A 3D Coordination Polymer based on *syn-anti* Bridged $[Mn(RCOO)_2]_n$ Chains Showing Spin-Canting with High Coercivity and an Ordering Temperature of 14 K

Soumen Kumar Dubey,[1] Maxcimilan Patra,[1] Kajal Gupta,[1] Subham Bhattacharjee,[1*] Rajat Saha,[1,2*] Carlos J Gómez García,[2*]

1- Department of Chemistry, Kazi Nazrul University, Asansol-713340, Paschim Bardhaman, West Bengal, India

2- Departamento de Química Inorgánica. Universidad de Valencia. Dr Moliner 50, 46100 Burjasot (Valencia) Spain

Table S1. Structural data of all the reported structures with 6-hydroxypicolinic acid.

CCDC	M	Form	Structure	Ref
AYIVIO	Cs(I)	*Keto*	3D	1
BEGXOC	Ru(II)	*Enol*	Monom	2
BOPXOU	Cu(II)	*Keto*	Monom	3
DICFEC	Cu(II)	*Keto*	Monom	4
EXOYIZ	Mn(III)	L^{2-}	Dimer	5
FEFGIH	Cu(II)	*Enol*	Monom	6
JOFZUC	Cu(II)	L^{2-}	Dimer	7
JOGBAL	Cd(II)	L^{2-}	1D	
MIWJIM	Cu(II)	L^{2-}	2D	8
MIWJOS	Cu(II)	L^{2-}	Dimer	
MIWJUY	Cu(II)	L^{2-}	2D	
MUTFIT	Dy(III)	L^{2-}	Trimer	9
QEFRIE	Ru(II)	*Enol*	Monom	10
RIYDEJ	Na(I)	*Keto*	3D	11
RUWCAO	Ni(II)	*Enol*	Monom	12
RUWCIW	Ni(II)	*Enol*	Monom	
ULEYAL	Re(II)	L^{2-}	Dimer	13
ULEYEP	Re(II)	L^{2-}	Dimer	
VAGXAF	Re(III)	*Enol*	Monom	14
VAGXEJ	Re(V)	*Enol*	Monom	
VAHZEM	Re(IV)	L^{2-}	Dimer	
VAJPEE	Re(IV)	L^{2-}	Dimer	
VUSNON	Ru(II)	*Enol*	Monom	15
XAMHUP	Er(III)	L^{2-}	Trimer	16
XAMJAX	Tb(III)	L^{2-}	Trimer	
XIZYUB	Co(II)	*Enol*	Monom	17
XOLCEH	Zn(II)	L^{2-}	Dimer	18
XOLCIL	Zn(II)	L^{2-}	Dimer	
XOLCOR	Zn(II)	L^{2-}	2D	
1	Mn(II)	*Keto*	3D	This work

Table S2. Coordination bond lengths (Å) and angles (°) in complex **1**.

Atoms	**Distance (Å)**	**Atoms**	**Distance (Å)**
Mn1-O1	2.140(2)	Mn1-O8	2.126(3)
Mn1-O1^{1}	2.140(2)	Mn1-O8^{1}	2.126(3)
Mn1-O9^{4}	2.211(3)	Mn1-O9^{6}	2.211(3)
Mn2-O2	2.137(3)	Mn2-O4	2.152(2)
Mn2-O7	2.152(2)	Mn2-O6^{2}	2.224(3)
Mn2-O3^{5}	2.219(3)	Mn2-O5^{8}	2.144(3)
N1-H1N1	0.98(4)	N2-H2N2	0.83(4)
N3-H3N3	0.90(4)		
Atoms	**Angle (º)**	**Atoms**	**Angle (º)**
O1-Mn1-O8	89.42(10)	O1-Mn1-O1^{1}	174.00(10)
O1-Mn1-O8^{1}	86.83(10)	O1-Mn1-O9^{4}	82.71(9)
O1-Mn1-O9^{6}	101.97(9)	O1^{1}-Mn1-O8	86.83(10)
O8-Mn1-O8^{1}	102.35(11)	O8-Mn1-O9^{4}	165.00(10)
O8-Mn1-O9^{6}	89.99(10)	O1^{1}-Mn1-O8^{1}	89.42(9)
O1^{1}-Mn1-O9^{4}	101.97(9)	O1^{1}-Mn1-O9^{6}	82.71(9)
O8^{1}-Mn1-O9^{4}	89.99(10)	O8^{1}-Mn1-O9^{6}	165.00(10)
O9^{4}-Mn1-O9^{6}	79.25(10)	O2-Mn2-O4	82.69(9)
O2-Mn2-O7	96.30(9)	O2-Mn2-O6^{2}	89.57(10)
O2-Mn2-O3^{5}	176.70(10)	O2-Mn2-O5^{8}	102.60(10)
O4-Mn2-O7	172.31(9)	O4-Mn2-O6^{2}	81.50(9)
O3^{5}-Mn2-O4	95.54(10)	O4-Mn2-O5^{8}	100.26(9)
O6^{2}-Mn2-O7	90.87(9)	O3^{5}-Mn2-O7	85.08(9)
O5^{8}-Mn2-O7	87.41(9)	O3^{5}-Mn2-O6^{2}	87.42(10)
O5^{8}-Mn2-O6^{2}	167.81(10)	O3^{5}-Mn2-O5^{8}	80.42(10)

1 = -x, y, 1/2-z; 2 = -x, y, 1/2-z; 3 = x, -y, 1/2+z; 4 = -1/2+x, -1/2+y, z; 5 = 1/2+x, 1/2+y, z; 6 = 1/2-x, -1/2+y, 1/2-z; 7 = 1/2-x, 1/2+y, 1/2-z; 8 = 1/2-x, 1/2-y, 1-z

Table S3. Hydrogen bond dimensions for complex **1**.

D-H···A	D-H/(Å)	H···A/(Å)	D···A/(Å)	<D-H···A/(°)	symmetry
N3-H3N3···O7	0.90(4)	2.40(5)	2.718(4)	101(3)	
N3-H3N3···O3	0.90(4)	2.00(4)	2.894(4)	171(4)	1/2+x, 1/2+y, z
N2-H2N2···O4	0.83(4)	2.33(5)	2.698(4)	108(3)	
N2-H2N2···O6	0.83(4)	2.02(4)	2.830(4)	167(4)	1-x, -y, 1-z
N1-H1N1···O1	0.98(4)	2.33(5)	2.682(4)	100(3)	
N1-H1N1···O9	0.98(4)	1.90(4)	2.868(4)	174(4)	-1/2+x, -1/2+y, z
C5-H5···O4	0.95	2.35	3.040(8)	129	-1/2+x, -1/2+y, z
C16-H16···N2	0.95	2.56	3.306(5)	136	-1/2+x, 1/2-y, -1/2+z
C17-H17···O1	0.95	2.57	3.268(4)	131	1/2-x, 1/2+y, 1/2-z

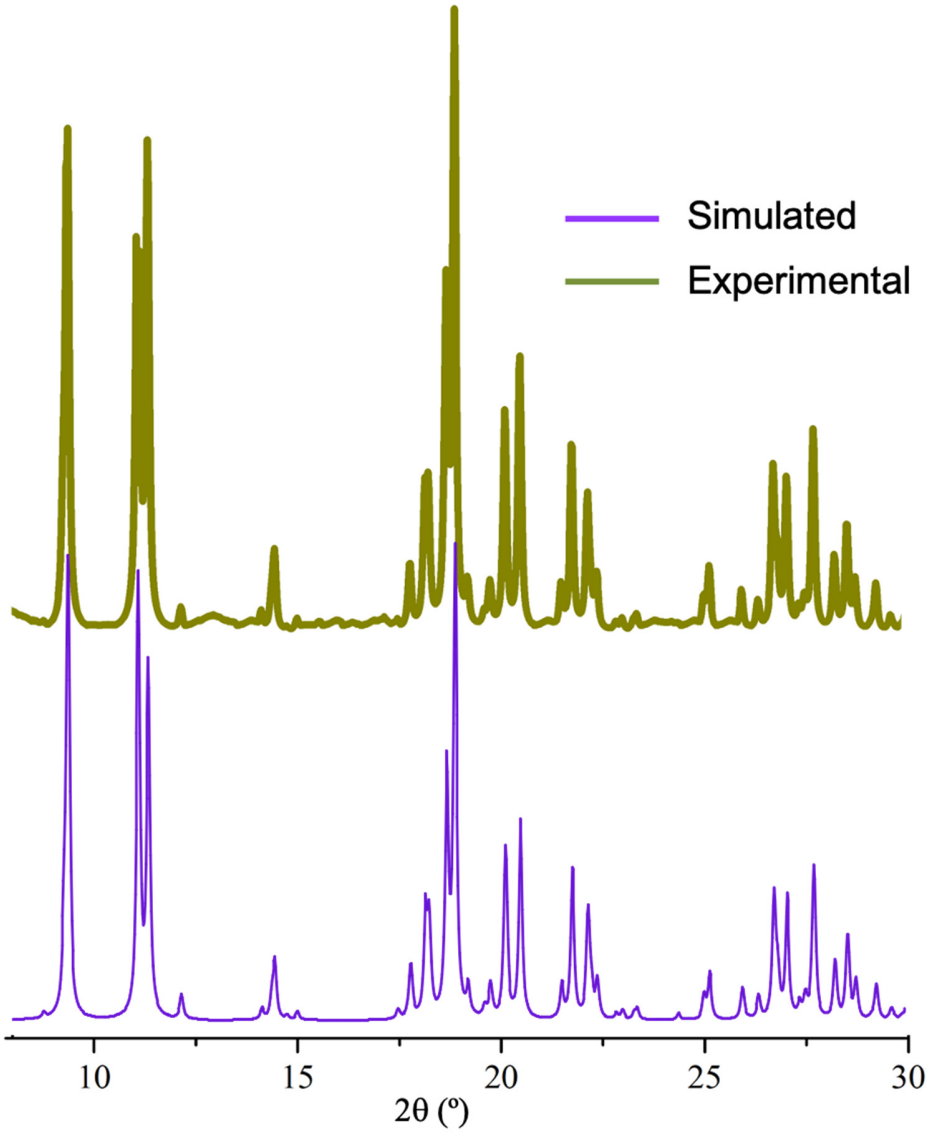

Figure S1. Simulated and experimental X-ray powder diffractograms for compound **1**.

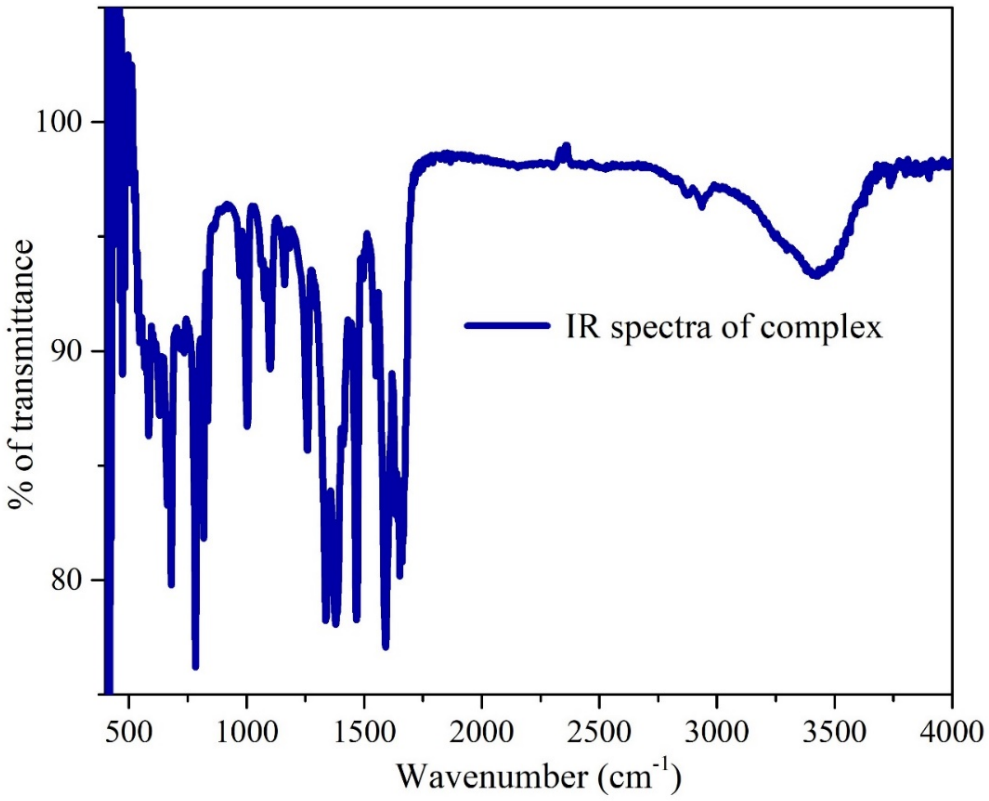

Figure S2. IR spectra of compound [Mn(HL)$_2$] (**1**).

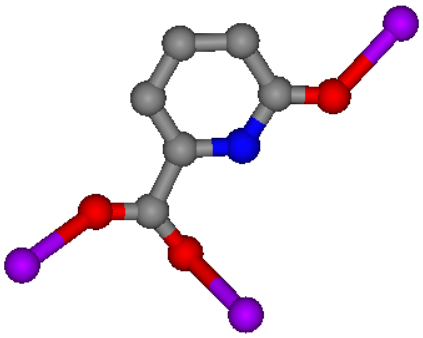

Figure S3. μ_3-bridging mode of the ligand through carboxylato and hydroxy groups. Colour code: C = grey, O = red, N = blue and Mn = purple).

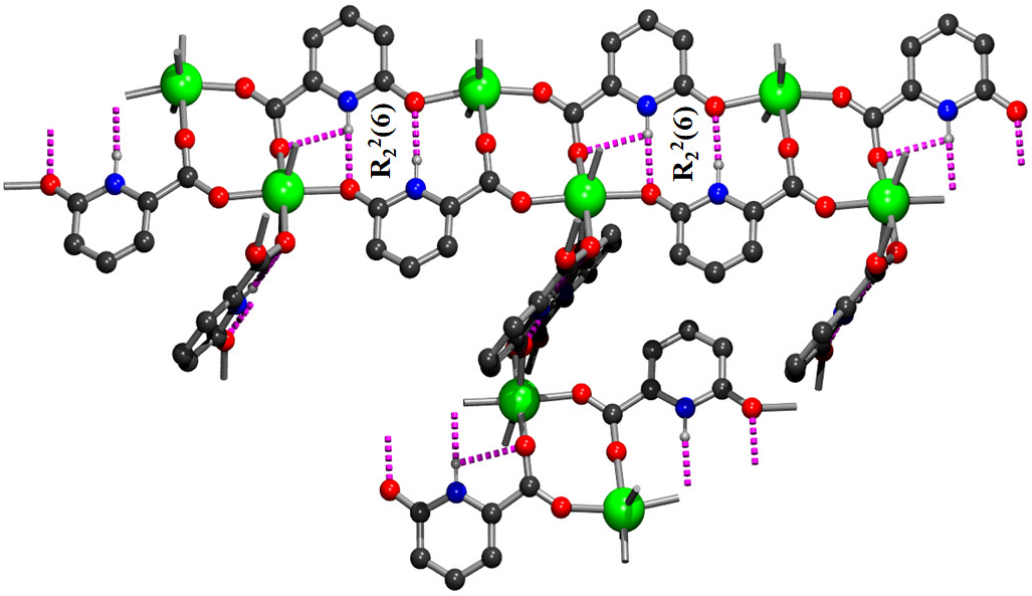

Figure S4. Hydrogen bonding interactions present in the complex. Colour code: C = black, O = red, N = blue and Mn = green. Pink lines indicate the H-bonds.

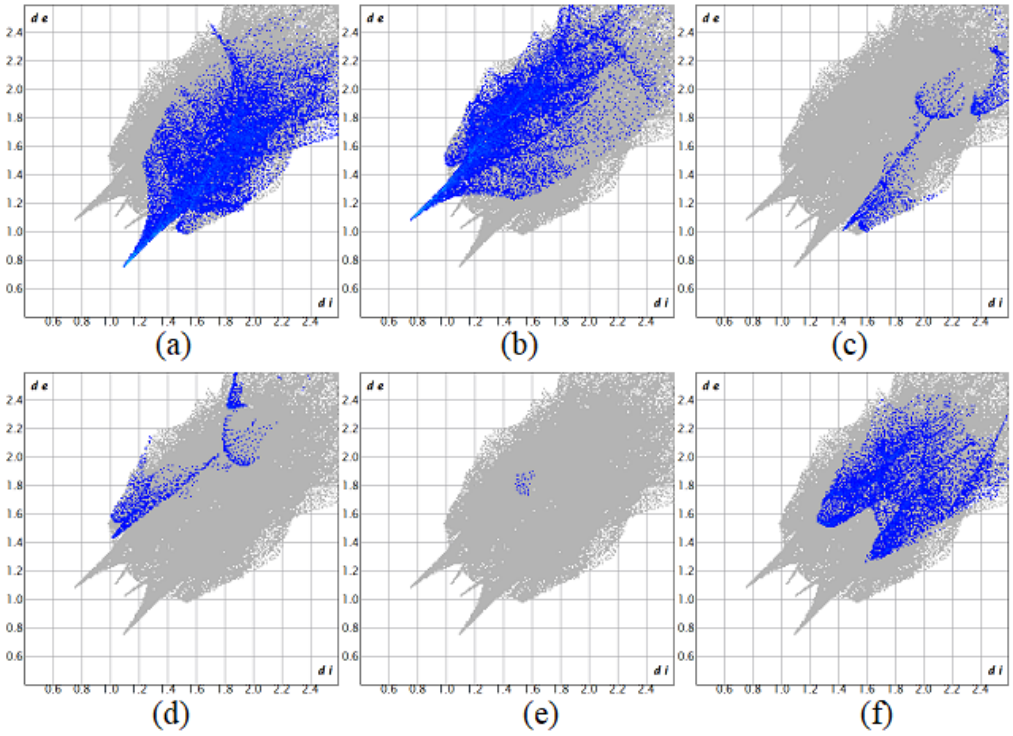

Figure S5. 2D fingerprint plots for a) O···H, b) H···O, c) N···H, d) H···N, e) N···O and f) O···O interactions.

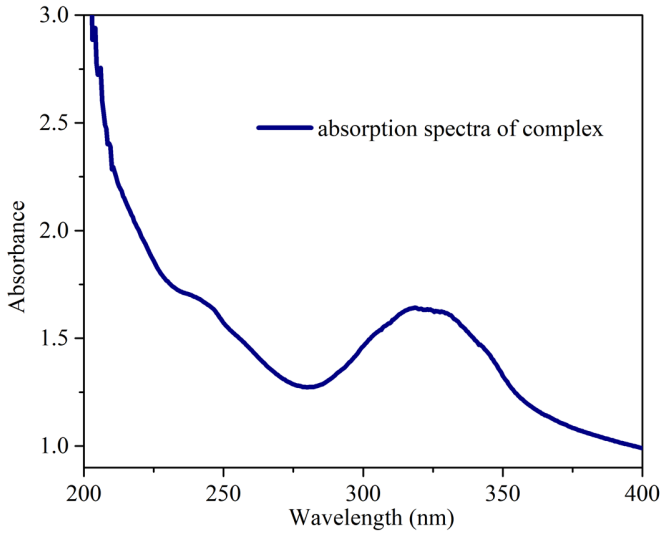

Figure S6. Solid-state absorption spectra of compound **1**.

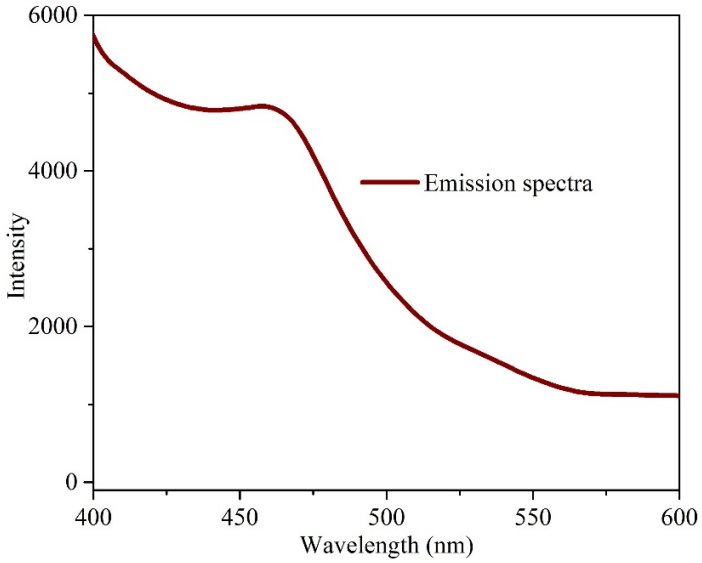

Figure S7. Solid-state emission spectra of compound **1**.

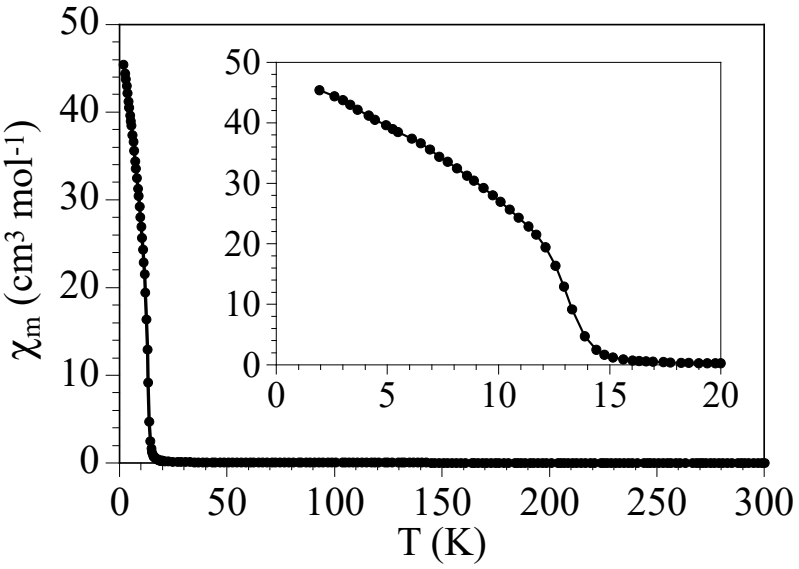

Figure S8. Thermal variation of $\chi_m T$ for compound **1**. Inset shows the low temperature region.

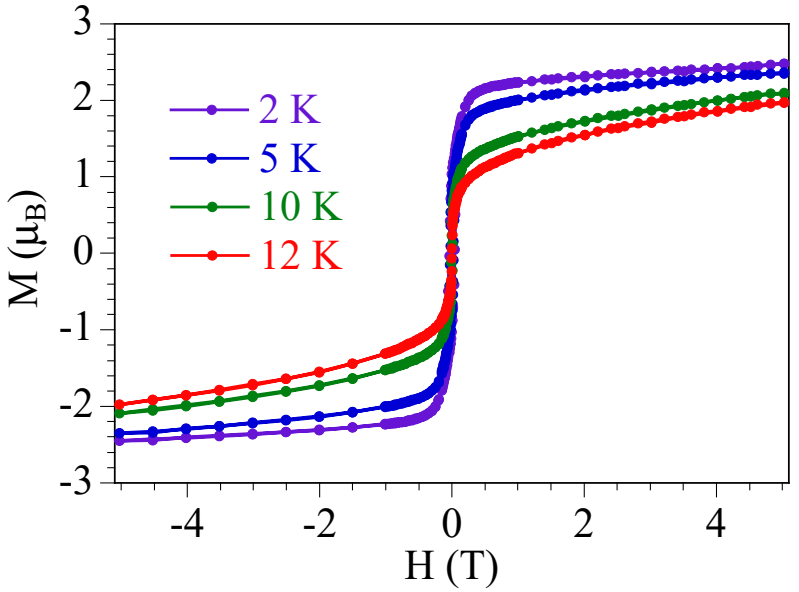

Figure S9. Isothermal magnetization at different temperatures for compound **1**.

References

1- Kang, S. K.; Shim, Y. S. Poly[(m6-6-Oxidopyridinium-2-Carboxylato)Caesium]. *Acta Cryst. E* **2011**, *67*, m1237.

2- Małecki, J. G.; Krompiec, S.; Maroń, A.; Penkala, M. Synthesis, Molecular, Spectroscopic and Catalytic Characterization of Ruthenium(II) Complexes with Pyridine-2-Carboxylic Acid Derivatives Ligands. *Polyhedron* **2012**, *48*, 21-30.

3- Kukovec, B.-M., Popovic, Z., & Pavlovic, G. Copper(II) Complexes with 3- and 6-hydroxypicolinic Acid. Preparation, Structural, Spectroscopic and Thermal Study. *Acta Chimica Slovenica*, **2008**, *55*, 779-787

4- B.-M. Kukovec, B. M.; Kaksa, M.; Popovic, Z. Synthesis and Characterization of a Copper(II) Complex with 6-Hydroxypicolinic Acid and 3-Picoline *Croatica Chemica Acta*, **2012**, *85*, 479-483

5- Bian, G.; Kuroda-Sowa, T.; Konaka, H.; Maekawa, M.; Munakata, M. Bis(m-6-Hydroxy-Picolinato)-m-Oxo-Bis-[Di-Pyridine-Manganese(III)] Monohydrate. *Acta Cryst. E* **2004**, *60*, m338-m340

6- Sengül, A.; Büyükgüngör, O. Trans-Di-Aqua-Bis(6-Hydroxy-Picolinato-k^2-N,O^2)Copper(II). *Acta Cryst. E* **2005**, *61*, m119-m121.

7- You-Zhu Yu, Song-Yang Chang, Xi Han, Guang-Xin Chen, Ya-Wei Xuan, Xian-Li Wu, Fang Wang, Hydrothermal Syntheses, Crystal Structures and Luminescence Properties of Cu(II) and Cd(II) Complexes Assembled by 6-Hydroxypicolinic Acid and 1,10-Phenanthroline *Jiegou Huaxue*, **2019**, *38*, 651-659.

8- Sun, C.; Zhou, J.; Li, W.; Jin, L. Supramolecular Stuctures from Mononuclear, Binuclear and 2D Net of Copper(II) Complexes with 6-Hydroxypicolinic Acid. *Z. anorg. allg. Chem.* **2008**, *634*, 549-554.

9- Su, W.; Guo, Y.; Yu, Y.; Wang, Y. Synthesis, Structure and Magnetic Property of a Linear Trinuclear Dy(III) Single Molecular Magnet. *Inorg. Chem. Commun.* **2020**, *120*, 108161.

10- Nakasone, T.; Nishioka, T.; Asato, E.; Kinoshita, I.; Takara, S. Synthesis and Structural Characterization of Novel Ruthenium(II) Complexes Bearing Hydroxypicolinato Ligands. *Polyhedron* **2012**, *45*, 152-157.

11- Casas, J. S.; Castellano, E. E.; Ellena, J.; García-Tasende, M. S.; Sánchez, A.; Sordo, J.; Toma, M. Dimethylthallium(III) Complexes with Picolinic Acid and its Hydroxyl Derivatives. *Polyhedron* **2008**, *27*, 1296-1302.

12- Kukovec, B.; Vaz, P. D.; Calhorda, M. J.; Popović, Z. Disappearing and Concomitant Polymorphism of Nickel(II) Complexes with 6-Hydroxypicolinic Acid. Structural and Density Functional Theory Studies. *Cryst. Growth Des.* **2010**, *10*, 3685-3693.

13- Chattopadhyay, S.; Fanwick, P. E.; Walton, R. A. Reactions of the Triply-Bonded Complex c*is*-$Re_2(\mu\text{-}O_2CCH_3)_2Cl_2(\mu\text{-}Dppm)_2$ with Pyridine Carboxylic Acids. the Isolation and Structural Characterization of a Third Structural Isomer of $Re_2(Dipic)Cl_2(\mu\text{-}Dppm)_2$ (Dipic = Pyridine-2,6-Dicarboxylate). *Dalton Trans.* **2003**, 3617-3621.

14- Mukiza, J.; Hosten, E. C.; Gerber, T. I. A. Rhenium(III), (IV) and (V) Complexes with 6-Hydroxypicolinic Acid. *Polyhedron* **2016**, *110*, 106-113.

15- Nakama, Y.; Nishioka, T.; Nakasone, T.; Asato, E.; Kinoshita, I.; Takara, S. Synthesis And Crystal Structure of [RuCl(6-hydroxypicolinato)(2,2′;6′,2″-terpyridine)]·(*N*,*N*-dimethylformamide). *X-ray Structure Analysis Online* **2010**, *26*, 33-34.

16- Sun, C.; Jin, L. Supramolecular Architectures from the Self-Assembly of Lanthanide Ions with 6-Hydroxypicolinic Acid and 1,10-Phenanthroline. *J. Mol. Struct.* **2005**, *741*, 241-247

17- Kukovec, B.; Popović, Z.; Pavlović, G.; Rajić Linarić, M. Synthesis and Structure of Cobalt(II) Complexes with Hydroxyl Derivatives of Pyridinecarboxylic Acids: Conformation Analysis of Ligands in the Solid State. *J. Mol. Struct.* **2008**, *882*, 47-55.

18- Sun, C.; Zheng, X.; Li, W.; Wang, M.; Fang, C. Assembly of Supramolecular Networks with the Inclusion of Water Chains, Cyclic Hepta and Octa Water Clusters. *Z. anorg. allg. Chem.* 2008, *634*, 2663-2669.