**Supplementary Materials for the paper**

**Incorporation of Hexanuclear Mn(II,III) carboxylate clusters with a {Mn6O2} core in polymeric structures**

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**Table S1.** Selected bond distances (Å) in **1** – **6**.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| 1 | 2 | 3 | 4 | 5 | 6 |
| Mn(1)-O(1) 1.8908(14)  Mn(2)-O(1) 1.9009(14)  Mn(4)-O(1) 2.1623(14)  Mn(5)-O(1) 2.1609(14)  Mn(1)-O(2) 1.8918(14)  Mn(2)-O(2) 1.8880(14)  Mn(3)-O(2) 2.1812(14)  Mn(6)-O(2) 2.1435(14)  Mn(1)-O(39) 1.9405(15)  Mn(1)-O(33) 1.9705(15)  Mn(1)-O(35) 2.2383(14)  Mn(1)-O(43) 2.2457(15)  Mn(2)-O(16) 1.9497(15)  Mn(2)-O(18) 1.9761(15)  Mn(2)-O(14) 2.2326(14)  Mn(2)-O(31) 2.2366(15)  Mn(3)-O(15) 2.1131(16)  Mn(3)-O(40) 2.1214(15)  Mn(3)-O(38) 2.1797(15)  Mn(3)-O(4) 2.2166(16)  Mn(3)-O(35) 2.2933(14)  Mn(4)-O(36) 2.1102(16)  Mn(4)-O(17) 2.1177(15)  Mn(4)-O(23) 2.2008(15)  Mn(4)-O(11) 2.2328(16)  Mn(4)-O(14) 2.2944(14)  Mn(5)-O(32) 2.0972(16)  Mn(5)-O(24) 2.1216(16)  Mn(5)-O(34) 2.2215(16)  Mn(5)-O(12) 2.2264(16)  Mn(5)-O(43) 2.2800(15)  Mn(6)-O(42) 2.0937(16)  Mn(6)-O(37) 2.1270(16)  Mn(6)-O(19) 2.1946(16)  Mn(6)-O(21) 2.2067(16)  Mn(6)-O(31) 2.3379(15)  Mn(1)…Mn(2) 2.8235(4)  Mn(1)…Mn(3) 3.1419(4)  Mn(1)…Mn(5) 3.1541(4)  Mn(2)…Mn(4) 3.1515(4)  Mn(2)…Mn(6) 3.1549(4) | Mn(1)-O(1) 1.890(2)  Mn(2)-O(1) 2.180(2)    Mn(1)-O(2) 1.892(1)  Mn(3)-O(2) 2.173(2)  Mn(1)-O(4) 1.949(3)  Mn(1)-O(3) 1.971(3)  Mn(1)-O(5) 2.249(3)  Mn(1)-O(6)1 2.254(3)  Mn(2)-O(7) 2.123(3)  Mn(2)-O(11) 2.127(4)  Mn(2)-O(8) 2.125(3)  Mn(2)-O(12) 2.265(4)  Mn(2)-O(5) 2.342(3)  Mn(3)-O(10) 2.091(4)  Mn(3)-O(13) 2.108(4)  Mn(3)-O(9) 2.189(3)  Mn(3)-O(14) 2.249(5)  Mn(3)-O(6) 2.342(3)  Mn(1)…Mn(1)12.819(1)  Mn(1)…Mn(2) 3.162(1)  Mn(1)…Mn(3)13.166(1)  #1 -x+1,y,-z+1/2 | Mn(1)-O(1) 1.894(2)  Mn(2)-O(1) 1.889(2)  Mn(4)-O(1) 2.172(2  Mn(5)-O(1) 2.161(2)  Mn(1)-O(2) 1.888(2)  Mn(2)-O(2) 1.890(2)  Mn(3)-O(2) 2.168(2)  Mn(6)-O(2) 2.176(2)  Mn(1)-O(8) 1.945(2)  Mn(1)-O(20) 1.963(2)  Mn(1)-O(5) 2.225(2)  Mn(1)-O(21) 2.261(2)  Mn(2)-O(15) 1.940(2)  Mn(2)-O(11) 1.978(2)  Mn(2)-O(10) 2.220(2)  Mn(2)-O(13) 2.248(2)  Mn(3)-O(14) 2.107(2)  Mn(3)-O(18) 2.108(2)  Mn(3)-O(19) 2.201(2)  Mn(3)-O(25) 2.236(3)  Mn(3)-O(21) 2.324(2)  Mn(4)-O(22) 2.131(2)  Mn(4)-O(4) 2.132(2)  Mn(4)-O(12) 2.203(2)  Mn(4)-O(23) 2.257(2)  Mn(4)-O(13) 2.264(2)  Mn(5)-O(9) 2.128(2)  Mn(5)-O(3) 2.134(2)  Mn(5)-O(7) 2.143(2)  Mn(5)-O(27) 2.190(2)  Mn(5)-O(5) 2.399(2)  Mn(6)-O(6) 2.139(2)  Mn(6)-O(17) 2.141(2)  Mn(6)-O(16) 2.141(2)  Mn(6)-O(28) 2.240(3)  Mn(6)-O(10) 2.327(2)  Mn(1)…Mn(2) 2.8185(6)  Mn(1)…Mn(3) 3.1746(6)  Mn(1)…Mn(5) 3.1900(6)  Mn(2)…Mn(4) 3.1421(6)  Mn(2)…Mn(6) 3.1555(6) | Mn(1)-O(1) 1.895(4)  Mn(2)-O(1) 1.883(4)  Mn(4)-O(1) 2.149(4)  Mn(5)-O(1) 2.208(4)  Mn(1)-O(2) 1.885(4)  Mn(2)-O(2) 1.883(4)  Mn(3)-O(2) 2.214(4)  Mn(6)-O(2) 2.155(4)  Mn(1)-O(4) 1.943(5)  Mn(1)-O(3) 1.958(5)  Mn(1)-O(5) 2.218(4)  Mn(1)-O(10) 2.220(4)  Mn(2)-O(7) 1.956(5)  Mn(2)-O(6) 1.964(5)  Mn(2)-O(12) 2.235(5)  Mn(2)-O(9) 2.250(5)  Mn(3)-O(25) 2.129(6)  Mn(3)-O(28) 2.148(6)  Mn(3)-O(14) 2.159(5)  Mn(3)-O(26) 2.223(5)  Mn(3)-O(5) 2.269(5)  Mn(4)-O(19) 2.112(5)  Mn(4)-O(11) 2.119(5)  Mn(4)-O(17) 2.139(6)  Mn(4)-O(9) 2.341(5)  Mn(4)-N(2) 2.375(6)  Mn(5)-O(13) 2.129(6)  Mn(5)-O(16) 2.143(5)  Mn(5)-O(24) 2.163(6)  Mn(5)-O(18) 2.207(5)  Mn(5)-O(10) 2.258(4)  Mn(6)-O(23) 2.107(5)  Mn(6)-O(8) 2.117(5)  Mn(6)-O(22) 2.133(6)  Mn(6)-O(12) 2.369(5)  Mn(6)-N(1) 2.375(6)  Mn(1)…Mn(2) 2.812(2)  Mn(1)…Mn(3) 3.158(1)  Mn(1)…Mn(5) 3.162(1)  Mn(2)…Mn(4) 3.147(1)  Mn(2)…Mn(6) 3.142(1) | Mn(1)-O(1) 1.886(2)  Mn(2)-O(1) 1.894(2)  Mn(4)-O(1) 2.194(2)  Mn(5)-O(1) 2.150(2)  Mn(1)-O(2) 1.892(2)  Mn(2)-O(2) 1.893(2)  Mn(3)-O(2) 2.148(2)  Mn(6)-O(2) 2.181(2)  Mn(1)-O(11) 1.954(2)  Mn(1)-O(17) 1.957(2)  Mn(1)-O(7) 2.236(2)  Mn(1)-O(15) 2.239(2)  Mn(2)-O(20) 1.948(2)  Mn(2)-O(13) 1.950(2)  Mn(2)-O(21) 2.211(2)  Mn(2)-O(5) 2.250(2)  Mn(3)-O(22) 2.123(3)  Mn(3)-O(3) 2.125(3)  Mn(3)-O(12) 2.132(3)  Mn(3)-N(1) 2.355(3)  Mn(3)-O(7) 2.366(2)  Mn(4)-O(8) 2.142(2)  Mn(4)-O(9) 2.154(2)  Mn(4)-O(19) 2.174(2)  Mn(4)-O(1W) 2.194(3)  Mn(4)-O(21) 2.244(2)  Mn(5)-O(6) 2.113(2)  Mn(5)-O(18) 2.128(3)  Mn(5)-O(10) 2.133(2)  Mn(5)-O(15) 2.316(2)  Mn(5)-N(2) 2.348(3)  Mn(6)-O(4) 2.107(2)  Mn(6)-O(16) 2.151(3)  Mn(6)-O(14) 2.169(3)  Mn(6)-O(5) 2.273(2)  Mn(6)-N(3) 2.350(3)  Mn(1)…Mn(2) 2.8179(7)  Mn(1)…Mn(3) 3.1643(7)  Mn(1)…Mn(5) 3.1474(7)  Mn(2)…Mn(4) 3.1569(7)  Mn(2)…Mn(6) 3.1558(7) | Mn(1)-O(1) 1.893(4)  Mn(2)-O(1) 1.888(4)  Mn(4)-O(1) 2.175(4)  Mn(5)-O(1) 2.158(4)  Mn(1)-O(2) 1.892(4)  Mn(2)-O(2) 1.890(4)  Mn(3)-O(2) 2.155(4)  Mn(6)-O(2) 2.156(4)  Mn(1)-O(13) 1.953(5)  Mn(1)-O(26) 1.959(5)  Mn(1)-O(16) 2.224(5)  Mn(1)-O(29) 2.227(5)  Mn(2)-O(20) 1.935(5)  Mn(2)-O(12) 1.947(5)  Mn(2)-O(10) 2.237(4)  Mn(2)-O(22) 2.275(5)  Mn(3)-O(9) 2.115(5)  Mn(3)-O(7) 2.121(5)  Mn(3)-O(4) 2.185(5)  Mn(3)-O(8) 2.263(6)  Mn(3)-O(16) 2.276(5)  Mn(4)-O(18) 2.130(5)  Mn(4)-O(15) 2.142(5)  Mn(4)-O(19) 2.148(5)  Mn(4)-N(1) 2.314(5)  Mn(4)-O(10) 2.334(5)  Mn(5)-O(21) 2.107(6)  Mn(5)-O(17) 2.135(5)  Mn(5)-O(14) 2.159(6)  Mn(5)-O(29) 2.291(4)  Mn(5)-O(23A)2.23(2)  Mn(5)-O(23B)2.27(3)  Mn(6)-O(3) 2.126(5)  Mn(6)-O(6) 2.130(5)  Mn(6)-O(11) 2.159(5)  Mn(6)-O(22) 2.232(5)  Mn(6)-O(5) 2.298(5)  Mn(1)…Mn(2) 2.8126(13)  Mn(1)…Mn(3) 3.1566(14)  Mn(1)…Mn(5) 3.1357(15)  Mn(2)…Mn(4) 3.1818(13)  Mn(2)…Mn(6) 3.1331(12) |

**Table S2.** The parameters of O−H…O hydrogen bonds in the crystal structure **1 – 6.**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| D-H∙∙∙A | Distances, Å | | | Angles, deg |
| D−H | H∙∙∙A | D∙∙∙A | DHA |
|  |  | **1** |  |  |
| O4− H4∙∙∙ O22 | 0.76(3) | 1.97(3) | 2.717(3) | 164(3) |
| O10−H10∙∙∙O23 | 0.84 | 1.73 | 2.567(2) | 171.1 |
| O13−H13∙∙∙O34 | 0.84 | 1.76 | 2.584(2) | 167.7 |
| O20−H20∙∙∙O19 | 0.84 | 1.84 | 2.668(2) | 169.0 |
| O44−H44∙∙∙O38 | 0.84 | 1.85 | 2.655(3) | 159.7 |
| **2** | | | | |
| O(12)-H(12)...O(16A) | 0.85(1) | 1.98(4) | 2.740(17) | 148(7) |
| O(12)-H(12)...O(16B) | 0.85(1) | 1.84(2) | 2.68(2) | 167(3) |
| O(15A)-H(15X)...O(9) | 0.82 | 1.94 | 2.664(8) | 147.5 |
| O(15B)-H(15Y)...O(13) | 0.82 | 1.85 | 2.64(3) | 160.5 |
| **3** | | | | |
| O1W-H1WA…O22 | 0.90(6) | 1.96(6) | 2.838(4) | 165(5) |
| O1W-H1WB…O4 | 0.86(6) | 2.12(6) | 2.882(4) | 149(5) |
| O30-H30…O1W | 0.84 | 1.86 | 2.691(4) | 169.6 |
| O24-H24…O12 | 0.84 | 1.76 | 2.587(3) | 169.6 |
| O26-H26…O19 | 0.84 | 1.80 | 2.630(5) | 167.7 |
| O27-H27…O301 | 0.78(5) | 1.90(5) | 2.642(4) | 159(5) |
| O28-H28…O2S | 0.78(5) | 2.03(5) | 2.742(18) | 152(5) |
| O28-H28…O1S | 0.78(5) | 1.93(5) | 2.628(9) | 153(5) |
| 1 -x+1/2, y-1/2, -z+3/2 | | | | |
| **4** | | | | |
| O18-H18…O161 | 0.852(10) | 1.921(19) | 2.739(7) | 160(3) |
| O26-H26…O142 | 0.849(10) | 1.889(16) | 2.722(7) | 167(4) |
| 1 -x,1-y,-z |  |  |  |  |
| 2  1-x,2-y,1-z |  |  |  |  |
| **5** | | | | |
| O2W-H2W2 O19 | 0.93 | 1.99 | 2.742(5) | 137.6 |
| O2W-H2W1 O81 | 0.99 | 1.92 | 2.899(6) | 170.2 |
| O1W-H1W1 O91 | 0.82(5) | 1.89(5) | 2.688(4) | 165(5) |
| O1W-H1W2 O2W | 0.73(4) | 2.02(4) | 2.713(6) | 159(5) |
| 1 -x+1, -y, -z+1 |  |  |  |  |
| **6** | | | | |
| O(28)-H(28P)...O(4) | 0.84 | 1.73 | 2.559(8) | 166.8 |
| O(24A)-H(24A)...O(17) | 0.84 | 1.83 | 2.609(13) | 154.6 |
| O(24B)-H(24B)...O(14) | 0.84 | 2.04 | 2.835(16) | 158.4 |

|  |  |
| --- | --- |
|  |  |
| **1** | **2** |
|  | |
| **3** | |

Figure S1. View of clusters **1**-**3** illustrates the diverse combination of capped ligands attached to peripheral MnII atoms. The carbon atoms of capped ligands are highlighted in green.