Exploring Supramolecular Architectures in Mn(III) Two-Compartment o–vanhd Schiff Base Complexes: Insights from Apical Aqua Ligands and Bond Valence Sum Analysis

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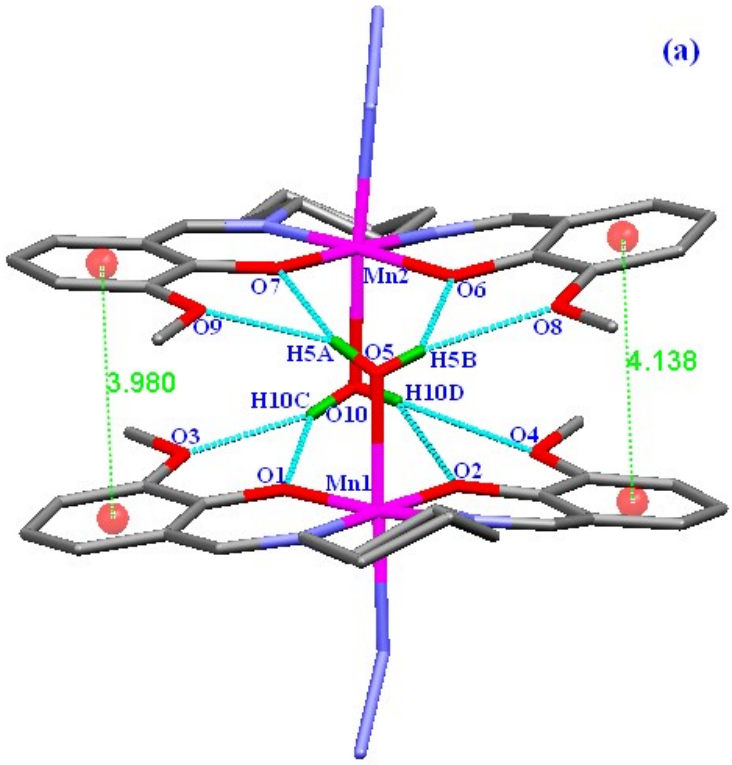
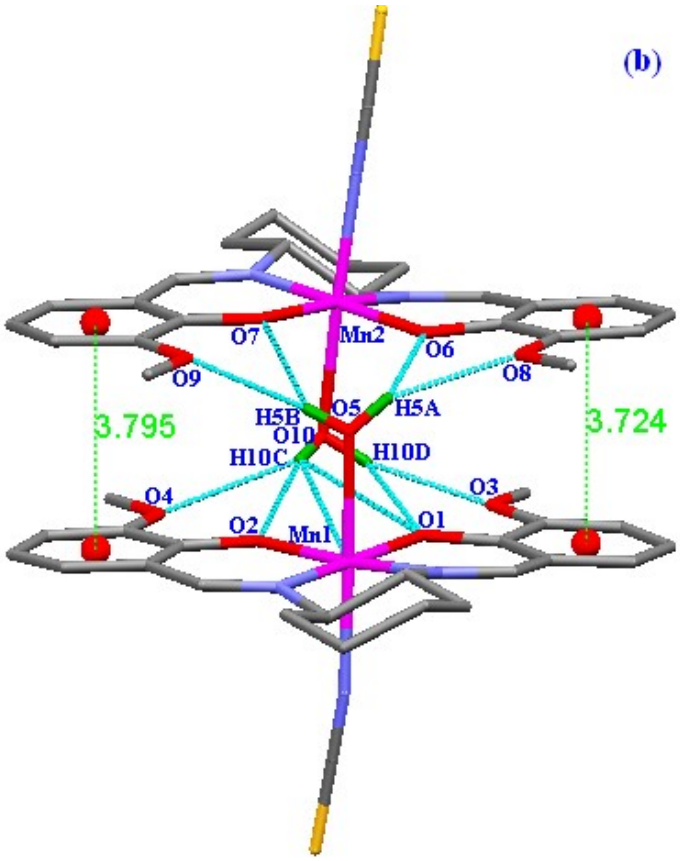



(b)
O7
Mn2
O6
O9
O8
3.795
H5B
O5
H5A
O10
3.724
H10C
H10D
O4
O3
O2
Mn1
O1

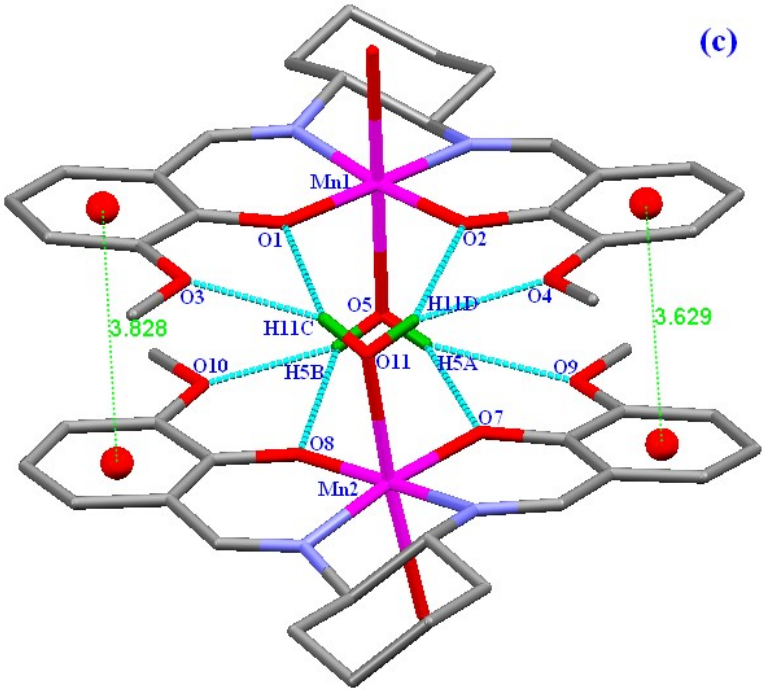
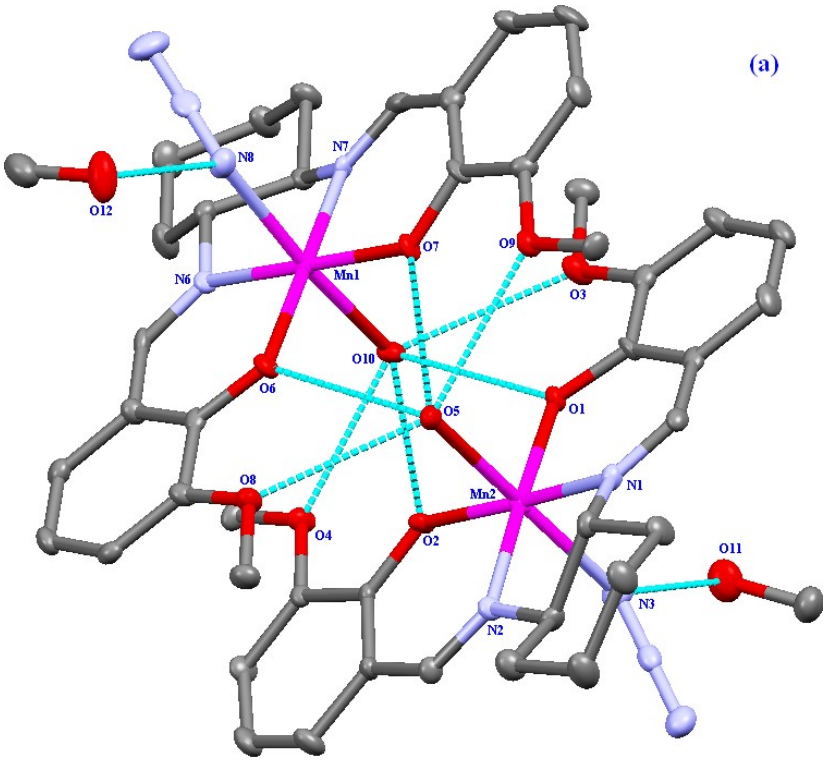
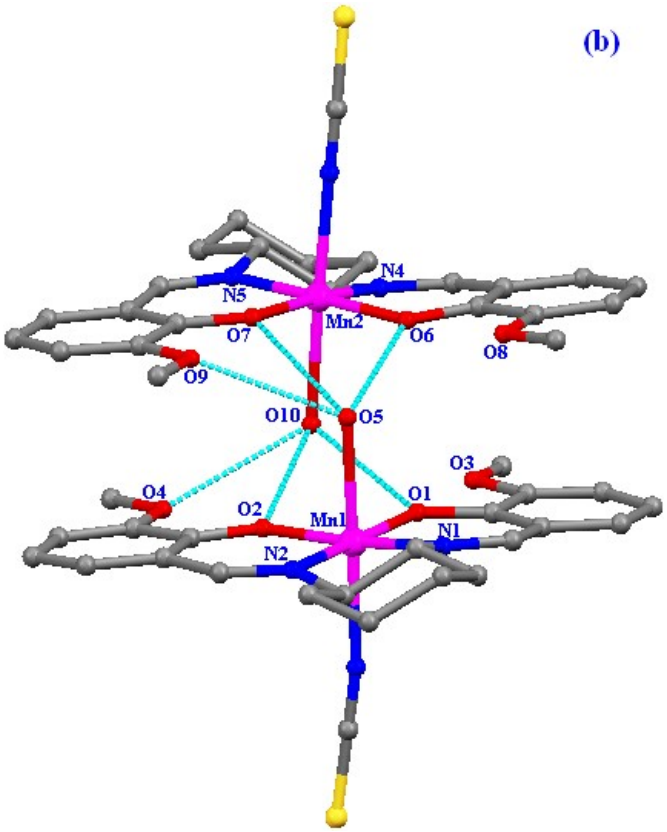


Fig. S1 Formation of the supramolecular dimer of (a) [Mn(*o*-vanhd)(N_3)(H_2O)]·CH_3OH (Solvated methanol molecules and hydrogen atoms are omitted for clarity), (b) [Mn(o-vanhd)(NCS)(H_2O)]. 2CH_3CN (Solvated acetonitrile molecules and hydrogen atoms are omitted for clarity), (c) [Mn(*o*-vanhd)(H_2O)$_2$] ClO_4 ·H_2O.


(a)
N8
N7
O12
O7
O9
Mn1
N6
O3
O10
O6
O5
O1
O8
Mn2
N1
O4
O2
O11
N3
N2


(b)
N4
N5
Mn2
O7
O6
O8
O9
O10
O5
O3
O4
O2
O1
Mn1
N1
N2

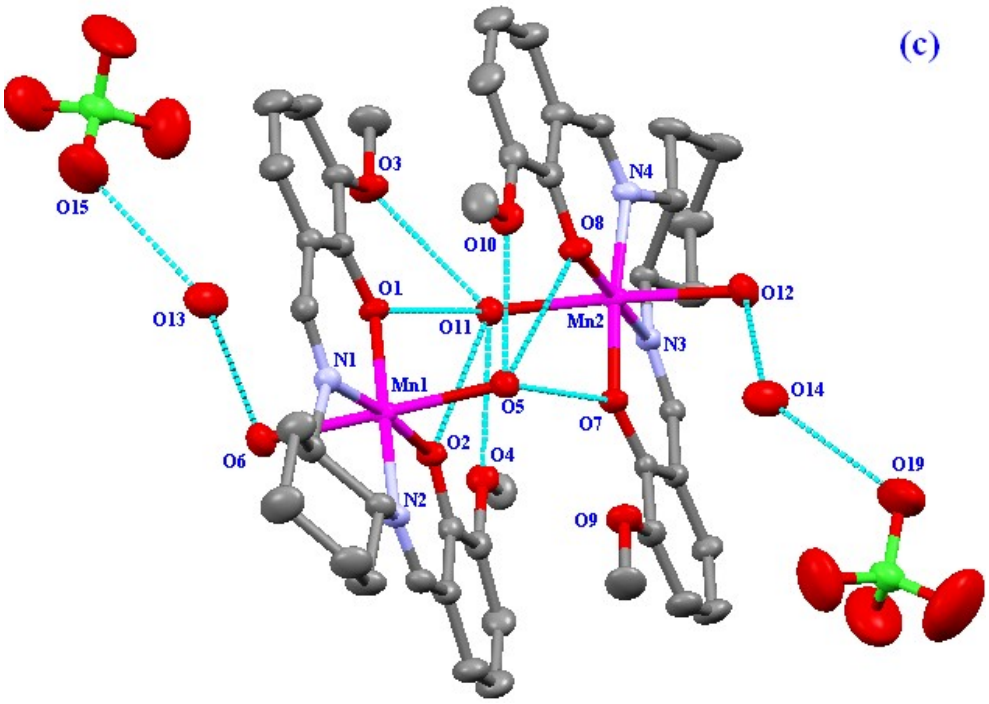
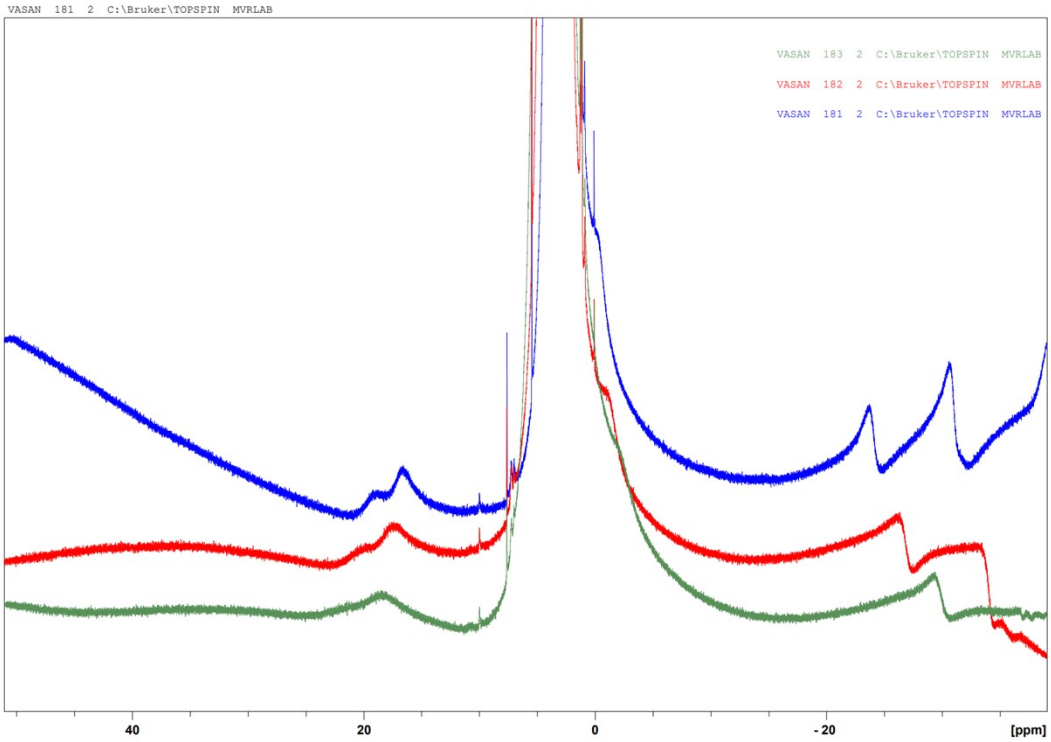


Fig. S2 π-π Stacking interactions within the supramolecular dimer of [Mn(*o*-vanhd)(N_3)(H_2O)]·CH_3OH (Solvated methanol molecules and hydrogen atoms are omitted for clarity), (b) [Mn(o-vanhd)(NCS)(H_2O)]. 2CH_3CN (Solvated acetonitrile molecules and hydrogen atoms are omitted for clarity), (c) [Mn(*o*-vanhd)(H_2O)$_2$] ClO_4 ·H_2O.

^{1}H NMR

Mn N3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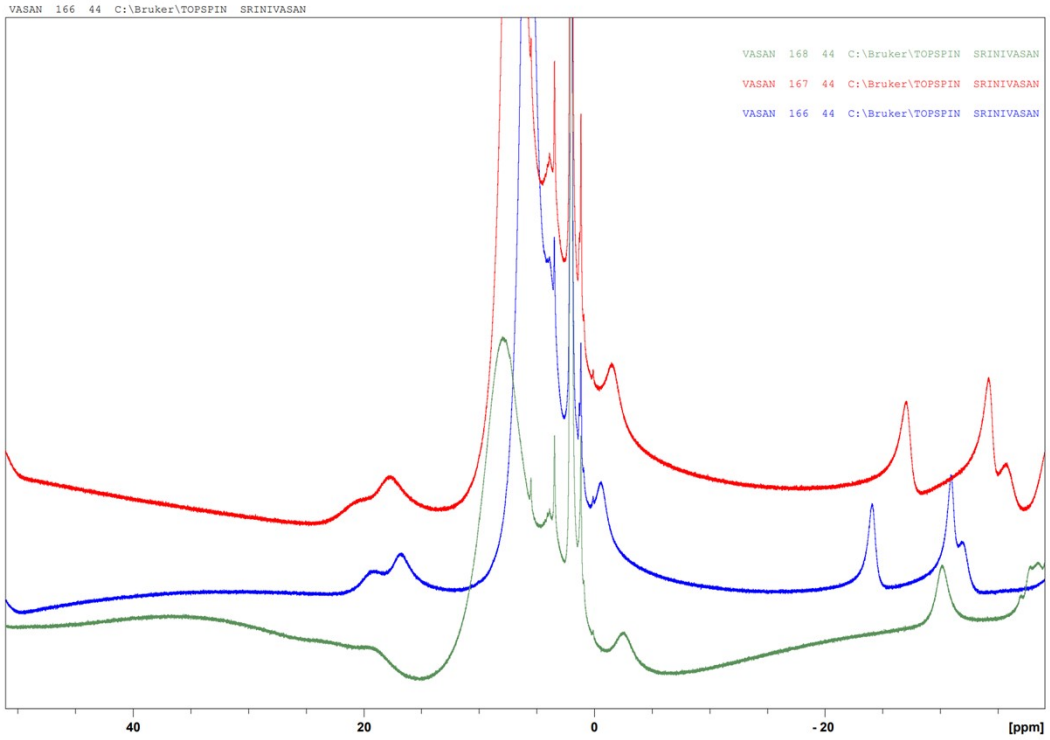
40
20
0
- 20
[ppm]

Mn ClO4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VASAN 166 44 C:\Bruker\TOPSPIN SRINIVASAN
40
20
0
- 20
[ppm]

Fig. S3 ^{1}H NMR spectra of [Mn(o–vanhd)(N_3)(H_2O)]·CH_3OH(**1**) and [Mn(o–vanhd)(H_2O)]· ClO_4· H_2O (**3**) complexes.

BOND VALENCE SUM ANALYSIS (BVS)

Manganese is an interesting metal not only in application part and its structural aspects. It exhibits different oxygen states in the complexes. For that, we decided to use bond valence sum analysis to predict formal oxidation number as well as to check the quality of crystal data and interactions of molecules. Many programs are involved in calculating the formal oxidation number and quality of a crystal by using certain parameters like bond lengths of the metal center.

Table S1 Selected Bond Distances (Å) in MnO_4N_2 units and Bond valence sum

Complex	Bond	d(A)	Expo2014 BV (v.u.)	Calculated BVS (S_{ij})	Bond	d(A)	Expo2014 BV (v.u.)	Calculated BVS (S_{ij})
[Mn(*o*-vanhd)(N_3)-(H_2O)]·CH_3OH(**1**)	Mn1-O1	1.889	0.693	0.654	Mn2-O6	1.884	0.701	0.663
	Mn1-O2	1.886	0.698	0.660	Mn2-O7	1.866	0.736	0.696
	Mn1-O5	2.265	0.251	0.237	Mn2-O10	2.258	0.256	0.241
	Mn1-N1	1.992	0.632	0.658	Mn2-N6	1.988	0.638	0.665
	Mn1-N2	1.982	0.648	0.676	Mn2-N7	1.990	0.635	0.661
	Mn1-N3	2.238	0.325	0.338	Mn2-N8	2.242	0.321	0.335
			3.247	**3.223**			**3.287**	**3.261**
[Mn(*o*-vanhd)(NCS)-(H_2O)]· 2CH_3CN (**2**)	Mn1-O1	1.904	0.666	0.628	Mn2-O6	1.875	0.719	0.679
	Mn1-O2	1.891	0.688	0.651	Mn2-O7	1.879	0.711	0.670
	Mn1-O5	2.292	0.233	0.220	Mn2-O10	2.309	0.223	0.210
	Mn1-N1	1.992	0.632	0.658	Mn2-N4	1.992	0.631	0.661
	Mn1-N2	1.987	0.640	0.646	Mn2-N5	1.972	0.667	0.698
	Mn1-N3	2.221	0.340	0.354	Mn2-N6	2.207	0.354	0.365
			3.199	**3.157**			**3.305**	**3.283**
[Mn(*o*-vanhd)(H_2O)]· ClO_4· H_2O (**3**)	Mn1-O1	1.874	0.721	0.681	Mn2-O7	1.884	0.701	0.663
	Mn1-O2	1.875	0.720	0.679	Mn2-O8	1.878	0.714	0.674
	Mn1-O5	2.272	0.246	0.232	Mn2-O11	2.269	0.248	0.234
	Mn1-O6	2.318	0.217	0.205	Mn2-O12	2.273	0.245	0.232
	Mn1-N1	1.980	0.653	0.679	Mn2-N3	1.983	0.648	0.674
	Mn1-N2	1.979	0.654	0.681	Mn2-N4	1.982	0.649	0.676
			3.211	**3.157**			**3.205**	**3.153**