

Supporting Information

The role of intermolecular interactions involving halogens in the supramolecular architecture of a series of Mn(II) coordination compounds

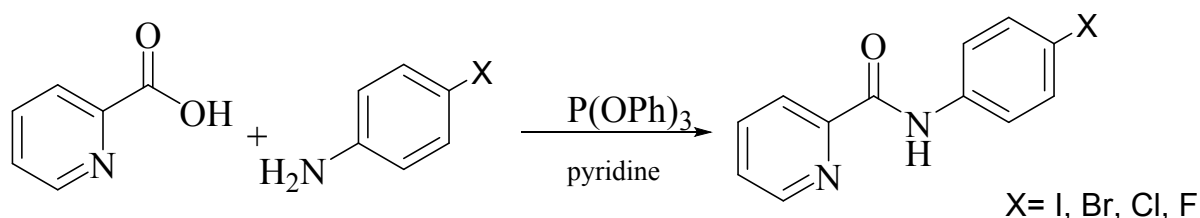
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Experimental Section

Synthesis of *N*-(4-iodo)phenyl picolinamide

A solution of 5 mmol of 4-iodoaniline in 15 mL pyridine was added to a solution of 5 mmol of 2-picolinic acid in 15 mL pyridine, equation 1. The solution was stirred at 313 K for 20 min, then 5 mmol of triphenyl phosphite (1.3 mL) was added dropwise, and the reaction mixture was stirred for 5 h at 373 K and then for 24 h at ambient temperature. The resulting solution was added to distilled water. A yellow solid resulted with a yield of 90%. Anal. Calcd for *N*-(4-iodophenyl) picolinamide: C, 44.47; H, 2.80; N, 8.64. Found: C, 44.35; H, 2.73; N, 8.58. Selected IR (KBr pellet, cm^{-1}): 3310, 1691, 1607, 1494, 1337, 1176, 846. (Melting point: 424-426 K).



Equation 1.

Synthesis of *N*-(4-bromo)phenyl picolinamide

A solution of 5 mmol of 4-bromoaniline in 15 mL pyridine was added to a solution of 5 mmol of 2-picolinic acid in 15 mL pyridine, equation 1. Then the solution was stirred at 313 K for 20 min, and 5 mmol of triphenyl phosphite (1.3 mL) was added dropwise, and the reaction mixture was stirred for 5 h at 373 K and then for 24 h at ambient temperature. Then the solution was added to distilled water. A yellow solid resulted with a yield of 85%. Anal. Calcd for *N*-(4-bromophenyl) picolinamide: C, 52.01; H, 3.27; N, 10.11. Found: C, 52.05; H, 3.32; N, 10.10. Selected IR (KBr pellet, cm^{-1}): 3324, 1683, 1593, 1480, 1386, 1225, 887.

Synthesis of *N*-(4-chloro)phenyl picolinamide

A solution of 5 mmol of 4-chloroaniline in 15 mL of pyridine was added to a solution of 5 mmol of 2-picolinic acid in 15 mL pyridine, equation 1. The solution was stirred at 313 K for 20 min, then 5 mmol of triphenyl phosphite (1.3 mL) was added dropwise, and the reaction mixture was stirred for 5 h at 373 K and then for 24 h at ambient temperature. The final solution was added to distilled water. A yellow solid resulted with a yield of 75%. Anal. Calcd for *N*-(4-

chlorophenyl)picolinamide: C, 61.95; H, 3.90; N, 12.04. Found: C, 61.90; H, 3.85; N, 12.00. Selected IR (KBr pellet, cm^{-1}): 3325, 1683, 1594, 1443, 1295, 1083, 751.

Synthesis of *N*-(4-fluoro)phenyl picolinamide

A solution of 5 mmol of 4-fluoroaniline in 15 mL pyridine was added to a solution of 5 mmol of 2-picolinic acid in 15 mL pyridine, Equation 1. The solution was stirred at 313 K for 20 min, then 5 mmol of triphenyl phosphite (1.3 mL) was added dropwise, and the reaction mixture was stirred for 5 h at 373 K and then for 24 h at ambient temperature. The resulting solution was added to distilled water. A yellow solid resulted with a yield of 90%. Anal. Calcd for *N*-(4-fluorophenyl) picolinamide: C, 66.66; H, 4.20; N, 12.96. Found: C, 66.58; H, 4.18; N, 12.90. Selected IR (KBr pellet, cm^{-1}): 3447, 1634, 1561, 1409, 1164, 1006, 901.

Synthesis of $[\text{MnCl}_2(\text{L}^{\text{Py-I}})_2]$:

This compound is obtained by the reaction of 0.2 mmol of methanolic solution of Mn(II) chloride tetra hydrate and 0.2 mmol of *N*-(4-iodophenyl)picolinamide ligand in 60 °C for 30 min. A suitable single crystal can be prepared by using slow evaporation after one week. Anal. Calcd for $\text{C}_{24}\text{H}_{18}\text{Cl}_2\text{I}_2\text{MnN}_4\text{O}_2$ complex: C, 37.24; H, 2.34; N, 7.24. Found: C, 37.25; H, 2.32; N, 7.24. Selected IR (KBr pellet, cm^{-1}): 3382, 1655, 1587, 1555, 1410, 1341, 1257, and 858. (Melting point > 543).

Synthesis of $[\text{MnCl}_2(\text{L}^{\text{Py-Br}})_2]$:

This compound is obtained by the reaction of 0.2 mmol of methanolic solution of Mn(II) chloride tetra hydrate and 0.2 mmol *N*-(4-bromophenyl) picolinamide ligand in 60 °C for 30 min. A suitable single crystal can be obtained by using slow evaporation after one week. Anal. Calcd for $\text{C}_{24}\text{H}_{18}\text{Br}_2\text{Cl}_2\text{MnN}_4\text{O}_2$ complex: C, 42.39; H, 2.67; N, 8.24. Found: C, 42.42; H, 2.70; N, 8.34. Selected IR (KBr pellet, cm^{-1}): 3388, 1633, 1544, 1490, 1400, 1314, 1230, and 903. (Melting point > 543).

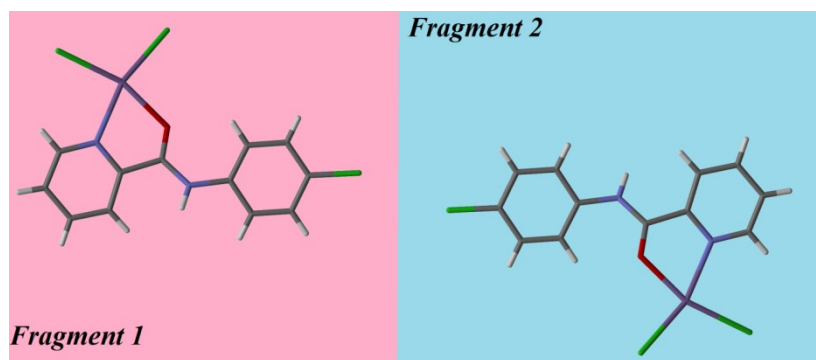
Synthesis of $[\text{MnCl}_2(\text{L}^{\text{Py-Cl}})_2]$:

This compound is gained by the reaction of 0.5 mmol acetonitrilic solution of Mn(II) chloride tetra hydrate and *N*-(4-chlorophenyl)picolinamide ligand in 60 °C. A suitable single crystal can be prepared by using an arm tube. The powder of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ and the ligand, were added to the bottom of a dry arm tube. The acetonitrile slowly was added by syringe until the arm tube filled with acetonitrile totally. Then, the tube was located in an oil bath with the temperature of 60 °C. After three days, crystals with the good quality can be obtained. Anal. Calcd for

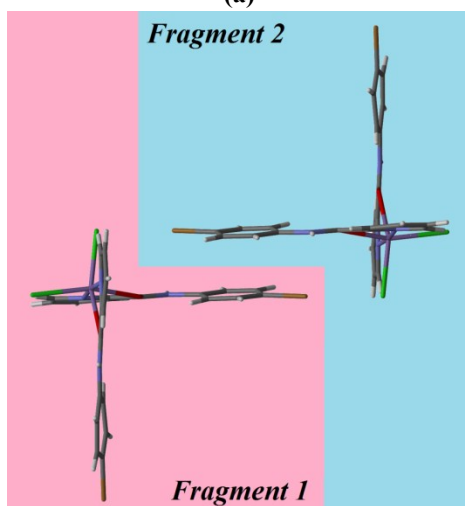
$C_{12}H_9Cl_3MnN_2O$ complex: C, 40.20; H, 2.53; N, 7.81. Found: C, 40.15; H, 2.48; N, 7.78. Selected IR (KBr pellet, cm^{-1}): 3350, 1684, 1593, 1487, 1410, 1303, 1177, and 900. (Melting point: 510-515).

Synthesis of $[MnCl_2(L^{Py-F})_2]$:

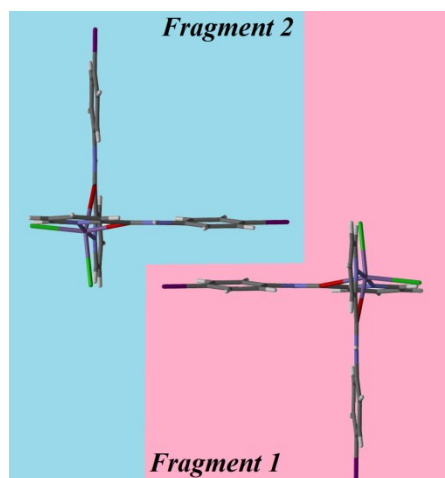
This compound is obtained by the reaction of 0.2 mmol of methanolic solution of Mn(II) chloride tetra hydrate and 0.2 mmol of *N*-(4-fluorophenyl) picolinamide ligand in 60 °C for 1 hour. A suitable single crystal can be prepared by using slow evaporation after one week. Anal. Calcd for $C_{24}H_{18}Cl_2F_2MnN_4O_2$ complex: C, 51.63; H, 3.25; N, 10.04. Found: C, 51.52; H, 3.20; N, 10.06. Selected IR (KBr pellet, cm^{-1}): 3480, 1650, 1580, 1425, 1200, 1100, 940. (Melting point: 485K).



(a)



(b)



(c)

Figure S1. Fragments selected for halogen bonding interaction energy analysis in complexes **2** (a), **3** (b) and **4** (c). Calculations were performed with the experimental structures as the starting point, at the BLYP-D3/TZP-ZORA level.

Table S1. Hydrogen bond geometries for complexes **1-4**.

Compound	D-H...A	d(D-H)/Å	d(H...A)/Å	d(D...A)/Å	<D-H...A/°	Sym. Code
1	C4-H4...C11	0.930	2.5518	3.479(4)	177	1.5-x, y, 1/2+z
	C12-H12...C11	0.930	2.6687	3.508(4)	151	1.5-x, y, 1/2+z
	N2-H2A...C11	0.860	2.5126	3.346(3)	164	1.5-x, y, 1/2+z
	C2-H2...F1	0.950	2.619	3.510(6)	160	1.5-x, -1/2+y, -1+z
	C8-H8...F1	0.950	2.561	3.281 (5)	135	x, -1.2+y, - 1/2+z
2	N2-H2A...C13	0.860	2.8905	3.718(7)	162	-1/2+x, 1.5-y, -1/2+z
	C1-H1...C12	0.950	2.810	3.518(9)	134	1-x, 1-y, 2-z
	C3-H3...O1	0.950	2.709	3.357(10)	128	1/2-x, 1/2+y, 1.5- z
	C8-H8...C13	0.950	2.865	3.490(7)	126	-x, 1- y, 2-z
	C9-H9...C13	0.950	2.8437	3.478(7)	127	-x, 1- y, 2-z
	C4-H4...C13	0.950	3.036	3.846(8)	147	-1/2+x, 1.5-y, -1/2+z
3	C4-H4...C11	0.950	2.561	3.488(13)	173	x, 1/2-y, 1/2+z
	C12-H12...C11	0.950	2.796	3.611(14)	147	x, 1/2-y, 1/2+z
	N2-H2A...C11	0.860	2.571	3.386(9)	158	x, 1/2-y, 1/2+z
	C16-H16...C12	0.950	2.546	3.471(12)	173	x, -1/2-y, 1/2+z
	C24-H24...C12	0.950	2.760	3.569(11)	146	x, -1/2-y, 1/2+z
	N4-H4B...C12	0.860	2.564	3.389(9)	161	x, -1/2-y, 1/2+z
4	C4-H4...C11	0.950	2.5653	3.495(5)	178	1/2-x, -1/2+y, z
	C12-H12...C11	0.950	2.796	3.611(14)	147	1/2-x, -1/2+y, z
	N2-H2A...C11	0.860	2.571	3.386(9)	158	1/2-x, -1/2+y, z

Table S2. Relative contributions of various non-covalent contacts to the Hirshfeld surface area in complexes 1-4.

Compound	H···H	C···H	C···C	N···H	O···H	X···H	X···C	X···X
1	25.9	24.8	5.0	3.1	2.8	Cl···H=17.8 F···H=12.6	Cl···C=2.0 F···C=1.2	F···Cl=0.7
2	19.0	15.0	4.7	3.5	4.7	Cl···H=30.9	Cl···C=7.3	2.7
3	28.4	22.5	4.7	2.9	1.3	Cl···H=13.9 Br···H=15.3	Cl···C=1.1 Br···C=1.5	2.8
4	27.6	22.4	4.5	2.9	1.3	Cl···H=13.9 I···H=15.3	Cl···C=1.0 I···C=1.8	2.6
Ref code: AMIQES (3-Cl)	30.1	18.6	3.5	2.5	1.9	Cl···H=30.7	Cl···C=9.7	-
Ref code: EGIZOK (4-H)	38.6	25.4	5.6	4.0	3.3	Cl···H=18.6	Cl···C=0.9	-
Ref code: FIXDEW (4-CH3)	45.7	22.9	4.7	3.4	3.1	Cl···H=16.4	Cl···C=0.9	-