

Synthesis, Crystal Structure and Magnetic Properties of 1D Chain Complexes Based on Azo Carboxylate Oxime Ligand

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BVS calculations

Bond-valence sum values for Fe and Mn ions in [M(L)₂]:

For a metal ion, the bond-valence sum (BVS) can be calculated according to Equation (1), where i is the coordination bond around the metal ion, r is the measured bond length, r_0 and B are empirical parameters. B is constant, 0.037 nm.

$$\text{BVS} = \sum \exp[(r_0 - r_i)/B] \quad (1)$$

Table S1. The r_0 values of some metal-ligand (M-L) bonds in HS metal ions

M-L	r_0/nm	M-L	r_0/nm
Mn²⁺-O	0.1765	Mn²⁺-N	0.1849
Mn³⁺-O	0.1732	Mn³⁺-N	0.1837
Mn ⁴⁺ -O	0.1750	Mn ⁴⁺ -N	0.1822
Mn ⁵⁺ -O	0.1773	Mn ⁵⁺ -N	0.1845
Fe ²⁺ -O	0.1700	Fe ²⁺ -N	0.1769
Fe³⁺-O	0.1765	Fe³⁺-N	0.1815

1. For Fe ion in Fe(L)₂ unit of complex **1**, Fe(III) ion is coordinated with two oxygen atoms and four nitrogen atoms. Assuming the band valence of Fe ion is HS +3, $r_0(\text{Fe}^{3+}\text{-O}) = 0.1765$, $r_0(\text{Fe}^{3+}\text{-N}) = 0.1815$.

$$\begin{aligned} \text{BVS} = & \exp[(0.1765-0.1935)/0.037] + \exp[(0.1765-0.1929)/0.037] + \\ & \exp[(0.1815-0.1895)/0.037] + \exp[(0.1815-0.1887)/0.037] + \\ & \exp[(0.1815-0.1904)/0.037] + \exp[(0.1815-0.1895)/0.037] = 4.49 \end{aligned}$$

This divergence indicates that Fe ion in complex 1 is LS +3, instead of HS Fe(III).

2. For Mn ion in Mn(L)₂ unit of complex **2**, Mn ion is coordinated with two

oxygen atoms and four nitrogen atoms. Assuming the band valence of Mn ion is HS +3, $r_0(\text{Mn}^{3+}\text{-O}) = 0.1732$, $r_0(\text{Mn}^{3+}\text{-N}) = 0.1837$.

$$\begin{aligned} \text{BVS} = & \exp[(0.1732-0.1939)/0.037] + \exp[(0.1732-0.1929)/0.037] + \\ & \exp[(0.1837-0.1924)/0.037] + \exp[(0.1837-0.1950)/0.037] + \\ & \exp[(0.1837-0.1934)/0.037] + \exp[(0.1837-0.1953)/0.037] = 4.19. \end{aligned}$$

This value deviates greatly from the average value of HS Mn^{III} ions, indicating that Mn in complex **2** is LS +3, rather than HS Mn(III).

3. For Mn1 ion in complex **1**, Mn1 ion is coordinated with six oxygen atoms.

Assuming the band valence of Mn1 ion is HS +2, $r_0(\text{Mn}^{2+}\text{-O}) = 0.1765$.

$$\begin{aligned} \text{BVS} = & \exp[(0.1765-0.2183)/0.037] + \exp[(0.1765-0.2183)/0.037] + \\ & \exp[(0.1765-0.2192)/0.037] + \exp[(0.1765-0.2192)/0.037] + \\ & \exp[(0.1765-0.2181)/0.037] + \exp[(0.1765-0.2193)/0.037] = 1.92. \end{aligned}$$

This value is in good agreement with the average oxidation state of HS Mn^{II} ions, indicating Mn1 in complex **1** is HS +2.

4. For Mn2 ion in complex **2**, Mn2 ion is coordinated with six oxygen atoms.

Assuming the band valence of Mn2 ion is HS +2, $r_0(\text{Mn}^{2+}\text{-O}) = 0.1765$.

$$\begin{aligned} \text{BVS} = & \exp[(0.1765-0.2151)/0.037] + \exp[(0.1765-0.2151)/0.037] + \\ & \exp[(0.1765-0.2162)/0.037] + \exp[(0.1765-0.2162)/0.037] + \\ & \exp[(0.1765-0.2167)/0.037] + \exp[(0.1765-0.2167)/0.037] = 2.06. \end{aligned}$$

This value is in good agreement with the average oxidation state of HS Mn^{II} ions, indicating Mn2 in complex **2** is HS +2.

Table S2. The results calculated by SHAPE software.

Complex	Lable	Symmetry	Shape	Deviation value
1-Fe^{III}	HP-6	D _{6h}	Hexagon	29.090
	PPY-6	C _{5v}	Pentagonal pyramid	25.277
	OC-6	O_h	Octahedron	0.588
	TPR-6	D _{3h}	Trigonal prism	13.523
	JPPY-6	C _{5v}	Johnson pentagonal pyramid J2	29.018
1-Mn^{II}	HP-6	D _{6h}	Hexagon	32.164
	PPY-6	C _{5v}	Pentagonal pyramid	24.152
	OC-6	O_h	Octahedron	1.459
	TPR-6	D _{3h}	Trigonal prism	9.607
	JPPY-6	C _{5v}	Johnson pentagonal pyramid J2	27.953
2-Mn^{III}	HP-6	D _{6h}	Hexagon	32.687
	PPY-6	C _{5v}	Pentagonal pyramid	26.027
	OC-6	O_h	Octahedron	0.807
	TPR-6	D _{3h}	Trigonal prism	12.797
	JPPY-6	C _{5v}	Johnson pentagonal pyramid J2	30.224
2-Mn^{II}	HP-6	D _{6h}	Hexagon	30.968
	PPY-6	C _{5v}	Pentagonal pyramid	29.242
	OC-6	O_h	Octahedron	0.085
	TPR-6	D _{3h}	Trigonal prism	16.328
	JPPY-6	C _{5v}	Johnson pentagonal pyramid J2	32.612

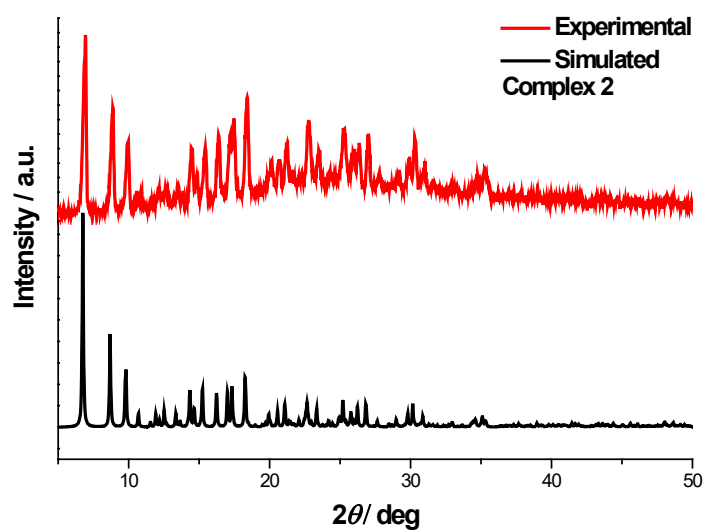
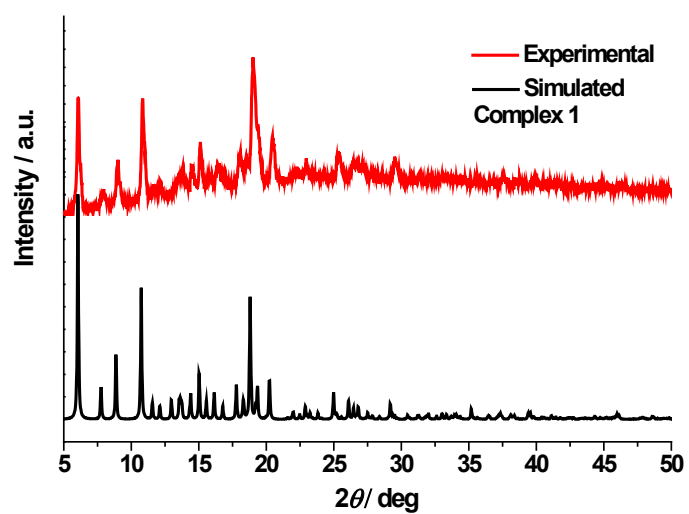


Figure S1. PXRD patterns for complexes 1 and 2 in the range of 5-50 degrees.

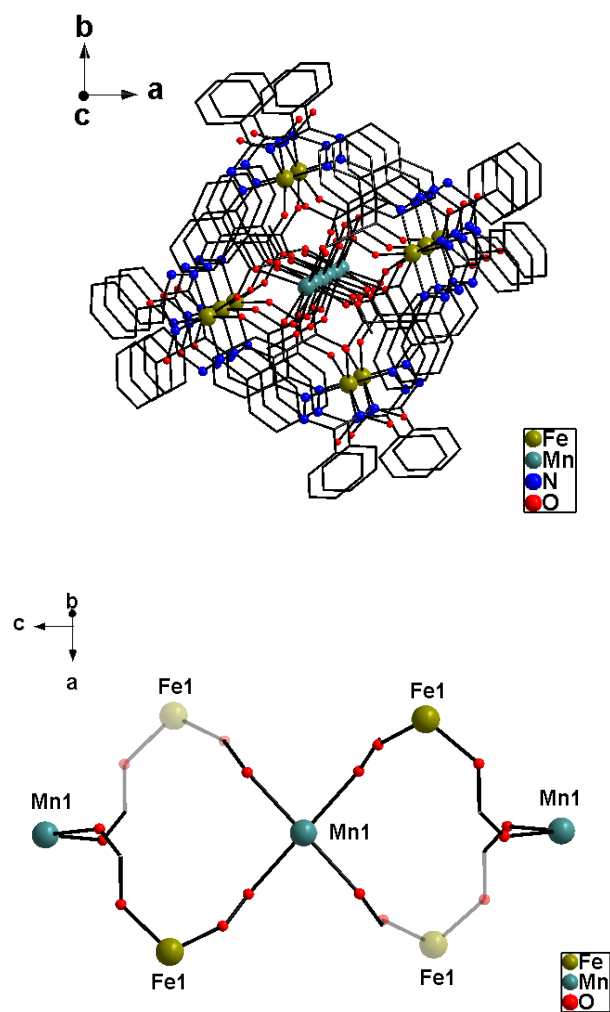


Figure S2. (top) Side view of complex **1** along *c* axis; (bottom) View of the 1D skeleton of Complex **1**. (Fe: dark yellow; Mn: cyan; C: gray; N: blue; O: red.)

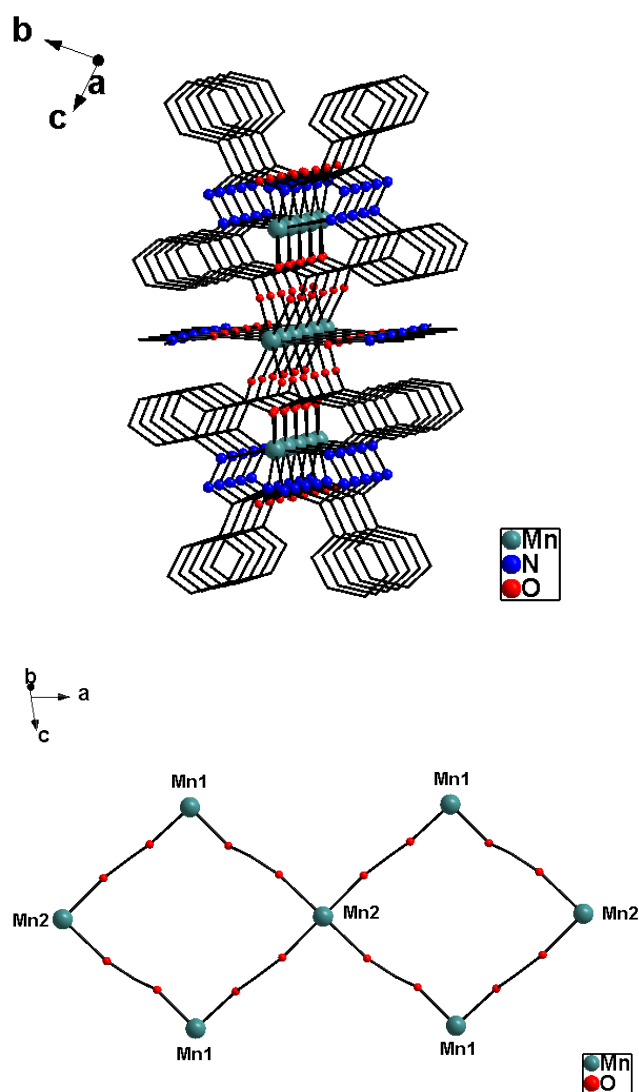


Figure S3. (top) Side view of complex 2 along *a* axis. (bottom) View of the 1D skeleton of Complex 2. (Mn: cyan; C: gray; N: blue; O: red.)

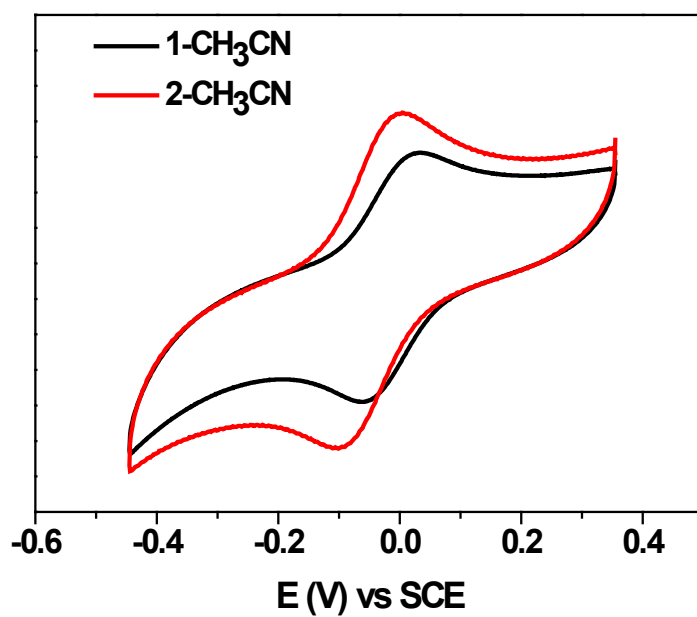


Figure S4. Cyclic voltammograms (scan rate 50 mV s^{-1}) of 10^{-3} M acetonitrile solutions of complexes **1** and **2** at 298 K.

$E(\text{SCE}) = E(\text{NHE}) - 0.242$, $E(\text{Ag}/\text{AgCl, sat. KCl}) = E(\text{NHE}) - 0.197$. Thus, $E(\text{SCE}) = E(\text{Ag}/\text{AgCl, sat. KCl}) - 0.045$.

$E_{1/2}$ is calculated as the average of anodic (E_{pa}) and cathodic (E_{pc}) peak potentials.

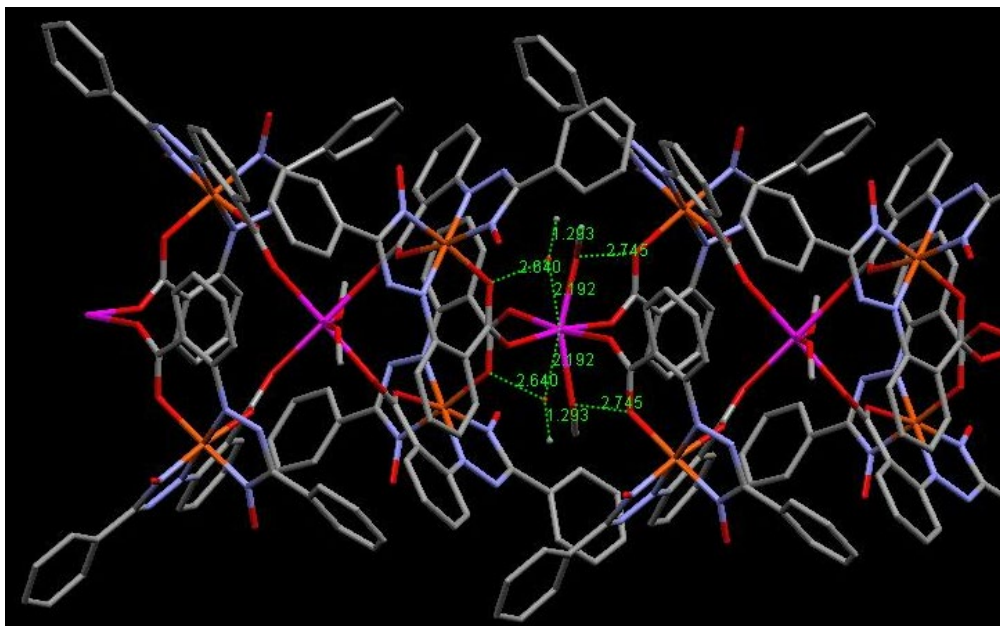


Figure S5. The intrachain hydrogen bonding interaction between the disordered methanol oxygen and the carboxylate oxygen atoms of L²⁻ in complex **1**.