

Hydroxy double salts intercalated with Mn(II) complexes as potential contrast agents

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Table S1: X-ray diffraction data for Mn(L¹) intercalates formed with varied reaction conditions.

Molar ratio [Zn ₅ -Cl : Mn(L ¹)]	Volume of water / ml	1 st guest	Interlayer spacing / Å	2 nd guest	Interlayer spacing / Å
5 : 1	10	/	/	Cl ⁻	7.75
5 : 2	10	/	/	Cl ⁻	7.86
5 : 3	10	/	/	Cl ⁻	7.77
5 : 1	5	[Mn(L ¹)] ²⁻	9.73	Cl ⁻	7.71
5 : 2	5	/	/	Cl ⁻	7.71
5 : 3	5	/	/	Cl ⁻	7.71
5 : 1	2	/	/	Cl ⁻	7.82
5 : 2	2	/	/	Cl ⁻	7.77
5 : 3	2	/	/	Cl ⁻	7.77
5 : 1	1	/	/	Cl ⁻	7.75
5 : 2	1	/	/	Cl ⁻	7.84
5 : 3	1	/	/	Cl ⁻	7.86

Table S2: X-ray diffraction data for Mn(L²) intercalates formed with varied reaction conditions.

Molar ratio [Zn ₅ -Cl : Mn(L ²)]	Volume of water / ml	1 st guest	Interlayer spacing / Å	2 nd guest	Interlayer spacing / Å
5 : 1	10	[Mn(L ²)] ²⁻	11.73	Cl ⁻	7.88
5 : 2	10	[Mn(L ²)] ²⁻	11.93	Cl ⁻	7.86
5 : 3	10	[Mn(L ²)] ²⁻	11.68	Cl ⁻	7.79
5 : 1	5	[Mn(L ²)] ²⁻	11.93	Cl ⁻	7.84
5 : 2	5	[Mn(L ²)] ²⁻	11.73	Cl ⁻	7.79
5 : 3	5	[Mn(L ²)] ²⁻	11.73	Cl ⁻	7.77
5 : 1	2	[Mn(L ²)] ²⁻	11.68	Cl ⁻	7.75
5 : 2	2	[Mn(L ²)] ²⁻	11.64	Cl ⁻	7.73
5 : 3	2	[Mn(L ²)] ²⁻	11.54	Cl ⁻	7.71
5 : 1	1	[Mn(L ²)] ²⁻	11.78	Cl ⁻	7.90
5 : 2	1	[Mn(L ²)] ²⁻	11.40	Cl ⁻	7.71
5 : 3	1	[Mn(L ²)] ²⁻	11.73	Cl ⁻	7.85

Table S3: X-ray diffraction data for $\text{Mn}(\text{L}^3)$ intercalates formed with varied reaction conditions.

Molar ratio [$\text{Zn}_5\text{-Cl}$: $\text{Mn}(\text{L}^3)$]	Volume of water / ml	1 st guest	Interlayer spacing / Å	2 nd guest	Interlayer spacing / Å
5 : 1	10	$[\text{Mn}(\text{L}^3)]^{2-}$	11.14	Cl^-	7.79
5 : 2	10	$[\text{Mn}(\text{L}^3)]^{2-}$	11.22	Cl^-	7.86
5 : 3	10	$[\text{Mn}(\text{L}^3)]^{2-}$	10.92	Cl^-	7.75
5 : 1	5	$[\text{Mn}(\text{L}^3)]^{2-}$	10.92	Cl^-	7.77
5 : 2	5	$[\text{Mn}(\text{L}^3)]^{2-}$	11.09	Cl^-	7.82
5 : 3	5	$[\text{Mn}(\text{L}^3)]^{2-}$	10.92	Cl^-	7.75
5 : 1	2	$[\text{Mn}(\text{L}^3)]^{2-}$	11.97	Cl^-	7.77
5 : 2	2	$[\text{Mn}(\text{L}^3)]^{2-}$	11.00	Cl^-	7.82
5 : 3	2	$[\text{Mn}(\text{L}^3)]^{2-}$	11.09	Cl^-	7.79
5 : 1	1	$[\text{Mn}(\text{L}^3)]^{2-}$	11.14	Cl^-	7.86
5 : 2	1	$[\text{Mn}(\text{L}^3)]^{2-}$	11.05	Cl^-	7.71
5 : 3	1	$[\text{Mn}(\text{L}^3)]^{2-}$	11.18	Cl^-	7.86

Table S4: X-ray diffraction data for $\text{Mn}_2(\text{L}^4)_2$ intercalates formed with varied reaction conditions.

Molar ratio [$\text{Zn}_5\text{-Cl}$: $\text{Mn}_2(\text{L}^4)_2$]	Volume of water / ml	1 st guest	Interlayer spacing / Å	2 nd guest	Interlayer spacing / Å
5 : 1	10	/	/	Cl^-	7.75
5 : 2	10	$[\text{Mn}_2(\text{L}^4)_2]^{2-}$	9.94	Cl^-	7.75
5 : 3	10	$[\text{Mn}_2(\text{L}^4)_2]^{2-}$	10.11	Cl^-	7.86
5 : 1	5	/	/	Cl^-	7.75
5 : 2	5	$[\text{Mn}_2(\text{L}^4)_2]^{2-}$	9.97	Cl^-	7.75
5 : 3	5	$[\text{Mn}_2(\text{L}^4)_2]^{2-}$	10	Cl^-	7.77
5 : 1	2	/	/	Cl^-	7.86
5 : 2	2	/	/	Cl^-	7.77
5 : 3	2	$[\text{Mn}_2(\text{L}^4)_2]^{2-}$	10.15	Cl^-	7.84
5 : 1	1	/	/	Cl^-	7.86
5 : 2	1	$[\text{Mn}_2(\text{L}^4)_2]^{2-}$	10.15	Cl^-	7.82
5 : 3	1	/	/	Cl^-	7.86

Table S5: Proton relaxivities of all Mn complex intercalates.

Complex	Molar ratio [Zn ₅ -Cl : Mn complex]	Volume of water / ml	[Mn] / mM	T_1 / ms	T_2 / ms	r_1 / s ⁻¹ mM ⁻¹	r_2 / s ⁻¹ mM ⁻¹
[Mn(L¹)]²⁻	5 : 1	5	0.83	1019.83 ± 13.20	69.32 ± 0.07	1.19 ± 0.02	17.43 ± 0.02
	5 : 1	5	1.80	421.50 ± 0.30	42.77 ± 0.03	1.32 ± 0.001	12.99 ± 0.009
[Mn(L²)]²⁻	5 : 1	10	0.79	1265.00 ± 3.00	113.87 ± 0.42	1.01 ± 0.002	11.19 ± 0.04
	5 : 3	10	2.55	336.67 ± 0.58	95.00 ± 0.10	1.17 ± 0.002	4.13 ± 0.004
	5 : 1	5	0.92	1369.00 ± 1.50	72.22 ± 0.10	0.79 ± 0.46	15.02 ± 0.01
	5 : 2	5	1.65	672.57 ± 1.01	54.99 ± 0.08	0.90 ± 0.001	11.00 ± 0.016
	5 : 3	5	2.12	983.67 ± 4.04	59.27 ± 0.12	0.48 ± 0.002	7.97 ± 0.016
	5 : 2	2	1.29	349.37 ± 1.17	37.24 ± 0.07	2.22 ± 0.007	20.87 ± 0.037
	5 : 3	2	2.66	296.43 ± 0.29	43.80 ± 0.03	1.27 ± 0.001	8.59 ± 0.006
	5 : 3	1	2.19	474.20 ± 1.30	51.92 ± 0.18	0.96 ± 0.003	8.78 ± 0.03
[Mn(L³)]²⁻	5 : 2	10	2.37	697.67 ± 12.74	86.13 ± 0.15	0.61 ± 0.01	4.90 ± 0.009
	5 : 3	10	2.20	494.67 ± 0.58	78.40 ± 0.10	0.92 ± 0.001	5.80 ± 0.007
	5 : 1	5	1.00	1479.00 ± 2.12	91.98 ± 0.20	0.67 ± 0.40	10.85 ± 0.02
	5 : 3	5	1.93	381.00 ± 1.15	63.90 ± 0.08	1.36 ± 0.004	8.10 ± 0.01
	5 : 1	2	0.28	1297.33 ± 10.69	79.13 ± 0.15	2.78 ± 0.023	45.21 ± 0.09
	5 : 2	2	1.57	568.03 ± 1.85	48.82 ± 0.07	1.12 ± 0.003	13.06 ± 0.02
	5 : 3	2	1.36	300.90 ± 0.60	53.22 ± 0.04	2.45 ± 0.004	13.86 ± 0.01
	5 : 2	1	2.05	432.67 ± 1.00	58.24 ± 0.02	1.13 ± 0.003	8.39 ± 0.003
[Mn₂(L⁴)₂]²⁻	5 : 3	1	2.34	243.53 ± 0.31	46.38 ± 0.05	1.75 ± 0.002	9.21 ± 0.01
	5 : 2	10	0.35	255.20 ± 0.61	48.64 ± 0.15	11.20 ± 0.03	58.74 ± 0.06
	5 : 3	10	0.63	150.40 ± 1.15	41.70 ± 0.10	10.64 ± 0.08	38.37 ± 0.09
	5 : 1	5	0.35	265.20 ± 0.20	48.43 ± 0.02	10.80 ± 0.004	58.90 ± 0.004
	5 : 2	5	0.43	212.67 ± 0.58	61.47 ± 0.15	11.06 ± 0.03	38.28 ± 0.10
	5 : 3	5	0.61	147.10 ± 0.28	40.49 ± 0.07	11.24 ± 3.24	40.82 ± 0.07
	5 : 3	2	0.61	96.53 ± 0.39	24.20 ± 0.03	17.12 ± 0.07	68.31 ± 0.08
	5 : 2	1	0.61	123.82 ± 0.54	25.01 ± 0.04	13.24 ± 0.06	65.55 ± 0.10