# Red/Green-light emission in continuous dielectric phase transitions materials: $[Me_3NVinyl]_2[MnX_4]$ (X = Cl, Br)

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**Synthesis of the title complexes**

**Synthesis of the complex 1**

Trimethylvinyl ammonium chloride (5 mmol, 0.612 g) and manganese chloride (5 mmol, 0.629 g) were dissolved in 12mL methanol solution with stirring. The resultant clear solution was allowed to stand at room temperature. Two days later, green block-shaped crystals of complex **1** were deposited from the solution in approximately 37.5% yield based on Mn. -Anal. calcd. (%) for $C_{10}H_{24}N_2Cl_4Mn$: C 32.54, H 6.55, N 7.59; found C 32.78, H 8.05, N 7.26. – FT-IR (KBr, $cm^{-1}$): 3450(w), 3110(m), 3026(s), 3000(m), 1660(s), 1462(s), 1412(m), 1248(w), 1070(w), 954(s), 896(s), 710(m).

**Synthesis of the complex 2**

Trimethylvinyl ammonium bromine (5 mmol, 0.830 g) and manganese bromide (5 mmol, 1.074 g) were dissolved in 20mL of 40% hydrobromic acid solution with stirring. The resultant clear solution was allowed to place at the temperature 48°C. One week later, orange block-shaped crystals of complex **2** were deposited from the solution in approximately 22.5% yield based on Mn. -Anal. calcd. (%) for $C_{10}H_{24}Br_4MnN_2$: C 21.96, H 4.42, N 5.12; found C 22.03, H 4.55, N 5.22. – FT-IR (KBr, $cm^{-1}$): 3462(w), 3112(m), 3024(s), 3004(m), 1660(s), 1486(s), 1412(m), 1246(w), 1066(w), 952(s), 894(s), 706(m).

**Figure Captions**

**Fig. S1** Infrared spectrum of solid complex **1** in KBr pellets recorded at room temperature.

**Fig. S2** Infrared spectrum of solid complex **2** in KBr pellets recorded at room temperature.

**Fig. S3** DSC curves of complex **2** obtained in the heating-cooling cycles from 280 to 400 K.

**Fig. S4** Molecular structure diagrams of complex **1** shown at different temperatures. (a) 200K, (b) 303 K, (c) 348 K

**Fig. S5** Hydrogen network diagrams of complex **1** at 200 K

**Fig. S6** Hydrogen network diagrams of complex **1** at 303 K

**Fig. S7** Hydrogen network diagrams of complex **2** at 348 K

**Fig. S8** Molecular structure diagrams of complex **2** shown at different temperatures. (a) 173K, (b) 223K

**Fig. S9** Hydrogen network diagrams of complex **2** at 173 K

**Fig. S10** Hydrogen network diagrams of complex **2** at 223 K

**Fig. S11** The dielectric losses of complex **1** at various frequencies with variation of the temperature.

**Fig. S12** DSC curves of complex **1** obtained in three heating-cooling cycles.

**Fig. S13** DSC curves of complex **2** obtained in three heating-cooling cycles.

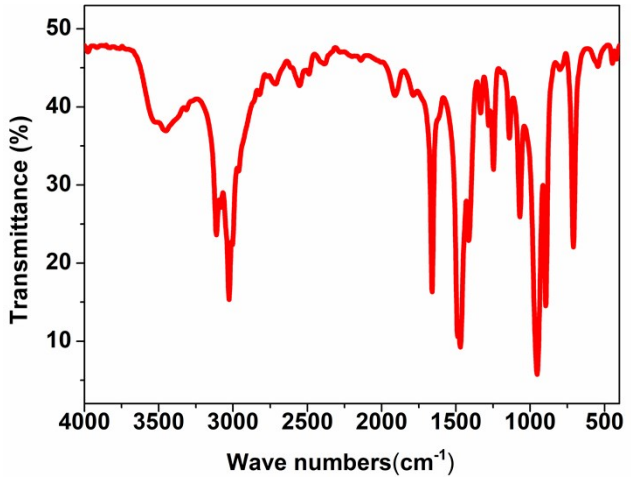


**Figure S1**

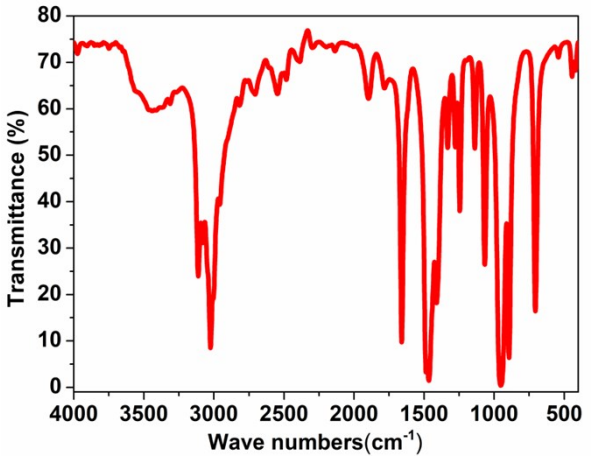


**Figure S2**

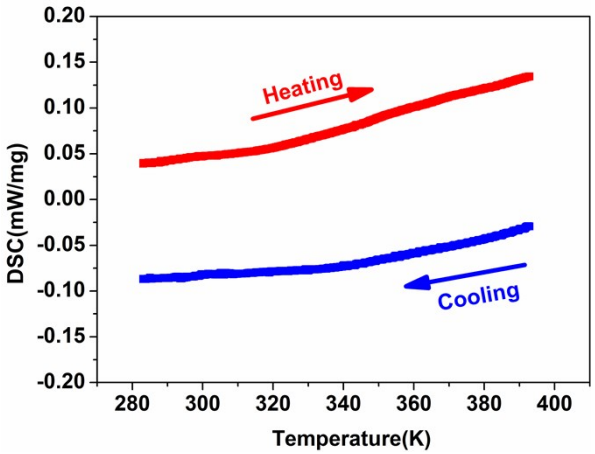


**Figure S3**

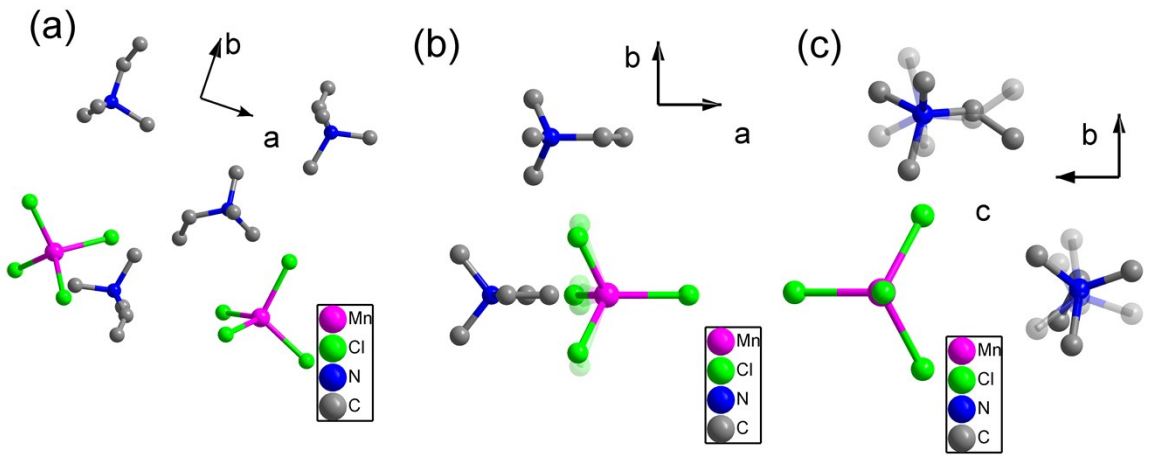


**Figure S4**

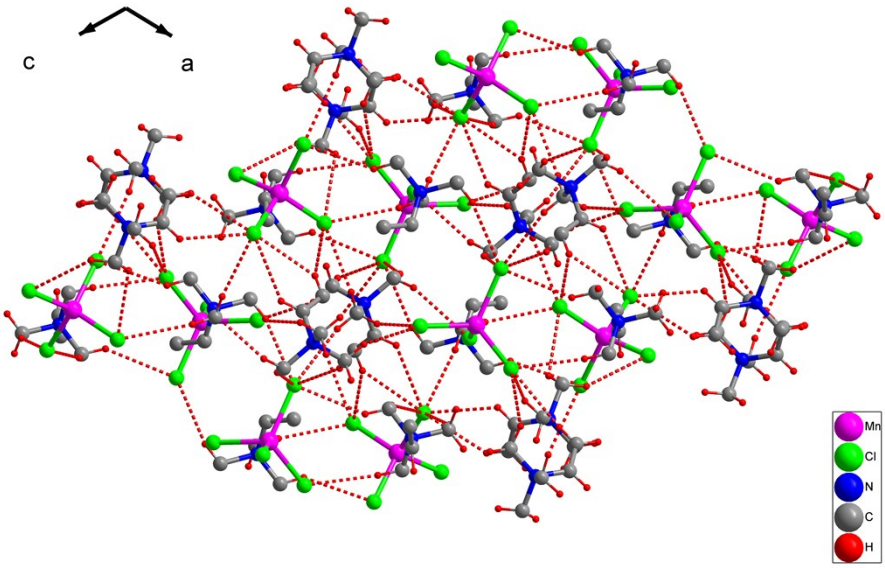


**Figure S5**

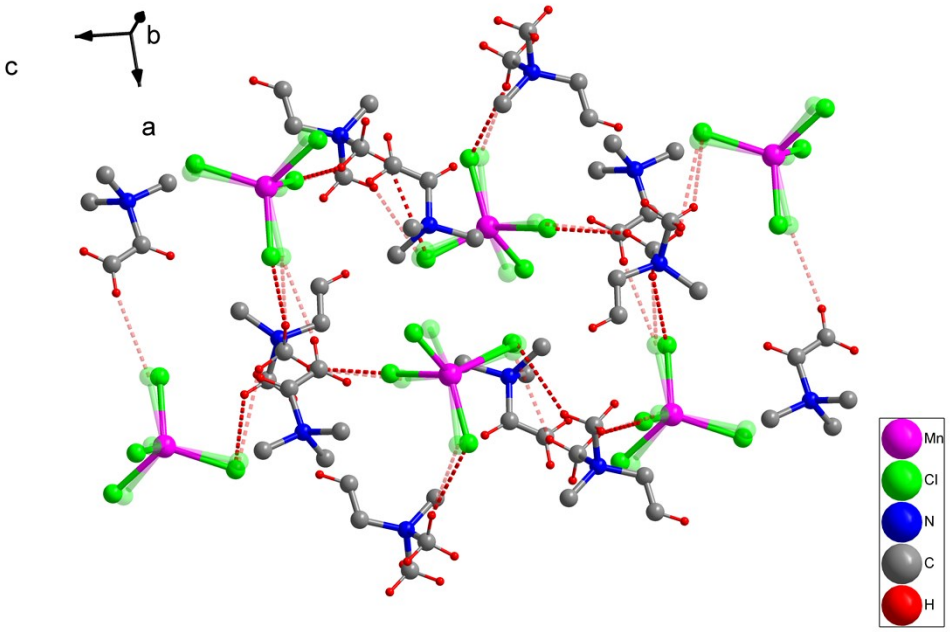


**Figure S6**

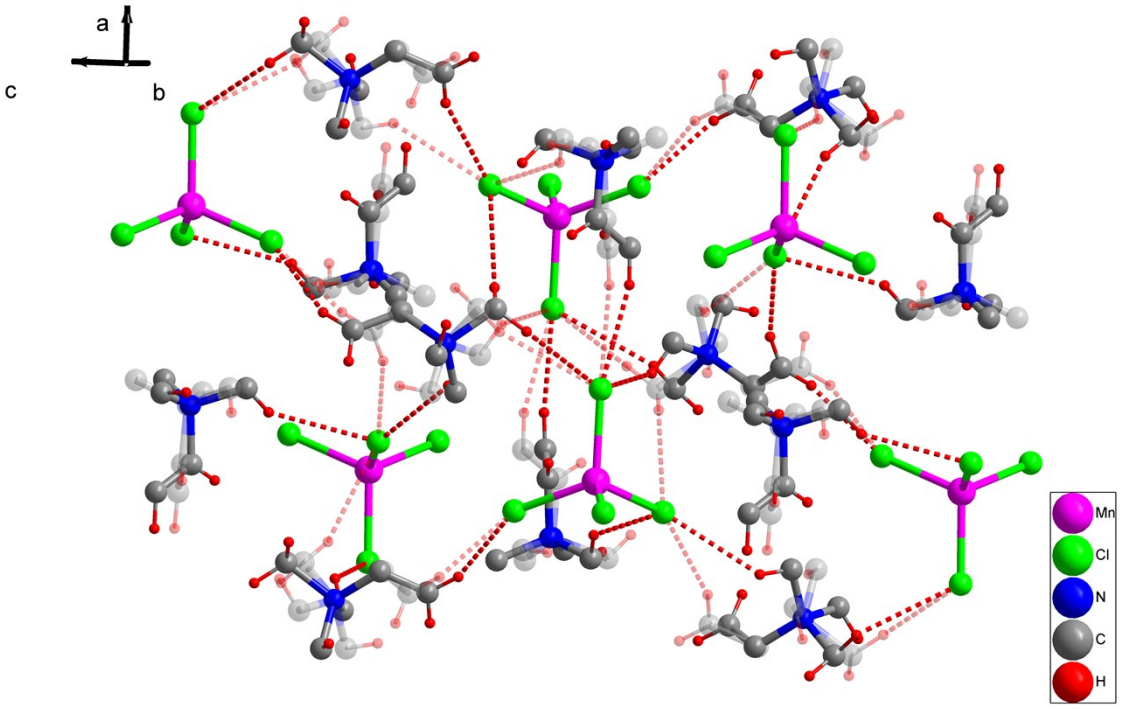


**Figure S7**

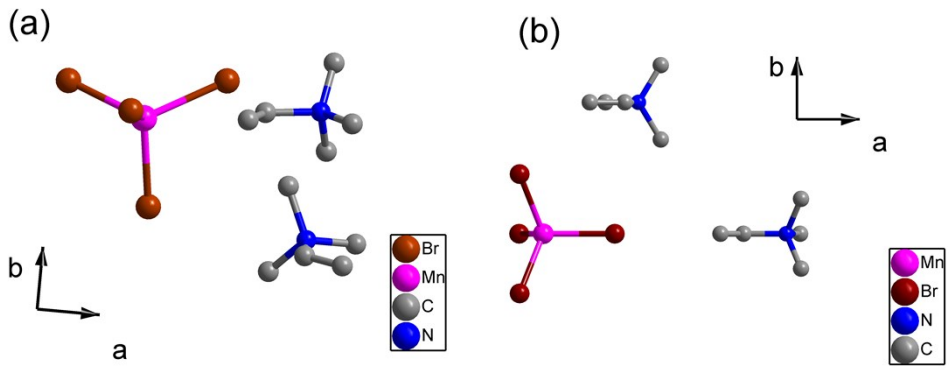


**Figure S8**

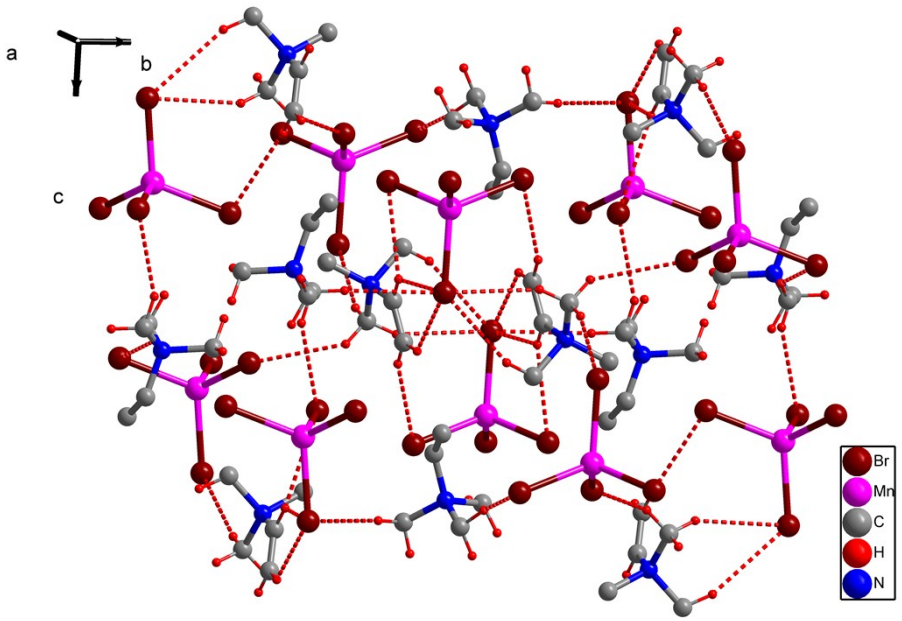


**Figure S9**

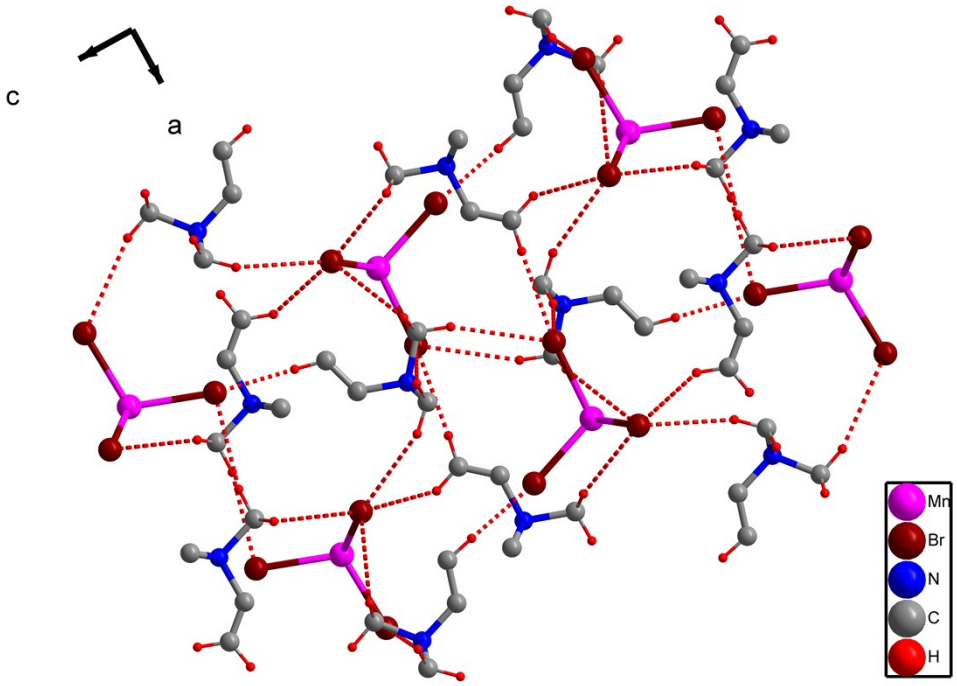


**Figure S10**

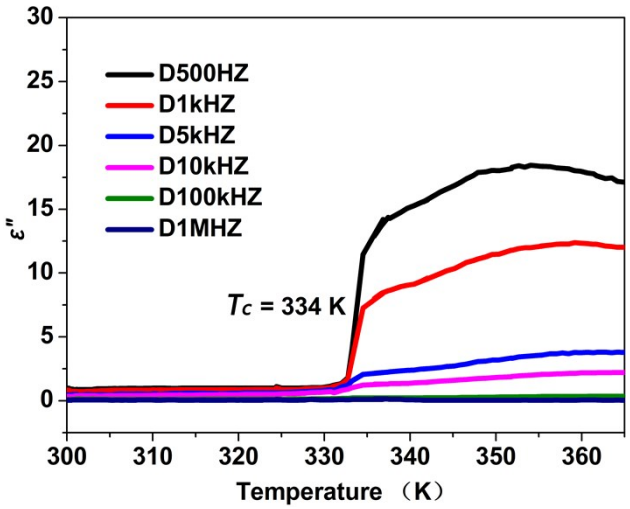


**Figure S11**

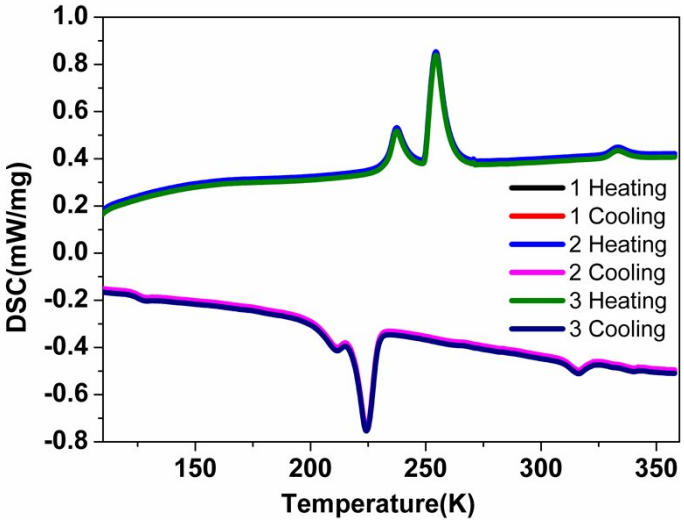


**Figure S12**

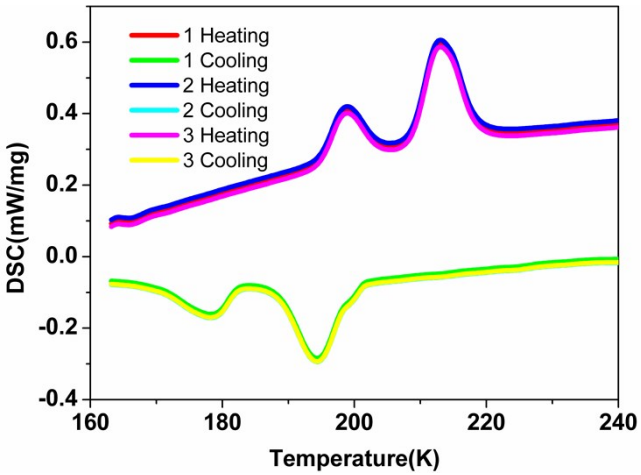


**Figure S13**

**Table S1**. Summary of crystallographic data for complex **1**

| **1** | $\delta$ phase (200 K) | $\beta$ *Phase* (303K) | $\alpha$ phase (348K) |
|---|---|---|---|
| Empirical formula | $C_{10}H_{24}N_2Cl_4Mn$ | $C_{10}H_{24}N_2Cl_4Mn$ | $C_{10}H_{24}N_2Cl_4Mn$ |
| Formula weight | 369.05 | 369.05 | 369.06 |
| T, K | 200.00(10) | 303 | 348(2) |
| Crystal system, space group | Monoclinic, $P2_1/c$ | Orthorhombic, *Pnma* | Orthorhombic, *Pnma* |
| *a*, Å | 18.2344(10) | 13.1299(9) | 13.1016(14) |
| *b*, Å | 12.6038(4) | 8.8855(10) | 9.0403(12) |
| *c,* Å | 18.1345(10) | 16.1959(14) | 16.1804(19) |
| *β*, deg | 119.224(7) | 90 | 90 |
| *V*, Å$^{-3}$ | 3637.2(4) | 1889.5(3) | 1916.4(4) |
| *Z* | 8 | 4 | 4 |
| $D_{calc.}$, mg m$^{-3}$ | 1.348 | 1.297 | 1.283 |
| $\mu$, mm$^{-1}$ | 11.178 | 1.249 | 1.232 |
| *F* (000), e | 1528.0 | 764.0 | 768.0 |
| $2\vartheta$ range, deg | 5.554 → 154.514 | 3.994 → 50.994 | 4 → 60.202 |
| *hkl* range | -22 ⩽ *h* ⩽ 22 | -15 ⩽ *h* ⩽ 15 | -15 ⩽ *h* ⩽ 17 |
| | -15 ⩽ *k* ⩽ 15 | -9 ⩽ *k* ⩽ 10 | -11 ⩽ *k* ⩽ 11 |
| | -22 ⩽ *l* ⩽ 22 | -19 ⩽ l ⩽ 18 | -20 ⩽ *l* ⩽ 20 |
| Data/Restraints/parameters | 12898/221/320 | 1823/227/121 | 2365/166/139 |
| Reflections collected/unique | 12898 / 12898 | 10208 / 1823 | 10811 / 2365 |
| $R_{int}$ | 0.0326 | 0.0486 | 0.0472 |
| Goodness-of-fit on $F^2$ | 1.089 | 1.148 | 1.086 |
| $R_1/wR_2$ [$I > 2\sigma(I)$] | 0.0655 / 0.1787 | 0.0913 / 0.2426 | 0.0915 / 0.2407 |
| $R_1/wR_2$ (all data) | 0.0809 / 0.2027 | 0.1323 / 0.2602 | 0.1622 / 0.2765 |
| Largest peak and hole (e Å$^{-3}$) | 0.58/-0.58 | 0.83/-0.66 | 0.55/-0.40 |

**Table S2**. Selected bond lengths and bond angles of complex **1** at 200 K

| Bond lengths | Å | Bong angles | deg |
|---|---|---|---|
| Mn01-Cl03 | 2.370(18) | Cl03-Mn01-Cl06 | 111.10(7) |
| Mn01-Cl06 | 2.375(2) | Cl09-Mn01-Cl03 | 109.17(8) |
| Mn01-Cl09 | 2.362(18) | Cl09-Mn01-Cl06 | 108.20(8) |
| Mn01-Cl0A | 2.353(18) | Cl0A-Mn01-Cl03 | 111.57(8) |
| Mn1_5-Cl2_5 | 2.353(19) | Cl0A-Mn01-Cl06 | 107.55(8) |
| Mn1_5-Cl3_5 | 2.361(17) | Cl0A-Mn01-Cl09 | 109.17(9) |
| Mn1_5-Cl4_5 | 2.344(19) | Cl2_5-Mn1_5-Cl3_5 | 107.54(7) |
| Mn1_5-Cl1_5 | 2.358(18) | Cl2_5-Mn1_5-Cl1_5 | 107.99(8) |
| C4_2-C5_2 | 1.299(9) | Cl4_5-Mn1_5-Cl3_5 | 112.97(9) |
| C4_3-C5_3 | 1.294(8) | Cl4_5-Mn1_5-Cl3_5 | 109.29(7) |
| C4_1-C5_1 | 1.304(7) | Cl4_5-Mn1_5-Cl1_5 | 109.12(8) |
| C4_4-C5_4 | 1.281(9) | Cl1_5-Mn1_5-Cl3_5 | 109.89(8) |

**Table S3.** Selected bond lengths and bond angles of complex **1** at 303 K

| Bond lengths | Å | Bong angles | deg |
|---|---|---|---|
| Mn1-Cl1 | 2.303(10) | Cl2-Mn1-Cl3 | 107.8(14) |
| Mn1-Cl1A | 2.342(4) | Cl1-Mn1-Cl2 | 114.1(15) |
| Mn1-Cl2 | 2.306(10) | Cl1-Mn1-Cl3 | 115.0(15) |
| Mn1-Cl2A | 2.335(4) | Cl3A-Mn1-Cl1A | 112.4(5) |
| Mn1-Cl3 | 2.311(10) | Cl2A-Mn1-Cl1A | 107.6(3) |
| Mn1-Cl3A | 2.341(5) | Cl2A-Mn1-Cl3A | 111.9(4) |
| C3-C4 | 1.193(9) | $Cl1^{\#1}$-Mn1-Cl2 | 114.1(15) |
| C7-C8 | 1.209(9) | $Cl1^{\#1}$-Mn1-Cl3 | 115.0(15) |

Symmetry transformations used to generate equivalent atoms: $^{\#1}$ +*X*, -1/2-*Y*, +*Z*

**Table S4.** Selected bond lengths and bond angles of complex **1** at 348 K

| Bond lengths | Å | Bong angles | deg |
|---|---|---|---|
| Mn1-Cl3 | 2.325(3) | Cl3-Mn1-Cl2 | 111.62(16) |
| Mn1-Cl1 | 2.332(2) | Cl3-Mn1-Cl1 | 108.20(11) |
| Mn1-Cl2 | 2.353(3) | Cl1-Mn1-Cl2 | 107.94(10) |

| | | | |
|---|---|---|---|
| C4_2-C5_2 | 1.337(9) | C4_1-C5_1 | 1.342(9) |

**Table S5**. Summary of crystallographic data for complex **2**

| **2** | $\gamma$ phase (173 K) | $\alpha$ phase (223 K) |
|---|---|---|
| Empirical formula | $C_{10}H_{24}N_2Br_4Mn$ | $C_{10}H_{24}N_2Br_4Mn$ |
| Formula weight | 546.89 | 546.89 |
| *T*, K | 173(2) | 223(2) |
| Crystal system, space group | Monoclinic, $P2_1/c$ | Orthorhombic, *Pnma* |
| *a*, Å | 9.2339(6) | 13.4500(3) |
| *b*, Å | 15.1859(10) | 9.1134(2) |
| *c,* Å | 13.7409(8) | 16.4176(5) |
| *β*, deg | 91.494(6) | 90 |
| *V*, Å$^{-3}$ | 1926.2(2) | 2012.40(9) |
| *Z* | 4 | 4 |
| $D_{calc.}$, mg m$^{-3}$ | 1.886 | 1.805 |
| $\mu$, mm$^{-1}$ | 8.969 | 14.522 |
| *F* (000), e | 1052 | 1052.0 |
| $2\vartheta$ range, deg | 3.998 → 50.018 | 8.498 →153.886 |
| *hkl* range | $-10 \leqslant h \leqslant 10$ | $-11 \leqslant h \leqslant 16$ |
| | $-18 \leqslant k \leqslant 18$ | $-10 \leqslant k \leqslant 11$ |
| | $-16 \leqslant l \leqslant 16$ | $-20 \leqslant l \leqslant 20$ |
| Data/Restraints/parameters | 3390 / 0 / 160 | 2135/113/96 |
| Reflections collected/unique | 15699 / 3390 | 7663 / 2135 |
| $R_{int}$ | 0.1208 | 0.0430 |
| Goodness-of-fit on $F^2$ | 1.121 | 1.051 |
| $R_1/wR_2$ [$I > 2\sigma(I)$] | 0.1271/ 0.2087 | 0.1182 / 0.2712 |
| $R_1/wR_2$ (all data) | 0.1680 / 0.2253 | 0.1417 / 0.2835 |
| Largest peak and hole (e Å$^{-3}$) | 1.50 / -0.72 | 1.24/-0.80 |

**Table S6.** Selected bond lengths and angles of complex **2** at 173 K

| Bond lengths | Å | Bong angles | deg |
|---|---|---|---|
| Br1-Mn1 | 2.505(3) | Br4-Mn1-Br1 | 118.26(12) |
| Br2-Mn1 | 2.535(3) | Br4-Mn1-Br3 | 105.57(11) |
| Br3-Mn1 | 2.510(3) | Br1-Mn1-Br3 | 107.14(11) |
| Br4-Mn1 | 2.500(3) | Br4-Mn1-Br2 | 106.37(11) |
| C4-C5 | 1.29(3) | Br1-Mn1-Br2 | 105.50(11) |
| C9-C10 | 1.26(3) | Br3-Mn1-Br2 | 114.36(12) |

**Table S7.** Selected bond lengths and angles of complex **2** at 223 K

| Bond lengths | Å | Bong angles | deg |
|---|---|---|---|
| Br1-Mn1 | 2.472(2) | Br1-Mn1-Br2 | 107.50(10) |
| Br3-Mn1 | 2.474(3) | Br1-Mn1-Br3 | 108.14(9) |
| Br2-Mn1 | 2.502(4) | Br3-Mn1-Br2 | 112.05(15) |
| C3-C4 | 1.221(18) | $Br1^{\#1}$-Mn1-Br2 | 107.50(10) |
| C8-C7 | 1.263(17) | $Br1^{\#1}$-Mn1-Br1 | 113.60(15) |

Symmetry transformations used to generate equivalent atoms: $^{\#1}$ +*X*, 1/2-*Y*, +*Z*