Coordination chemistry of manganese and iron with N,O-donor ligands: oxidation catalysis and magnetochemistry of clusters

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Appendix A1

Table 1: ESI-MS analysis of complex $[Mn_2(Etsalim)_4(HEtsalim)_2](ClO_4)_2$ (**1**) in ethanol and deuterated ethanol. (Chapter 2)

Complex (C_2H_5OH)		**Complex (C_2D_5OD/ C_2H_5OH)**	
Observed peaks(relative intensity)	***Calculated peaks and assignments***	***Observed peaks(relative intensity)***	***Calculated peaks and assignments***
383.15(62%)	383.08, $[MnL_2]^+$	383.15(36%)	383.08, $[MnL_2]^+$
		388.19(72%)	388.11, $[Mn(L)(d_5\text{-}L)]^+$
		393.23(37%)	393.14, $[Mn(d_5\text{-}L)_2]^+$
429.22(100%)	429.12, $[MnL_2(EtOH)]^+$	429.23(45%)	429.12, $[Mn(L)_2(EtOH)]^+$
		434.26(100%)	434.15, $[Mn(L)(d_5\text{-}L)\ (EtOH)]^+$
		439.29(62%)	439.19, $[Mn(d_5\text{-}L)_2\ (EtOH)]^+$
801.31(6%)	801.17, $[Mn_2L_4Cl]^+$	811.46(1%)	811.20, $[Mn_2L_4(EtOH)–H^+]^+$
811.35(2%)	811.20, $[Mn_2L_4(EtOH)–H^+]^+$	816.46(3%)	816.23, $[Mn_2(L)_3(d_5\text{-}L)(EtOH)–H^+]^+$
		821.49(5%)	821.26, $[Mn_2(L)_2(d_5\text{-}L)_2(EtOH)–H^+]^+$
		826.52(4%)	826.29, $[Mn_2(L)(d_5\text{-}L)_3(EtOH)–H^+]^+$
		831.58(1%)	831.32, $[Mn_2(d_5\text{-}L)_4(EtOH)–H^+]^+$
865.30(5%)	865.11 $\{[Mn_2L_4](ClO_4)\}^+$	865.33(<1%)	865.11, $\{[Mn_2(L)_4](ClO_4)\}^+$
		870.32(1%)	870.14, $\{[Mn_2(L)_3(d_5\text{-}L)](ClO_4)\}^+$
		875.36(2%)	875.17, $\{[Mn_2(L)_2(d_5\text{-}L)_2](ClO_4)\}^+$
		880.39(<1%)	880.20, $\{[Mn_2(L)(d_5\text{-}L)_3](ClO_4)\}^+$
		885.38(<1%)	885.23, $\{[Mn_2(d_5\text{-}L)_4](ClO_4)\}^+$

L = Etsalim

All manganese ions are in +III oxidation state unless otherwise stated.

d_5-L = (d_5-Et)salim; d_5-L is caused by exchange reaction of the ethoxy group in Etsalim with deuterated solvent ethanol.

Table 2: ESI-MS analysis of the solution containing the complex $[Mn_2(Etsalim)_4(HEtsalim)_2](ClO_4)_2$ (**1**) + 5 eq NaOH in ethanol and deuterated ethanol. (Chapter 2)

Complex + 5eq NaOH (C_2H_5OH)		**Complex + 5eq NaOH (C_2D_5OD/ C_2H_5OH)**	
Observed peaks(relative intensity)	***Calculated peaks and assignments***	***Observed peaks(relative intensity)***	***Calculated peaks and assignments***
383.19((26%)	383.08, $[MnL_2]^+$	383.22(4%)	383.08, $[MnL_2]^+$
		388.22(10%)	388.11, $[Mn(L)(d_5\text{-}L)]^+$
		393.23(4%)	393.14, $[Mn(d_5\text{-}L)_2]^+$
429.28(100%)	429.12, $[MnL_2(EtOH)]^+$	429.27(5%)	429.12, $[MnL_2(EtOH)]^+$
		434.27(12%)	434.15, $[Mn(L)(d_5\text{-}L)(EtOH)]^+$
		439.27(7%)	439.19, $[Mn(d_5\text{-}L)_2(EtOH)]^+$
451.26(54%)	451.11, $\{Na^+[Mn(L)_2(EtOH)–H^+]\}^+$	451(10%)	451.11, $\{Na^+[Mn(L)_2(EtOH)–H^+]\}^+$
		456.26(24%)	456.14, $\{Na^+[Mn(L)(d_5\text{-}L)(EtOH)–H^+]\}^+$
		461.26(16%)	461.17, $\{Na^+[Mn(d_5\text{-}L)_2(EtOH)–H^+]\}^+$
		468.41(100%)	468.21, $\{Na^+[Mn(d_6\text{-}L)_2(d_6\text{-}EtOH)–H^+]\}^+$
497.28(48%)	497.15, $\{Na^+[Mn(L)_2(EtOH)_2–H^+]\}^+$	497.26(3%)	497.15, $\{Na^+[Mn(L)_2(EtOH)_2–H^+]\}^+$
		502.32(5%)	502.18, $\{Na^+[Mn(L)(d_5\text{-}L)(EtOH)_2–H^+]\}^+$
		507.31(5%)	507.21, $\{Na^+[Mn(d_5\text{-}L)_2(EtOH)_2–H^+]\}^+$
570.35(23%)	570.14, $\{Na^+[Mn(L)_3]\}^+$	570.33(2%)	570.14, $\{Na^+[Mn(L)_3]\}^+$
		575.34(6%)	575.17, $\{Na^+[Mn(L)_2(d_5\text{-}L)]\}^+$
		580.37(8%)	580.20, $\{Na^+[Mn(L)(d_5\text{-}L)_2]\}^+$
		585.38(4%)	585.23, $\{Na^+[Mn(d_5\text{-}L)_3]\}^+$
787.47(8%)	787.14, $\{Na^+[Mn_2(L)_4–2H^+]\}^+$	787.43(<1%)	787.14, $\{Na^+[Mn_2(L)_4–2H^+]\}^+$
		792.42(4%)	792.17, $\{Na^+[Mn_2(L)_3(d_5\text{-}L)–2H^+]\}^+$
		797.45(8%)	797.20, $\{Na^+[Mn_2(L)_2(d_5\text{-}L)_2–2H^+]\}^+$
		802.47(6%)	802.23, $\{Na^+[Mn_2(L)(d_5\text{-}L)_3–2H^+]\}^+$
		807.52(2%)	807.26, $\{Na^+[Mn_2(d_5\text{-}L)_4–2H^+]\}^+$
811.49(12%)	811.20, $[Mn_2L_4(EtOH)–H^+]^+$	811(<2%)	811.20, $[Mn_2L_4(EtOH)–H^+]^+$
		816(<2%)	816.23, $[Mn_2L_3(d_5\text{-}L)(EtOH)–H^+]^+$
		821.53(4%)	821.26, $[Mn_2L_2(d_5\text{-}L)_2(EtOH)–H^+]^+$
833.46(29%)	833.18, $\{Na^+[Mn_2(L)_4(EtOH)–2H^+]\}^+$	833.51(<1%)	833.18, $\{Na^+[Mn_2(L)_4(EtOH)–2H^+]\}$
		838.46(5%)	838.21, $\{Na^+[Mn_2(L)_3(d_5\text{-}L)(EtOH)–2H^+]\}$
		843.51(10%)	843.24, $\{Na^+[Mn_2(L)_2(d_5\text{-}L)_2(EtOH)–2H^+]\}$
850.52(2%)	850.18, $\{Na^+[Mn_2(L)_4(EtOH)(O)–H^+]\}^+$	848(8%)	848.27, $\{Na^+[Mn_2(L)(d_5\text{-}L)_3(EtOH)–2H^+]\}$
		850.55(8%)	850.181, $\{Na^+[Mn_2(L)_4(EtOH)(O)–H^+]\}^+$
		855.63(10%)	855.21, $\{Na^+[Mn_2(L)_3(d_5\text{-}L)(EtOH)(O)–H^+]\}^+$
		860.70(6%)	860.24, $\{Na^+[Mn_2(L)_2(d_5\text{-}L)_2(EtOH)(O)–H^+]\}^+$
952.57(5%)	952.21, $\{Na^+[Mn_2(L)_5–H^+]\}^+$		952.21, $\{Na^+[Mn_2(L)_5–H^+]\}^+$
		959.60(3%)	959.20, $\{Na^+[Mn^{IV}{}_2(L)_4(EtOH)_3(O)_2]\}^+$
		964.56(<2%)	964.24, $\{Na^+[Mn^{IV}{}_2(L)_3(d_5\text{-}L)(EtOH)_3(O)_2]\}^+$
		969.61(<2%)	969.27, $\{Na^+[Mn^{IV}{}_2(L)_2(d_5\text{-}L)_2(EtOH)_3(O)_2]\}^+$
		974.64(<2%)	974.30, $\{Na^+[Mn^{IV}{}_2(L)(d_5\text{-}L)_3(EtOH)_3(O)_2]\}^+$

L = Etsalim

All manganese ions are in +III oxidation state unless otherwise stated.

Appendix A2

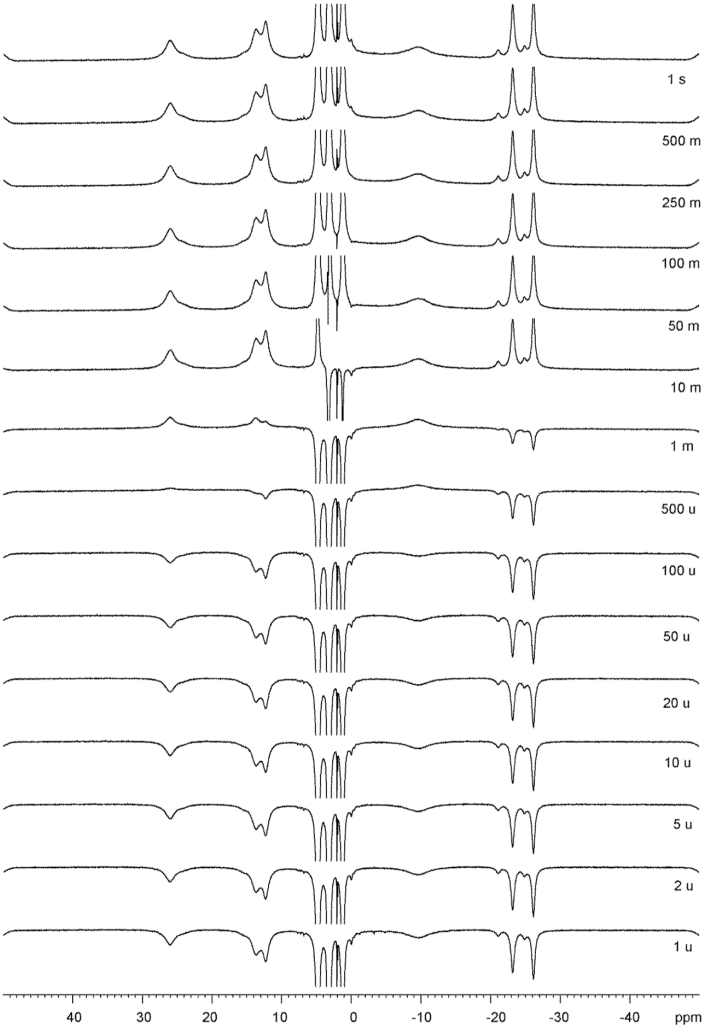

Figure 1: Inversion recovery pulse sequence NMR for the complex $(HNEt_3)$ *trans*-[Mn(*R*-phoxCOO)(*S*-phoxCOO)$(H_2O)_2$] (**RS-5**). (Chapter 3)

Appendix A3

Table 1: Selected bond angles of complex $[Mn_6O_4(OMe)_2(OAc)_4(Mesalim)_4]$ (**3**). (See Chapter 5)

O1–Mn1–O2	89.63(7)	O53–Mn3–O63	98.16(8)
O2_a–Mn2–N39	167.92(8)	O52–Mn1–O71	163.83(7)
O1–Mn1–O52	89.73(8)	O2_a–Mn3–O53	171.73(8)
O1–Mn3–O2	78.31(7)	O52–Mn1–N19	100.66(8)
O1–Mn1–O71	81.52(7)	O53–Mn3–O71_a	92.55(8)
O1–Mn3–O53	94.45(8)	O71–Mn1–N19	88.92(8)
O1–Mn1–N19	169.35(9)	O2_a–Mn3–O63	90.11(7)
O1–Mn3–O63	96.71(8)	O1–Mn2–O37	175.60(8)
O2–Mn1–O17	174.17(8)	O63–Mn3–O71_a	98.94(7)
O1–Mn3–O2_a	84.59(8)	O1–Mn2–O62	88.15(8)
O2–Mn1–O52	89.99(8)	O2_a–Mn3–O71_a	86.06(8)
O1–Mn3–O71_a	161.75(8)	O1–Mn2–O71	79.77(7)
O2–Mn1–O71	76.45(7)	Mn1–O1–Mn2	111.74(9)
O2–Mn3–O53	92.44(7)	O1–Mn2–N39	89.21(8)
O2 –Mn1–N19	92.69(8)	Mn1–O1–Mn3	100.98(9)
O2 –Mn3–O63	168.64(7)	O1–Mn2–O2_a	83.06(8)
O17 –Mn1–O52	95.15(8)	Mn2–O1–Mn3	95.48(8)
O2 –Mn3–O2_a	79.32(7)	O37–Mn2–O62	96.23(8)
O17–Mn1–O71	98.03(8)	Mn1–O2–Mn3	85.53(6)
O2–Mn3–O71_a	84.58(7)	O37–Mn2–O71	95.86(7)
O17–Mn1–N19	89.06(9)	Mn1–O2–Mn2_a	163.06(10)
O2_a–Mn2–O37	97.10(8)	O37–Mn2–N39	89.90(9)
Mn2_a–O2–Mn3	94.25(7)	Mn1–O2–Mn3_a	104.24(8)
O62–Mn2–O71	167.84(7)	Mn2_a–O2–Mn3	94.25(7)
O62–Mn2–N39	95.83(8)	Mn3–O2–Mn3_a	100.68(7)
O2_a–Mn2–O62	93.20(7)	Mn2_a–O2–Mn3_a	92.47(7)
O71–Mn2–N39	85.47(8)	Mn2–O71–Mn3_a	96.56(7)
Mn1–O71–Mn3_a	93.14(8)	Mn1–O71–Mn2	86.85(6)

a = Symmetry code: a: –x, –y, 2–z.

Table 2: Selected Bond angles for complex $[Mn_8O_2(OH)_2(OMe)_{12}(OAc)_2(Mesalim)_4]$ (**4**). (See Chapter 5)

O3–Mn1–O17	175.8(3)	O1–Mn2–O3	76.1(2)
O3–Mn1–O93	85.7(3)	O1–Mn2–O122	101.5(2)
O3–Mn1–O122	76.6(2)	O1–Mn2–O138	153.1(2)
O3–Mn1–O124	85.1(3)	O1–Mn2–O140	98.1(2)
O3–Mn1–N19	91.3(3)	O2–Mn2–O3	92.4(2)
O17–Mn1–O93	98.4(3)	O2–Mn2–O122	175.6(2)
O17–Mn1–O122	99.3(3)	O2–Mn2–O138	77.1(2)
O17–Mn1–O124	93.9(3)	O2–Mn2–O140	84.6(2)
O17–Mn1–N19	89.5(3)	O3–Mn2–O122	84.9(3)
O93–Mn1–O122	162.0(2)	O3 –Mn2–O138	89.0(2)
O93–Mn1–O124	2.166(7)	O3 –Mn2–O140	173.8(2)
O93–Mn1–N19	89.3(3)	O122–Mn2–O138	99.3(2)
O122–Mn1 –O124	92.8(3)	O122–Mn2–O140	98.4(3)
O122–Mn1–N19	86.4(3)	O138–Mn2–O140	95.6(2)
O124–Mn1–N19	90.5(3)	O1–Mn2–O3	76.1(2)
O1–Mn2–O2	175.7(3)	O1–Mn2–O122	101.5(2)
O1–Mn3–O3	84.7(2)	O2–Mn5–O130	97.7(2)
O1–Mn3–O94	167.8(3)	O2–Mn5–O132	102.1(2)
O1–Mn3–O124	99.7(3)	O4–Mn5–O128	88.4(2)
O1–Mn3–O126	84.4(2)	O4–Mn5–O130	173.8(2)
O1–Mn3–O130	76.7(2)	O4–Mn5–O132	84.8(2)
O3–Mn3–O94	93.0(2)	O128–Mn5–O130	96.5(2)
O3–Mn3–O124	79.4(2)	O130–Mn5–O132	98.2(3)
O3–Mn3–O126	164.7(3)	O1–Mn7–O57	176.6(3)
O3–Mn3–O130	96.8(2)	O1–Mn7–O114	84.7(2)
O94–Mn3–O124	91.6(3)	O1–Mn7–O126	76.6(2)
O94–Mn3–O126	99.9(3)	O1–Mn7–O128	87.3(2)
O94–Mn3–O130	91.7(3)	O1–Mn7–N59	89.7(3)
O124–Mn3–O126	92.0(2)	O57–Mn7–O114	92.1(3)
O124–Mn3–O130	175.1(2)	O57–Mn7–O126	106.5(3)
O126–Mn3–O130	91.0(2)	O57–Mn7–O128	93.8(3)
O1–Mn5–O2	80.8(2)	O57–Mn7–N59	89.1(3)
O1–Mn5–O4	93.4(2)	O114–Mn7–O126	161.3(2)
O1–Mn5–O128	77.3(2)	O114–Mn7–O128	85.1(2)
O1–Mn5–O130	84.0(2)	O114–Mn7 –N59	92.7(3)
O1–Mn5–O132	176.1(2)	O126–Mn7–O128	93.1(2)
O2–Mn5–O4	76.3(2)	O126–Mn7–N59	88.1(3)
O2–Mn5–O128	152.4(2)	O128–Mn7–N59	176.4(3)
Mn2–O1–Mn3	91.9(2)	Mn2–O2–Mn6	100.6(3)
Mn2–O1–Mn5	99.0(2)	Mn2–O2–Mn8	103.1(2)
Mn2–O1–Mn7	150.7(3)	Mn5–O2–Mn6	92.0(2)
Mn3–O1–Mn5	100.7(3)	Mn1–O3–Mn2	102.9(3)
Mn3–O1–Mn7	103.3(2)	Mn1–O3–Mn3	100.2(2)
Mn5–O1–Mn7	102.5(3)	Mn2–O3–Mn3	106.6(3)
Mn2–O2–Mn5	99.0(2)	Mn3–O126–Mn7	94.7(2)
Mn3–O130–Mn5	98.1(3)	Mn5–O128–Mn7	92.8(2)

Table 3: Selected bond angles for complex $[Fe_{10}O_4(OMe)_{14}Cl_2(Mesalim)_6]$ (**5**).(See Chapter 5)

O1–Fe1–O17	104.96(12)	O1–Fe2–O111	80.38(10)
O1–Fe1–O71	81.84(11)	O1–Fe2 –N39	97.20(13)
O1–Fe1–O81	82.33(11)	O37–Fe2–O71	103.30(12)
O1–Fe1–O91	93.96(11)	O37–Fe2–O101	99.84(11)
O1–Fe1–N19	166.16(12)	O37–Fe2–O111	96.14(12)
O17–Fe1–O71	96.12(13)	O37–Fe2–N39	86.38(14)
O17–Fe1–O81	171.99(12)	O71–Fe2–O101	156.27(12)
O17–Fe1–O91	98.38(12)	O71–Fe2–O111	90.27(12)
O17–Fe1–N19	86.32(12)	O71–Fe2–N39	87.10(14)
O71–Fe1–O81	88.10(11)	O101–Fe2–O111	92.45(11)
O71–Fe1–O91	165.49(12)	O101–Fe2–N39	89.17(14)
O71–Fe1–N19	89.11(12)	O111–Fe2–N39	176.72(13)
O81–Fe1–O91	77.56(10)	Cl1–Fe3 –O1	102.77(8)
O81–Fe1–N19	86.95(12)	Cl1–Fe3–O2	171.84(8)
O91–Fe1–N19	92.24(12)	Cl1–Fe3–O101	94.77(8)
O1–Fe2 –O37	175.61(12)	Cl1–Fe3 –O121	94.42(8)
O1–Fe2–O71	79.49(12)	Cl1–Fe3–O131	100.87(8)
O1–Fe2–O101	77.74(11)	O1–Fe3 –O2	81.13(11)