for preparation of dihydrazone Schiff bases with multiple coordination sites, giving rise to metal complex compounds with exclusive geometries.

Four Mn(II) coordination compounds based on the 2,6-diacetylpyridine bis(isonicotinoylhydrazone) (H_2L^1) and 2,6-diacetylpyridine bis(nicotinoylhydrazone) (H_2L^2), were prepared using different synthetic conditions and starting manganese salts: discrete mononuclear $[Mn(H_2L^1)_2(H_2O)_2](NO_3)_2$ (**1**) and trinuclear $[Mn_3(H_2L^1)_2(NCS)_2Cl_4(H_2O)_2]$ (**2**) complexes and two 2D coordination polymers $\{[Mn_3(L^1)_3(H_2O)_2] \cdot 1.5C_2H_5OH\}_n$ (**3**) and $\{[MnL^2] \cdot dmf\}_n$ (**4**).

The crystals of discrete coordination compounds **1** and **2** suitable for single-crystal diffraction analysis were obtained by template assembly of components, while 2D coordination polymers **3** and **4** by the direct reaction between pre-synthesized H_2L^1 and H_2L^2 ligands and manganese sulfate salt. The results of this study and our recent publications showed that the addition of N,N-dimethylformamide (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** and **2**), while the addition of dmf led to the fabrication of coordination compounds with higher dimensionality (**3** and **4**).

Schematic representation of Mn(II) coordination compounds preparation

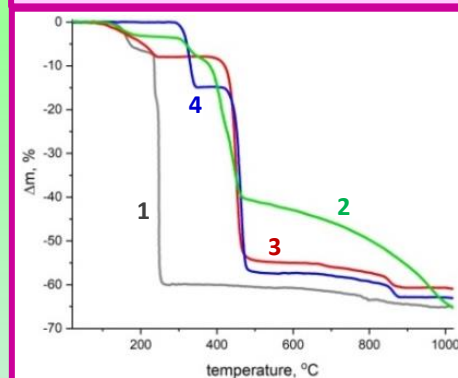


Schiff bases behave as neutral (**1** and **2**) and bideprotonated (**3** and **4**) ligands and coordinate to the Mn(II) ion through azomethine and central pyridyl nitrogen atoms, as well as through carbohydrazide oxygen atoms, while isonicotinic/nicotinic pyridine rings increase the structure dimensionality (2D) in **2-4**.

Infrared spectroscopy (IR)

	$\nu(NH)$	$\nu(C=O)$	$\nu(C=N)$	$\nu(C=C)$	$\nu(NO_3^-)$	$\nu(CN)$
H_2L^1	3184	1671	1569	1601, 1495, 1444	-	-
1	3124	1645	1656	1604, 1556, 1492	1323-1299	-
2	3193	1693	1623	1605, 1491, 1462	-	2070
3	-	1668	1567	1602, 1591, 1500	-	-
H_2L^2	3186	1666	1568	1594, 1484, 1443	-	-
4	-	1651	1551	1594, 1582, 1495	-	-

Thermal analysis (TGA)



The TGA has 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 than the H_2L^1 ligand due to the nitrate ion oxidizing effect. The chloride ion, on the other hand, increases the thermal stability of the coordinating compound. In the absence of the inorganic anions, it was noticed that compounds begin to decompose at a temperature close or slightly higher to the ligand.